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Molecular Energy Transfer Processes in Nonequilibrium Hypersonic Flows

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14. ABSTRACT Newly developed Cavity Ring Down Spectroscopy (CRDS) and Tunable Diode Laser Spectroscopy (TDLAS) have been employed for absolute time-resolved populations of N₂ in the excited A³Σ⁺ electronic state, generated in a repetitive ns pulse discharge in nitrogen. CRDS measurements of N₂(A³Σ⁺,v=0-2) populations are made in the discharge afterglow at pressures of 22 and 39 Torr. The data reduction procedure takes into account the linewidth of the pulsed laser source, which is comparable with the absorption linewidth and results in a non-single exponential ring down decay. Peak N₂(A³Σ⁺,v=0-2) populations after a 10-pulse ns discharge burst are in the range of 10¹² - 10¹³ cm⁻³. In the afterglow, these populations exhibit a relatively slow decay with the characteristic time of approximately 500 ns, most likely due to the quenching by N atoms. TDLAS data have been taken at a higher pressure of 132 Torr. Absolute time-resolved N₂(A³Σ⁺,v=0,1) number densities are measured during ns pulse discharge bursts up to 5 pulses long and in the afterglow, peaking at 6×10¹² cm⁻³ and 3×10¹³ cm⁻³, respectively. The results indicate that N₂(A³Σ⁺) is generated after every discharge pulse on a 20-50 ns time scale, much longer compared to the discharge pulse duration of ~100 ns, and subsequently decays between the pulses. The decay rate increases during the discharge burst. In the afterglow, N₂(A³Σ⁺,v=0,1) population decay significantly more rapidly compared to the low pressure CRDS conditions, with the characteristic time of approximately 160 ns after a 5-pulse discharge burst. Absolute, time-resolved populations of N₂(A³Σ⁺,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 H₂-N₂, O₂-N₂, and NO-N₂ plasmas are compared with kinetic modeling predictions, identifying the mechanisms of N₂(A³Σ⁺) generation and decay during the discharge pulses and in the afterglow. Comparison with the modeling predictions indicates that electron impact dissociation of N₂ from the ground electronic state significantly underpredicts the yield of N atoms.					
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MOLECULAR ENERGY TRANSFER PROCESSES IN NONEQUILIBRIUM HYPERSONIC FLOWS

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Final Report

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Abstract

Newly developed Cavity Ring Down Spectroscopy (CRDS) and Tunable Diode Laser Spectroscopy (TDLAS) have been employed for absolute time-resolved populations of N_2 in the excited $A^3\Sigma_u^+$ electronic state, generated in a repetitive ns pulse discharge in nitrogen. CRDS measurements of $N_2(A^3\Sigma_u^+, v=0-2)$ populations are made in the discharge afterglow at pressures of 22 and 39 Torr. The data reduction procedure takes into account the linewidth of the pulsed laser source, which is comparable with the absorption linewidth and results in a non-single exponential ring down decay. Peak $N_2(A^3\Sigma_u^+, v=0-2)$ populations after a 10-pulse ns discharge burst are in the range of $10^{12} - 10^{13} \text{ cm}^{-3}$. In the afterglow, these populations exhibit a relatively slow decay with the characteristic time of approximately 500 μs , most likely due to the quenching by N atoms. TDLAS data have been taken at a higher pressure of 132 Torr. Absolute time-resolved $N_2(A^3\Sigma_u^+, v=0,1)$ number densities are measured during ns pulse discharge bursts up to 5 pulses long and in the afterglow, peaking at $6 \cdot 10^{12} \text{ cm}^{-3}$ and $3 \cdot 10^{13} \text{ cm}^{-3}$, respectively. The results indicate that $N_2(A^3\Sigma_u^+)$ is generated after every discharge pulse on a 20-50 μs time scale, much longer compared to the discharge pulse duration of $\sim 100 \text{ ns}$, and subsequently decays between the pulses. The decay rate increases during the discharge burst. In the afterglow, $N_2(A^3\Sigma_u^+, v=0,1)$ population decay significantly more rapidly compared to the low-pressure CRDS conditions, with the characteristic time of approximately 160 μs after a 5-pulse discharge burst.

Absolute, time-resolved populations of $N_2(A^3\Sigma_u^+, v=0-5)$ 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 H_2 - N_2 , O_2 - N_2 , and 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. Comparison with the modeling predictions indicates that electron impact dissociation of 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 $N_2(A^3\Sigma_u^+)$ 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 - N_2 mixture, it is shown that the $N_2(A^3\Sigma_u^+)$ decay is controlled by the rapid energy transfer to NO , resulting in its electronic excitation and UV emission ($NO \gamma$ 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.

Non-intrusive laser diagnostics are used for the measurements of metastable nitrogen molecules in the lowest excited electronic state, $N_2(A^3\Sigma_u^+)$, in a nonequilibrium flow, blowdown supersonic wind tunnel.

The tunnel is operated with nitrogen at plenum pressures of $P_0=200-250$ Torr, with the flow expanding through a two-dimensional contoured nozzle to the Mach number of $M=3.6-4.6$. The steady-state run time of the tunnel is approximately 10 s. The flow is excited by a repetitive ns pulse discharge operated in the plenum or in the nozzle throat. Time-resolved absolute $N_2(A^3\Sigma_u^+, v=0)$ populations in the plenum are measured by single-pass, continuous wave Tunable Diode Laser Absorption Spectroscopy (TDLAS). In the supersonic test section, absolute $N_2(A^3\Sigma_u^+, v=0-2)$ populations are measured by Cavity Ring Down Spectroscopy (CRDS), using a tunable pulsed laser system operated at 10 Hz. During each run, 50 single-shot ring down traces are acquired, demonstrating good shot-to-shot reproducibility. The results demonstrate that the cavity ring down time is not affected by the supersonic flow. $N_2(A^3\Sigma_u^+, v=0-2)$ populations and the flow temperature are inferred from the single-shot CRDS data. At the conditions when the flow is excited by the discharge in the nozzle throat, $N_2(A^3\Sigma_u^+, v=0)$ population in the supersonic test section is measured by both CRDS and TDLAS diagnostics. The two diagnostic techniques are complementary and can be used for characterization of nonequilibrium reacting flows over a wide range of pressures, including short run time high-enthalpy flow facilities.

Kinetics of O_2 vibrational excitation is studied during the O atom recombination in an O_2 -Ar mixture partially dissociated by a burst of ns discharge pulses in a flow reactor, at $T = 380-650$ K. Time-resolved vibrational level populations of molecular oxygen in the ground electronic state, $O_2(X, v=8-20)$, are measured by ps Laser Induced Fluorescence on the O_2 Schumann Runge bands, with absolute calibration by NO LIF in a NO- N_2 mixture with a known composition, at quenching-free conditions. O atom number density in the same mixture is measured by ps Two-Photon absorption LIF (TALIF). The discharge generates a diffuse volumetric plasma, without well-pronounced filaments. The temperature in the plasma is measured by Tunable Diode Laser Absorption Spectroscopy (TDLAS) of excited Ar atoms. The results indicate a rapid initial decay of the $O_2(X, v=8-20)$ molecules generated by electron impact in the discharge, on ~ 100 μs time scale, due to the V-V exchange and V-T relaxation. This decay is followed by a much slower decay, on the time scale much longer compared to the characteristic time for V-V relaxation, up to several ms. This indicates an additional process of $O_2(v)$ generation by chemical reactions initiated by the O atom recombination. This effect is observed both in the non-preheated and preheated O_2 -Ar mixtures. However, comparison of the time-resolved $O_2(v=8-13, 17-20)$ vibrational level populations after the burst excitation of non-preheated and preheated exhibits significant differences. In the preheated mixtures, peak $O_2(v)$ populations during the slow decay following the excitation are significantly lower, suggesting a significant effect of O atom recombination via the reaction pathways involving ozone. Additional data need to be taken in preheated mixtures with the low O_2 mole fraction, $\sim 1\%$, and at higher pressures, at the conditions when the discharge excitation would result in dissociation of most of O_2 molecules in the mixture.

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PART I.

LASER DIAGNOSTICS DEVELOPMENT FOR TIME-RESOLVED, STATE-SPECIFIC MEASUREMENTS OF ELECTRONICALLY EXCITED, METASTABLE $N_2(A^3\Sigma_u^+,v)$ MOLECULES ¹

1. Introduction

The electronically excited metastable state of molecular nitrogen, $N_2(A^3\Sigma_u^+)$, plays an important role in kinetics of electric discharge plasmas, atmospheric pressure plasma jets, and high-temperature nonequilibrium reacting flows. In electric discharges in gas mixtures containing significant amounts of nitrogen and air, $N_2(A^3\Sigma_u^+)$ molecules are produced by direct electron impact and by the radiative and collisional decay of higher energy excited electronic states, such as $N_2(B^3\Pi_g)$ and $N_2(C^3\Pi_u)$ [1]. In atmospheric pressure argon plasma jets, $N_2(A^3\Sigma_u^+)$ population may also be affected by energy transfer from metastable Ar atoms and Ar₂ excimers to excited electronic states of N_2 [2]. In high-temperature hypersonic flows behind strong shock waves, $N_2(A^3\Sigma_u^+)$ molecules may also form by electron and heavy species impact, as well as by N atom recombination [3]. Collisional quenching of $N_2(A^3\Sigma_u^+,v)$ by O₂, H₂, CH₄, C₂H₄, and C₂H₆ is one of the major sources of O atoms, H atoms, and hydrocarbon radicals in air and fuel-air mixtures [4], which is essential for kinetics of low-temperature plasma assisted combustion. Reactions of $N_2(A^3\Sigma_u^+)$ with O₂ and O atoms are also among the dominant channels of O and NO formation in low-temperature air plasmas [5] and atmospheric pressure Ar plasma jets [6]. Both O atoms and NO are of considerable importance for plasma applications in chemistry and biology, due to their high reactivity and generation of other reactive oxygen and nitrogen species (RONS) [7]. Finally, rapid energy transfer from $N_2(A^3\Sigma_u^+)$ to nitric oxide and excitation of the NO($A^2\Sigma$) state, with its subsequent radiative decay, generate NO γ band emission in air and $N_2:O_2$ plasmas [8,9], and may also be responsible for NO γ band emission from strong shock waves in air [3].

Quantitative measurements of absolute populations of $N_2(A^3\Sigma_u^+)$ are challenging, due to its long radiative life time and relatively low number densities. Diagnostic techniques used over the last two decades include optical emission spectroscopy [10-12], Cavity Enhanced Absorption Spectroscopy (CEAS) [13], Cavity Ring Down Spectroscopy (CRDS) [14-15], and Laser Induced Fluorescence (LIF) [16-22]. While emission spectroscopy and LIF require absolute calibration, absorption spectroscopy and CRDS yield direct measurements of absolute number densities of the absorbing species. In the present work, we use CRDS and single-pass Tunable Diode Laser Absorption Spectroscopy (TDLAS) to measure absolute populations of vibrational states of $N_2(A^3\Sigma_u^+)$ in a repetitive, double dielectric barrier, ns pulse discharge in nitrogen between two parallel plate electrodes, at moderate pressures of 20-130 Torr. This type of discharge generates a diffuse, well-reproduced, transient plasma, which lends itself to time-resolved measurements of excited species and radicals, as well as kinetic modeling analysis using a zero-dimensional

¹ E.R. Jans, K. Frederickson, T.A. Miller, and I.V. Adamovich, "Time-Resolved Populations of $N_2(A^3\Sigma_u^+,v)$ in Nanosecond Pulse Discharge Plasmas", *Journal of Molecular Spectroscopy* 365 (2019) 111205

approximation. The TDLAS measurements complement the CRDS data at the conditions when the $N_2(A^3\Sigma_u^+)$ number density may be too high to measure by the ring down but sufficient to be detected by single-pass absorption. The objective of the present work is to obtain accurate data on the time evolution of absolute $N_2(A^3\Sigma_u^+, v)$ populations during the discharge pulse burst and in the afterglow. These results can be used for quantitative insight into the processes of their generation and decay, inferred from comparison with kinetic modeling.

2. Experimental

The schematic of the CRDS experiment is shown in Fig. 1. To produce a spectrally narrow tunable output for the CRDS spectrometer, a Nd:YAG laser (Continuum PowerLite Precision II), operated at 10 Hz, 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. Brillouin backscattering from the Raman cell, including first Stokes, second Stokes, anti-Stokes, and second anti-Stokes components, is separated from the fundamental pump beam by a dichroic mirror (see Fig. 1). The Stokes and anti-Stokes beams are dispersed by a Pellin-Broca prism, as shown in Fig. 1, isolating the first Stokes beam used for the CRDS measurements. 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 cavity 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 cavity length of 90 cm. The high reflectivity mirrors ($R=0.99997$, Layertec GmbH, radius of curvature of 1 m) are attached to the ends of the ring-down cavity using stainless steel adjustable mounts, for precision alignment. The present CRDS measurements have been made in 99.999% pure nitrogen at the pressures of 22 and 39 Torr and the flowrates of 237 and 1000 SCCM, respectively, monitored by a flow controller (MKS Flow Controller 1179A01313CS1BV). The combined leak rate of the cavity and the gas delivery system is approximately $1.6 \cdot 10^{15}$ molecules/s, over 5 orders of magnitude lower compared to the flow rate, $5.3 \cdot 10^{20}$ molecules/s, such that the upper bound oxygen and water vapor impurity level is $\sim 10^{-6}$ and $\sim 10^{-7}$ mole fraction, respectively. The experiment is controlled by a computer running a LabVIEW script, which (i) scans the dye laser grating to tune the output wavelength, (ii) records the wavelength and linewidth for each laser shot, and (iii) saves the ring down traces measured by the silicon avalanche photodiode (Thorlabs APD410A) and acquired by a DAQ card (PCI-DAS4020/12).

Figure 2 shows the TDLAS apparatus, which is using the same quartz channel / discharge cell as in the CRDS measurements, with the high-reflectivity mirrors replaced by BK-7 glass optical access windows. The windows are not wedged and do not have an anti-reflecting coating. An output beam of a 20 mW continuous wave diode laser (New Focus Velocity 6312), with a scan range from 765 to 781 nm and a nominal linewidth of less than 0.3 MHz, is directed along the discharge cell, as shown in Fig. 2. The laser wavelength is scanned by varying the voltage on the piezoelectric driver of the laser and is monitored by the wavemeter. The transmitted signal is measured by a silicon photodiode (Thorlabs DET36A) and monitored by an oscilloscope (Agilent DSO-X 4032A). The TDLAS measurements are done in 99.999% pure nitrogen, at a higher pressure of 132 Torr and a flowrate of 900 SCCM. At these conditions, the $N_2(A^3\Sigma_u^+)$ number density is significantly higher compared to the lower pressure conditions used for the CRDS

measurements, such that single-pass absorption becomes detectable. This experiment is controlled by a computer running a similar LabVIEW script, which (i) scans the piezoelectric driver voltage to tune the laser output wavelength, (ii) records the wavelength from the wavemeter for each trace, and (iii) saves the laser intensity trace from the oscilloscope.

Nitrogen in the CRDS / TDLAS test cell is excited by a double dielectric barrier discharge maintained between two rectangular parallel 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. The electrodes are attached to the walls by a silicon rubber adhesive, which also prevents corona discharge formation in ambient air, near the electrode surfaces. The discharge in the cell is sustained by a custom-built high-voltage pulse generator producing alternating polarity pulses with peak voltage up to 15 kV and pulse duration of approximately 100 ns FWHM, with the energy coupled to the plasma of approximately 0.2 mJ/pulse at 22 Torr and 0.3 mJ/pulse at 132 Torr. Typical discharge voltage and current traces at these conditions are shown in Fig. 3. In both cases, the discharge current is significantly higher compared to the capacitive current measured at the atmospheric pressure in the cell, when the plasma is not generated. In the present experiments, the pulse generator is operated in burst mode, with burst repetition rate of 10 Hz, pulse repetition rate of 10 kHz, and 5-10 pulses per burst. The voltage and current waveforms are reproduced well pulse to pulse, with the coupled energy per pulse varying over 5% during the burst.

The CRDS measurements are made in the afterglow after the burst, for different delays between the burst and the laser pulse, as shown schematically in Fig. 4. In contrast, the cw TDLAS measurements are made continuously, both during the discharge burst and in the afterglow (see Fig. 4). The TDLAS measurements require significant reduction of the electromagnetic noise from the discharge, to make possible detection of small variations in the absorption coefficient, down to 10^{-4} .

3. Data reduction

For the empty ring down cavity, the transmitted light source signal intensity is given as

$$I(t) = I_0 \exp\left(-\frac{ct(1-R)}{L_{cell}}\right), \quad (1)$$

where I_0 is the incident intensity, c is the speed of light, t is time, R is the reflectivity of the mirrors, and L_{cell} is the total length of the cavity. When an absorbing species is present inside the cavity and a spectrally narrow light source is resonant with an absorption transition, the transmitted signal intensity becomes

$$I(t) = I_0 \exp\left(-\frac{ct(1-R)}{L_{cell}}\right) \exp\left(-\frac{ct\alpha(\nu)L_{abs}}{L_{cell}}\right), \quad (2)$$

where $\alpha(\nu)$ is the spectral absorption coefficient and L_{abs} is the absorption path length. In the present work, L_{abs} is taken to be the same as the length of the discharge electrodes.

The Fabry-Pérot cavity formed by the two high reflectivity mirrors has the allowed longitudinal mode spacing formed by the length of the cavity as

$$\Delta\nu_m = \frac{c}{2L_{cell}}. \quad (3)$$

For the present experimental apparatus, the longitudinal cavity mode spacing is approximately 166 MHz. The spectral width of each mode is

$$FWHM_{cavity} = -\frac{c}{4\pi L_{cell}} \ln(R^2) = 2.6 \cdot 10^{-3} \text{ MHz}, \quad (4)$$

much lower than the mode spacing. For the average dye laser FWHM linewidth of 2100 MHz, the light is coupled to the cavity on about 30 modes. For the absorption transition FWHM linewidth of approximately 920 MHz (with the line shape dominated by the Doppler broadening at P=20 Torr and T=300 K), the light is absorbed on approximately 10 cavity modes, as shown schematically in Fig. 5. The exact frequencies of the longitudinal cavity modes in the cavity are not known precisely, due to mechanical vibrations and thermal fluctuations of the cavity length. To simplify the computations, the comb of the cavity modes is centered, with one of the modes always placed at the absorption transition frequency. Due to the fairly large number of the modes on which the light is absorbed, the result is essentially independent on the exact position of the modes. From Fig. 5, it is readily apparent that the absorption rate for each mode frequency ν_m is affected both by the laser source line shape, $g_S(\nu_0 - \nu_m)$, and by the absorption line shape, $g_A(\nu_0 - \nu_m)$, in addition to the number density of the absorbing species. Therefore, the net time-resolved signal measured by the detector becomes

$$\frac{I(t)}{I_0} = \exp\left(-\frac{ct(1-R)}{L_{cell}}\right) \sum_m g_S(\nu_0 - \nu_m) \exp\left(-\frac{ctg_A(\nu_0 - \nu_m)\alpha L_{abs}}{L_{cell}}\right), \quad (5)$$

where α is the line-integrated absorption coefficient (in $\text{cm}^{-1}\cdot\text{Hz}$), such that $\alpha(\nu) = g_A(\nu) \cdot \alpha$, and the sum is evaluated for all cavity modes overlapping with the absorption line (see Fig. 5). In Eq. (5), both line shapes (in Hz^{-1}) are normalized to one. It can be seen that the sum in Eq. (5) describes the deviation of the ring down signal from a simple exponential decay. The line-integrated absorption coefficient, α , is inferred by matching the ring down decay signal, $I(t)$, predicted by Eq. (5), to the experimental signal at the absorption line center. This approach is similar to the method used in Ref. [23], where the transmitted signal was integrated across the absorption line to quantify the effect of the finite laser linewidth on the ring down decay, which becomes multi-exponential.

Several previous studies, by Hancock *et al* [14], Foissac *et al* [24], and Western *et al* [25], are particularly helpful for deriving the $\text{N}_2(\text{A}^3\Sigma_u^+)$ vibrational populations from the measured intensities of rotationally resolved lines of the $\text{B}^3\Pi_g \leftarrow \text{A}^3\Sigma_u^+$ electronic transition. In the earlier studies, absolute number densities were obtained from the intensity measurements, and we use the Foissac *et al* analysis as a guide for our work. However, more than one approximation is contained in this analysis. For that reason, we also utilize the recent work of Western *et al*, which is the most thorough analysis in terms of the molecular parameters for the $\text{B}^3\Pi_g$ and $\text{A}^3\Sigma_u^+$ states of N_2 . However, in Ref. [25] little is said about the line intensities, particularly the absolute intensities. Nonetheless, such information can be obtained from the computer program pGopher [26], used for the analysis therein. Therefore, we have also run the calculation for the A and B states using the recommended molecular parameters and extracting the relevant intensity information from pGopher. It is instructive to compare the results of the two methods. One expects the results from

pGopher to possess greater numerical accuracy. On the other hand, one may argue that the results of Foissac *et al* provide physical interpretation more readily. In making these comparisons, one should note the caveat that Foissac *et al* use a case (b) basis set and accordingly label the spin-rotational eigenvalues with case (b) quantum numbers, i.e. N, J, and S, where $\mathbf{J}=\mathbf{N}+\mathbf{S}$ and, hence $J=N$, $N\pm 1$, except for $N=0$ for which $J=S=1$. Western *et al* use case (a) notation with $\mathbf{J}$ and its projection on the internuclear axis, $\Omega'' = 0, \pm 1$ (A state), $\Omega' = 0, \pm 1, \pm 2$ (B state). In labelling the eigenvalues, we shall use the generic notation $E(v, \gamma)$, where E is the energy, $\gamma = N, J$ for case (b), and $\gamma = J, \Omega$ for case (a). Specified rovibronic transitions in this paper will follow the case (b) standard spectroscopic notations [27], i. e. $^{\Delta N}\Delta J_{F_i, F_j}(J'')$, where F_i and F_j are spin substates for the $A^3\Sigma_u^+$ and $B^3\Pi_g$ states, respectively. There are 3 spin substates where the J levels are related to N as follows, $F_1: J=N+S$, $F_2: J=N$, $F_3: J=N-S$. The notations for different ΔN and ΔJ are given in Table 1.

Table 1. Rotational transition notations

ΔJ			-1	0	1		
ΔN	-3	-2	-1	0	1	2	3
Notation	N	O	P	Q	R	S	T

For example, the $^S R_{32}(12)$ transition used for CRDS measurements is a S form R branch transition.

The absolute population (number density) of a particular vibrational-rotational state of the absorbing species, $N(v'', \gamma'')$ (in cm^{-3}), is obtained from the absorption coefficient as follows [24]

$$N(v'', \gamma'') = N(v'') f_{\gamma''}^{v''} = \frac{\alpha}{k_{v_0}}, \quad (6)$$

where $N(v'')$ is the vibrational level population, $f_{\gamma''}^{v''}$ is the fractional rotational population in the γ'' eigenstate, and k_{v_0} is the line intensity (line-integrated cross section, in $\text{cm}^2 \cdot \text{Hz}$). Our analysis shows that for the CRDS experiment under the present conditions, accurate inference of the absorption coefficient and the absorbing species number density requires the knowledge of the laser line shape. This issue is discussed in greater detail in Section 4.

The spectral absorption coefficient, $\alpha(v)$, is measured directly by TDLAS,

$$\alpha(v) = \frac{1}{L_{abs}} \ln \left(\frac{I_o(v)}{I(v)} \right), \quad (7)$$

and is related to the number density of the absorbing species, $N(v'', \gamma'')$ in a similar way,

$$N(v'', \gamma'') = N(v'') f_{\gamma''}^{v''} = \frac{\alpha(v)}{k_{v_0} g_A(v)}. \quad (8)$$

The line-integrated absorption coefficient is related to the spectral absorption coefficient through integrating across the rotational line, $\alpha = \int_0^\infty \alpha(v) dv$. At higher pressures at which

TDLAS data are taken, pressure broadening of tightly packed rotational lines makes the use of Eq. (8) a preferable option. For this, accurate knowledge of the absorption line shape is required.

At low pressures (below $P \sim 20$ Torr), the absorption line shape, $g_A(\nu_0 - \nu_m)$, is dominated by Doppler broadening,

$$g_D(\nu - \nu_0) = \frac{\sqrt{4 \ln(2)}}{\pi} \frac{1}{\Delta \nu_D} e^{(-4 \ln(2) \frac{\nu - \nu_0}{\Delta \nu_D})}, \quad (9)$$

where $\Delta \nu_D = \nu_0 \sqrt{\frac{8 \ln(2) k_B T}{m c^2}} = 7.16 \times 10^{-7} \nu_0 \sqrt{\frac{T(K)}{M(amu)}}$ is the Doppler broadening factor (FWHM). At high pressures (~ 1 bar), when collisional broadening dominates, the line shape is Lorentzian,

$$g_L(\nu - \nu_0) = \frac{1}{2\pi} \frac{\Delta \nu_L}{(\nu - \nu_0)^2 + \left(\frac{\Delta \nu_L}{2}\right)^2}, \quad (10)$$

where $\Delta \nu_L = \sum N_i \sigma_i \sqrt{\frac{8 k_B T}{\pi \mu_i}}$, N_i is the number density of collision partner i , σ_i is the collisional dephasing cross section, and μ_i is the collision reduced mass. In the general case, the absorption line shape is a convolution of the Doppler and Lorentzian line shapes, given by the Voigt profile,

$$g_V(\nu) = \int g_D(\nu') g_L(\nu - \nu') d\nu'. \quad (11)$$

In addition, when the laser source linewidth, $g_S(\nu - \nu_{0S})$, is comparable with that of the absorption line, $g_A(\nu - \nu_{0A})$, as is the case for the CRDS measurements, the apparent line shape in the CRDS spectra is a convolution of the two line shapes,

$$g(\nu) = \int g_A(\nu' - \nu_{0A}) g_S(\nu' - \nu_{0S}) d\nu'. \quad (12)$$

Following Ref. [24], the line integrated rotational cross-section used in Eq. (6) is calculated from the following equation,

$$k_{\nu_0} = \frac{2\pi^2 \nu_0}{3\varepsilon_0 h c} \frac{S_{J',J''}}{2J'' + 1} \left| R_e^{v',v''} \right|^2 = \frac{2\pi^2 \nu_0}{3\varepsilon_0 h c} \frac{S_{J',J''}}{2J'' + 1} q_{v',v''} (R_e(\bar{r}_{v',v''}))^2, \quad (13)$$

where ε_0 is the dielectric permittivity of vacuum, h is the Planck constant, c is the speed of light, $S_{J',J''}$ is the Hönl-London factor (rotational line strength) [28], $\left| R_e^{v',v''} \right|^2$ is the electronic-vibrational transition moment, $q_{v',v''}$ is the Franck-Condon factor, and $R_e(\bar{r}_{v',v''})$ is the electronic transition moment, both taken from Ref. [29]. The electronic transition moment from Ref. [29] is multiplied by a conversion factor $8.47835326 \times 10^{-30} \text{ C} \cdot \text{m}$ to convert it from the atomic units to SI units. The values of $\left| R_e^{v',v''} \right|^2$ from [29] for the $(2 \leftarrow 0)$, $(3 \leftarrow 1)$, and $(4 \leftarrow 2)$ bands are $7.00 \cdot 10^{-$

⁶¹, $1.19 \cdot 10^{-60}$, and $1.25 \cdot 10^{-60} \text{ C}^2 \cdot \text{m}^2$, respectively, within 2% from the more accurate data in Western *et al* [25]. The values of the Hönl-London factors and k_{v_0} calculated in this way are given in columns I and III in Table 2. Alternatively, these values can be obtained directly from pGopher and the latter values are given in columns II and IV of Table 2.

Since the vibrational populations, $N(v'')$, are the desired quantities from the experimental measurement, we need to return to Eqs. (6,8), to relate these populations to the absorption coefficient for a transition from a given spin-rotational eigenvalue $E(v'', \gamma'')$ in the vibrational level v'' . If we assume a Boltzmann distribution among the rotational levels, the fractional rotational population in the γ'' eigenstate in Eq. (6) is

$$f_{\gamma''}^{v''} = \frac{N(v'', \gamma'')}{N(v'')} = \frac{(2J'' + 1)g_N}{Q} \exp\left(-\frac{E(\gamma'')hc}{kT}\right), \quad (14)$$

where Q is the corresponding rotational partition function and g_N is the nuclear spin weight for each eigenvalue, $g_N = 3$ for levels with $I_T = 1$ and $g_N = 6$ for levels with $I_T = 2$ or 0 . Note that ^{14}N is a boson with nuclear spin of 1, and hence N_2 rotational levels symmetric to nuclear exchange ($\gamma'' = J''$, odd N'' or $\gamma'' = J''$, Ω'') have a total nuclear spin function, $I_T = 2$ or 0 , while antisymmetric rotational levels require an antisymmetric nuclear spin function, $I_T = 1$.

Assuming rotational-translational equilibrium and following Ref. [30], the fractional population can be evaluated

$$f_{\gamma''}^{v''} = \frac{2\Phi hc B_{v''}}{3kT} (2J'' + 1) \exp\left(-\frac{E(\gamma'')hc}{kT}\right) \quad (15)$$

where $\Phi = \frac{1}{3}$ (even N'') or $\frac{2}{3}$ (odd N'') is the nuclear spin statistical weight factor which is obtained by canceling a common factor of 9 in g_N in the numerator and denominator inside the partition function of Eq. (14), $B_{v''}$ is the rotational constant of the v'' state [31], the factor of 2 in the numerator comes from the rotational partition function, $Q = kT/2B_{v''}$, and the factor of 3 in the denominator is due to the triplet structure of the $\text{A}^3\Sigma_u^+$ electronic state. Alternatively, the fractional population can be obtained directly from pGopher. These results are listed in columns V and VI of Table 2, respectively. The last two columns of Table 2 list the values of the cross-section for the vibrational population, $A_{\gamma''}^{v''} = k_{v_0} f_{\gamma''}^{v''}$, such that

$$N(v'') = \frac{\alpha}{A_{\gamma''}^{v''}} \quad (16a)$$

for CRDS measurements, and

$$N(v'') = \frac{\alpha(v_0)}{A_{\gamma''}^{v''} g_A(v_0)} \quad (16b)$$

for TDLAS measurements. In the latter case, the spectral absorption line shape (approximated by the Voigt profile), $g_A(v)$, was measured by scanning the tunable diode laser across the line centered at v_0 , and the vibrational populations were determined using the time-resolved values of the spectral absorption coefficient, $\alpha(v_0)$, measured with the laser parked on the line center.

Table 2. Parameters of selected vibrational-rotational absorption transitions.

Transition Name and Wavelength	Hönl-London Factor, $S_{J',J''}$		Rotational Cross Section, k_{v0} (cm ² Hz)		Fractional Population, $f_{\gamma''}^{v''}$		Vibrational Cross Section, $A_{\gamma''}^{v''}$ (cm ² Hz)	
	I ^a	II ^b	III ^c	IV ^b	V ^d	VI ^b	VII ^c	VIII ^b
$v''=0$, R ₁₁ (20), N''=19, J''=20, λ_0 (nm)=766.854	18.7	18.7	$4.67 \cdot 10^{-6}$	$4.74 \cdot 10^{-6}$	$8.81 \cdot 10^{-3}$	$8.80 \cdot 10^{-3}$	$4.12 \cdot 10^{-8}$	$4.17 \cdot 10^{-8}$
$v''=1$, ^S R ₃₂ (12), N''=12, J''=12, λ_0 (nm)= 753.646	3.65	3.78	$2.58 \cdot 10^{-6}$	$2.69 \cdot 10^{-6}$	$1.30 \cdot 10^{-2}$	$1.31 \cdot 10^{-2}$	$3.37 \cdot 10^{-8}$	$3.51 \cdot 10^{-8}$
$v''=2$, ^N P ₁₃ (6), N''=7, J''=6, λ_0 (nm)= 752.721	0.70	0.56	$9.80 \cdot 10^{-7}$	$8.08 \cdot 10^{-7}$	$2.75 \cdot 10^{-2}$	$2.69 \cdot 10^{-2}$	$2.69 \cdot 10^{-8}$	$2.17 \cdot 10^{-8}$
$v''=0$, Q ₁₁ (12), N''=11, J''=12, λ_0 (nm)=773.215	18.2	18.0	$7.40 \cdot 10^{-6}$	$7.40 \cdot 10^{-6}$	$3.09 \cdot 10^{-2}$	$3.08 \cdot 10^{-2}$	$2.29 \cdot 10^{-7}$	$2.27 \cdot 10^{-7}$
$v''=1$, ^O P ₁₂ (12), N''=12, J''=12, λ_0 (nm)=764.638	3.75	3.93	$2.61 \cdot 10^{-6}$	$2.75 \cdot 10^{-6}$	$1.30 \cdot 10^{-2}$	$1.31 \cdot 10^{-2}$	$3.39 \cdot 10^{-8}$	$3.60 \cdot 10^{-8}$

^a From program in Ref. [28]^b From pGopher program^c From column I and Eq. (13)^d From Ref. [24], Eq. (15)^e Product of Columns III and V

A synthetic spectrum code of the first positive system of molecular nitrogen has been used to compare with the experimental absorption spectra with the theoretical predictions. The line positions in the synthetic spectrum are calculated by diagonalizing the Hamiltonians for B³Π_g and A³Σ_u⁺ excited electronic states [31], with a corrected value of T_{Σ⁺eff} for v=1 of the A³Σ_u⁺ state of 1432.907 taken from Ref. [32]. The absorption line assignments used during the data reduction are obtained from the synthetic spectrum and verified using the line positions for the (2←0) band reported in Ref. [33].

4. Results and Discussion

Figures 6 and 7 show typical plasma emission images during a ns pulse discharge in nitrogen at pressures of 20 Torr and 132 Torr, respectively (pulses #1 and #10 in a 10-pulse discharge burst). It can be seen that at 20 Torr the plasma is diffuse, confined within the volume between the electrodes, and extends over the entire electrode length. This justifies the assumption

that the absorption path length is approximately equal to the length of the electrodes, $L_{abs} \approx 6$ cm. Although at 132 Torr the plasma becomes somewhat more constricted, such that it occupies only about half of the 22 mm x 10 mm channel cross section, the TDLAS beam, approximately 10 mm in diameter, is aligned to pass through the plasma near its center.

Figure 8 compares the typical ring down traces in the empty cavity and in nitrogen at a pressure of 22 Torr, 50 μ s after the last pulse in a 10-pulse discharge burst. Both traces are plotted on a semi-log scale, such that a single exponential decay in the empty cavity (ring down time of 115 μ s) is a straight line. It is evident, however, that the ring down trace in the discharge afterglow has a more complex shape and cannot be represented as a single exponential decay. As discussed in Section 3 and illustrated in Fig. 5, the multi-exponential decay in Fig. 8 is due to the laser linewidth being larger than the absorption linewidth (also see [23]). The line-integrated absorption coefficient, α , is inferred from the data such as shown in Fig. 8 using Eq. (5), minimizing the least-squares error and assuming the absorption path of $L_{abs} = 6$ cm.

Figure 9 plots typical CRDS spectra acquired 50 μ s after the last discharge pulse in the burst at a pressure of 22 Torr. Each spectral scan covers over 0.5 nm, incorporating between 15 and 30 rovibrational transitions in the ($2 \leftarrow 0$), ($3 \leftarrow 1$), and ($4 \leftarrow 2$) vibrational bands of the first positive system of nitrogen, $N_2(B^3\Pi_g \leftarrow A^3\Sigma_u^+)$. Note that the absorption transitions in Fig. 9 are labeled in different colors, red for $v''=0$, black for $v''=1$, and blue for $v''=2$. Each data point in the spectra in Fig. 9 is an average ring-down time of 25 laser shots sorted into 0.5 pm bins as the laser is scanned, and nearly every absorption transition has been identified, with selected transitions labeled for clarity. The experimental spectra plotted in Fig. 9 have been obtained by fitting the entire ring down trace at each wavelength with a single exponential, instead of a series of exponential terms given by Eq. (5), as illustrated in Fig. 8. The latter procedure can be used in a straightforward fashion only for isolated absorption lines, when the data reduction code infers the line-integrated absorption coefficient that provides the best fit to a set of experimental ringdown traces measured while scanning the laser across the line. Therefore the vertical axis in the experimental spectra of Fig. 9 is not linearly proportional to the vibrational-rotational level populations. Indeed, comparison of the experimental CRDS spectra to synthetic spectra in Fig. 9 exhibits differences between the experimental and predicted line intensities. From Fig. 9, it can be seen that stronger absorption lines are systematically underestimated compared to the weaker absorption lines, consistent with the theoretical predictions by Yalin and Zare [23]. The primary purpose of Fig. 9 is to demonstrate that the observed absorption lines have been identified as specific transitions in the N_2 first positive bands. The isolated rotational lines marked with an asterisk in Fig. 9, $R_{11}(20)$ for $v''=0$, $S_{32}(12)$ for $v''=1$, and $N_{13}(6)$ for $v''=2$, are used for the inference of the time-resolved vibrational populations of $N_2(A^3\Sigma_u^+)$. The data plotted in Fig. 9 are also shown in Fig. S1 in the supplemental material, where they are shown in greater detail for better illustration.

As stated in Section 3, accurate inference of the absorbing species number density requires the knowledge of the laser line shape, used in Eq. (5). In the present measurements, the laser line shape is assumed to have the Lorentzian profile with the average FWHM of 2100 MHz, measured by the wavemeter during the experiment. The validity of this assumption has been verified by matching the calculated convolution of the absorption line shape (Voigt profile) and the laser line shape (Lorentzian profile), calculated from Eq. (12), to the apparent absorption line shape measured in the experiment, showing good agreement, as shown in Fig. 10. The use of the best fit

Voigt laser line shape, with the same FWHM, resulted in a modest difference in the inferred number densities, less than 2% at P=22 Torr and approximately 15% at P=39 Torr.

The critical importance of using Eq. (5), rather than a single exponential fit of the ring down trace, for the inference of the line-integrated absorption coefficient α is illustrated in Fig. 11. This figure compares the spectral absorption coefficients obtained by these two methods, $\alpha(\nu)$, from the scans over three rotational-vibrational transitions used for the inference of $N_2(A^3\Sigma_u^+, v=0-2)$ vibrational populations, respectively. For illustration, the line-integrated spectral absorption coefficients inferred from Eq. (5) have been multiplied by the normalized convolution of the absorption line shape and laser line shape, such as plotted in Fig. 10. From Fig. 11, it can be seen clearly that the absorption coefficients obtained from Eq. (5) exceed the values inferred from the single-exponential fit by a factor of 4-5. In other words, the data obtained from the single exponential fits would underpredict the absorption coefficient, as well as the $N_2(A^3\Sigma_u^+)$ vibrational populations (see Eq. (16a)), by a factor of 4-5. These results are consistent with the theoretical predictions of Ref. [23], for the same normalized absorption strength of $\kappa = \alpha(\nu = \nu_0)L_{abs}/(1-R) \approx 3-14$ and $\Delta = (FWHM)_{laser}/(FWHM)_{abs} \approx 2$.

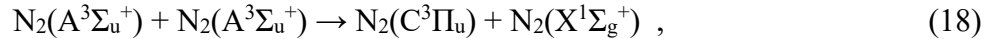
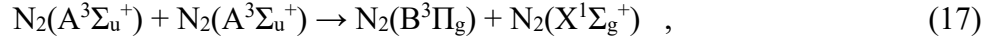
Time resolved CRDS data are taken in the discharge afterglow, by varying the time delay of the laser pulse with respect to the discharge burst, as shown in Fig. 4. Measurements during the discharge burst are considerably more challenging, due to the variation of the $N_2(A^3\Sigma_u^+)$ number density on the time scale comparable with the ring down time, and due to the significant EMI interference of the discharge with the dye laser and the data acquisition system. For each vibrational state, isolated rotational lines are used to infer the temporal evolution of the absolute populations of vibrational levels of $N_2(A^3\Sigma_u^+, v=0-2)$ at $t = 50 \mu s - 2.05 ms$ after the last discharge pulse. The results are plotted in Fig. 12. For these measurements, the probe beam is tuned to 766.8544 nm, 753.6459 nm, and 752.7218 nm, respectively, which corresponds to rovibrational transitions $R_{11}(20)$ for $N_2(B, v'=2 \leftarrow A, v''=0)$, $^S R_{32}(12)$ for $N_2(B, v'=3 \leftarrow A, v''=1)$, and $^N P_{13}(6)$ for $N_2(B, v'=4 \leftarrow A, v''=2)$ vibrational bands. During the measurements, the laser wavelength and linewidth are monitored continuously by the wavemeter. After the absorption transitions are identified, the number density of a particular vibrational level of $N_2(A^3\Sigma_u^+)$ is determined from Eq. (16a), using the vibrational cross section, $A_{\gamma}^{v''}$ in column VIII of Table 2 and assuming the temperature in the afterglow of $T=300 K$. The peak rotational and vibrational populations for CRDS at 22 Torr for 50 μs and TDLAS at 132 Torr are listed in Table 3.

The assumption of 300 K is justified by estimating an upper bound temperature rise in the plasma from the coupled pulse energy and the plasma volume at these conditions, $\sim 1 K/pulse$. It is also consistent with the temperature inferred from TDLAS scans taken at a higher pressure of 132 Torr, discussed below. The uncertainty of the inferred number densities for CRDS is evaluated from the standard deviation of the inferred line-integrated absorption coefficient, as the laser is scanned across the absorption line, at the peak of the transition with an average of 15 laser shots. The estimated uncertainty of the number densities inferred from the TDLAS measurements, based on the upper bound difference between the vibrational cross sections listed in Table 2, temperature uncertainty and the uncertainty in the plasma length, is approximately 10%.

Table 3. Selected vibrational-rotational and vibrational level populations

Transition	Absorption Coefficient, α (cm ⁻¹ ·Hz)	$N(v'', \gamma'')$ (cm ⁻³)	$N(v'')$ (cm ⁻³)
$v''=0$, R ₁₁ (20), N''=19, J''=20, λ_0 (nm) = 766.854	$1.04 \cdot 10^5$	$(2.20 \pm 0.72) \cdot 10^{10}$	$(2.51 \pm 0.82) \cdot 10^{12}$
$v''=1$, ^S R ₃₂ (12), N''=12, J''=12, λ_0 (nm)= 753.646	$1.47 \cdot 10^5$	$(5.45 \pm 3.04) \cdot 10^{10}$	$(4.18 \pm 2.32) \cdot 10^{12}$
$v''=2$, ^N P ₁₃ (6), N''=7, J''=6, λ_0 (nm) = 752.721	$4.74 \cdot 10^4$	$(5.87 \pm 1.94) \cdot 10^{10}$	$(2.18 \pm 0.72) \cdot 10^{12}$
$v''=0$, Q ₁₁ (12), N''=11, J''=12, λ_0 (nm) = 773.215	$1.50 \cdot 10^6$	$(2.03 \pm 0.20) \cdot 10^{11}$	$(6.61 \pm 0.66) \cdot 10^{12}$
$v''=1$, ^O P ₁₂ (12), N''=12, J''=12, λ_0 (nm) = 764.638	$1.09 \cdot 10^6$	$(4.96 \pm 0.62) \cdot 10^{11}$	$(3.02 \pm 0.47) \cdot 10^{13}$

From Fig. 12, plotting the time-resolved number densities of $N_2(A^3\Sigma_u^+, v=0-2)$, it can be seen that at the end of the discharge burst, the populations of vibrational levels $v=0,1$ exceed that of $v=2$ significantly. $N_2(A^3\Sigma_u^+, v=0,1)$ populations after the discharge burst appear to follow a single exponential decay with the characteristic time of 500 μ s, indicating that at these conditions, rapid energy pooling processes with nearly gas kinetic rates [1], such as



are insignificant, due to the low $N_2(A^3\Sigma_u^+, v=0,1)$ number densities. At the present conditions, the decay of $N_2(A^3\Sigma_u^+, v=0,1)$ populations in the afterglow is most likely due to the quenching by N atoms generated during the discharge burst.

The fact that the $N_2(A^3\Sigma_u^+, v=0-2)$ decay time after the discharge burst is much longer compared to the ring down time demonstrates that the non-single exponential ring down decay shown in Fig. 4 is due to the laser linewidth, rather than the temporal variation of the absorbing species number density. The effect of kinetic processes on time-resolved CRDS measurements, at the conditions when the lifetime of the absorbing species is shorter compared to the ring down decay time, have been analyzed previously [15,34,35]. However, at the present conditions this effect is minor compared to that of the laser linewidth.

To understand the $N_2(A^3\Sigma_u^+)$ population kinetics both during the ns discharge burst and in the afterglow, we used TDLAS measurements. Since the single pass absorption was below

detection limit of the present diagnostics for pressures below 80 Torr, TDLAS measurements were taken at a pressure of 132 Torr, during and after the discharge bursts 1-5 pulses long. Figure 13 shows a scan of the cw diode laser across six rotational lines in the $N_2(B, v'=2 \leftarrow A, v''=0)$ vibrational band and two rotational lines in the $N_2(B, v'=3 \leftarrow A, v''=1)$ vibrational band. These data are taken 40 μs after the last discharge pulse, and every data point is averaged over 50 discharge bursts. It can be seen that the peak absorption coefficient of $\sim 10^{-3}$ is measured, with the detection limit below $\sim 10^{-4}$. Figure 13 also compares these data with the best fit synthetic spectra, where the rotational line intensity distribution and a Voigt profile spectral line fit are used to infer the rotational-translational temperature and the pressure broadening parameter. The spectral line fit and the line intensity ratio for the two vibrational bands give a rotational-translational temperature of $T = 295 \pm 10$ K with the broadening parameter of $2\gamma = 0.19 \text{ cm}^{-1} \cdot \text{atm}^{-1}$ ($5.7 \text{ GHz} \cdot \text{atm}^{-1}$)

For time-resolved TDLAS measurements, the diode laser wavelength is tuned to the peak absorption of the rotational lines $Q_{11}(12)$ for $N_2(B, v'=2 \leftarrow A, v''=0)$ and $^oP_{12}(12)$ for $N_2(B, v'=3 \leftarrow A, v''=1)$, and the absorption signal, averaged over 200 bursts, is measured during the entire discharge pulse burst and in the afterglow, as shown schematically in Fig. 4. The results are plotted in Fig. 14, which shows absolute number densities of $N_2(A^3\Sigma_u^+, v=0,1)$ during and after the discharge, for a single pulse and for a 5-pulse burst. It can be seen that after each discharge pulse, the $N_2(A)$ populations increase, as expected. The rise time ranges from 20 to 50 μs , with that of the $v=0$ population noticeably longer compared to that of $v=1$. Since the discharge pulse duration is approximately 100 ns (see Fig. 3), this indicates that at the present conditions, $N_2(A^3\Sigma_u^+, v=0)$ molecules are produced primarily by radiative and collisional decay of higher energy excited electronic states, rather than by direct electron impact [1].

Between the pulses, the $N_2(A)$ populations first level off and then begin to decay. Peak $N_2(A^3\Sigma_u^+, v=0,1)$ number densities of $6 \cdot 10^{12} \text{ cm}^{-3}$ and $3 \cdot 10^{13} \text{ cm}^{-3}$ are detected after the pulses #3 and #4 and these values are listed in Table 3. The rate of the population decay accelerates during the discharge burst, from 460 μs after a single pulse to 160 μs after a 5-pulse burst (see Fig. 14), such that the peak number densities measured after pulse #5 are levelling off. This occurs in spite of the coupled discharge pulse energy remaining constant, within 5%, during the entire pulse burst, and suggests that the quenching species accumulate in the plasma during the burst. The population decay after the discharge is a single exponential, with the characteristic decay time of 160 μs for a 5-pulse burst, significantly faster compared to that inferred from the CRDS measurements after a 10-pulse burst at the pressure of 22 and 39 Torr (see Fig. 12). Although faster decay of $N_2(A^3\Sigma_u^+, v=0,1)$ number densities at the higher pressure of 132 Torr is expected, leveling off of the peak populations and acceleration of their decay during the discharge burst are not completely understood. This may be caused by accumulation of vibrationally excited N_2 molecules in the ground electronic state or N atoms, both generated by electron impact during the discharge burst. Comparison with the kinetic modeling predictions may provide quantitative insight into the state-specific processes of $N_2(A^3\Sigma_u^+)$ population and decay in a ns pulse discharge and the afterglow.

5. Summary

In the present work, absolute time-resolved populations of the metastable excited electronic state of nitrogen, $N_2(A^3\Sigma_u^+)$, generated in a diffuse repetitive ns pulse discharge in nitrogen have been measured by CRDS and TDLAS. CRDS measurements of $N_2(A^3\Sigma_u^+, v=0-2)$ populations have been made in the discharge afterglow at relatively low pressures of 22 and 39 Torr. The CRDS

data reduction procedure takes into account the effect of the laser linewidth, which is comparable with the absorption linewidth at the present conditions, on the ring down decay. A number of rovibrational absorption transitions in $N_2(B, v'=2 \leftarrow A, v''=0)$, $N_2(B, v'=3 \leftarrow A, v''=1)$, and $N_2(B, v'=4 \leftarrow A, v''=2)$ vibrational bands have been identified from the CRDS spectra. Peak $N_2(A^3\Sigma_u^+, v=0,1)$ populations measured after a 10-pulse ns discharge burst are in the range of 10^{12} - 10^{13} cm^{-3} . In the afterglow, these populations exhibit a relatively slow, single exponential decay with the characteristic time of approximately 500 μs , most likely due to quenching by N atoms. Complementary TDLAS data have been taken at a higher pressure of 132 Torr, when the $N_2(A^3\Sigma_u^+)$ number density is over an order of magnitude higher compared to the conditions used in the low-pressure CRDS measurements. Absolute time-resolved $N_2(A^3\Sigma_u^+, v=0,1)$ number densities are measured during ns discharge bursts of 1-5 pulses and in the afterglow, peaking at $6 \cdot 10^{12}$ cm^{-3} and $3 \cdot 10^{13}$ cm^{-3} , respectively. The results indicate that $N_2(A^3\Sigma_u^+)$ is generated after every discharge pulse, on a 20-50 μs time scale, and decays between the pulses. The decay rate increases during the discharge burst, indicating accumulation of the quenching species. In the afterglow, $N_2(A^3\Sigma_u^+, v=0,1)$ populations decay significantly more rapidly compared to the low-pressure CRDS conditions, exhibiting a single-exponential decay with the characteristic time of about 160 μs after a 5-pulse burst.

The results demonstrate that both CRDS and TDLAS diagnostics can be used for time-resolved, absolute $N_2(A^3\Sigma_u^+)$ measurements in transient nonequilibrium plasmas and the afterglow, with detection limit of $\sim 10^{10}$ - 10^{12} cm^{-3} , respectively. The data obtained using these two diagnostics are complementary, since TDLAS measurements can be used at the conditions when the $N_2(A^3\Sigma_u^+)$ populations may be too high, or vary too rapidly for the accurate CRDS measurements. The present results also show feasibility of the use of $N_2(A^3\Sigma_u^+)$ measurements by TDLAS and CRDS in more challenging environments, such as nonequilibrium supersonic flows, where vibrationally and electronically excited molecules are generated by a repetitively pulsed ns discharge overlapped with a DC discharge in the high-temperature plenum, upstream of the supersonic expansion [36,37].

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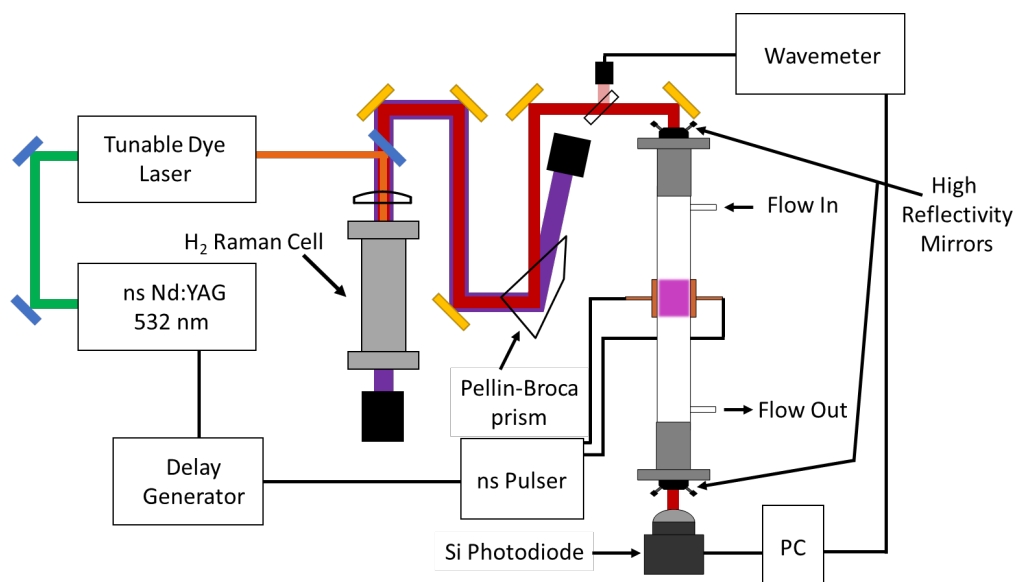


Figure 1. Schematic diagram of the Cavity Ring Down Spectroscopy experimental apparatus.

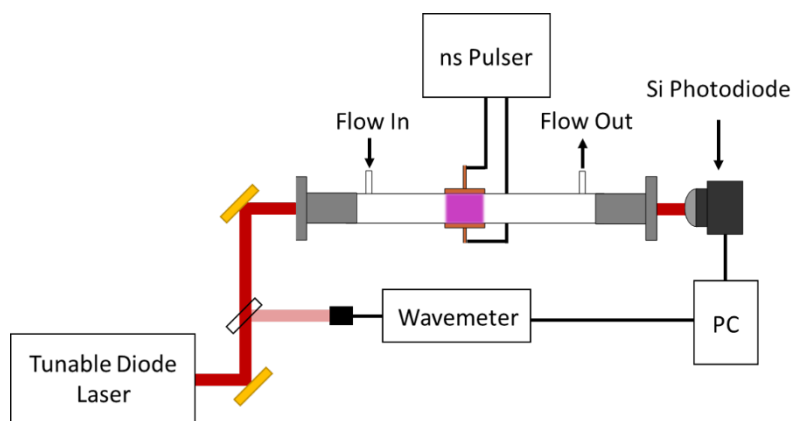


Figure 2. Schematic diagram of the Tunable Diode Laser Absorption Spectroscopy experimental setup.

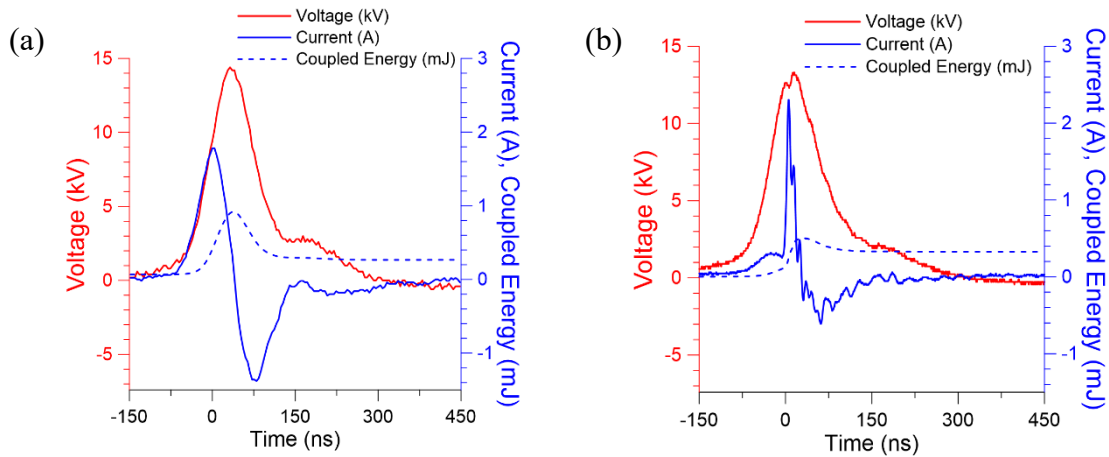


Figure 3. Typical ns pulse discharge voltage, current, and coupled energy waveforms, (a) P=22 Torr, and (b) P=132 Torr.

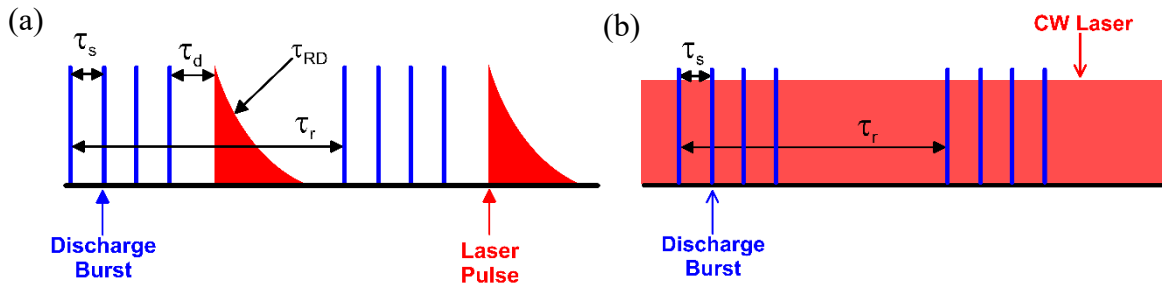


Figure 4. Discharge pulse and laser timing schemes for (a) CRDS and (b) TDLAS experiments. Time separation between the discharge pulses in the burst $\tau_s=100 \mu\text{s}$ (pulse repetition rate 10 kHz), time delay between the last discharge pulse in the burst and the laser pulse $\tau_d = 50 \mu\text{s} - 2.05 \text{ ms}$, empty cavity ring down time $\tau_{RD} = 115 \mu\text{s}$, time interval between the discharge bursts $\tau_r = 100 \text{ ms}$ (burst repetition rate 10 Hz).

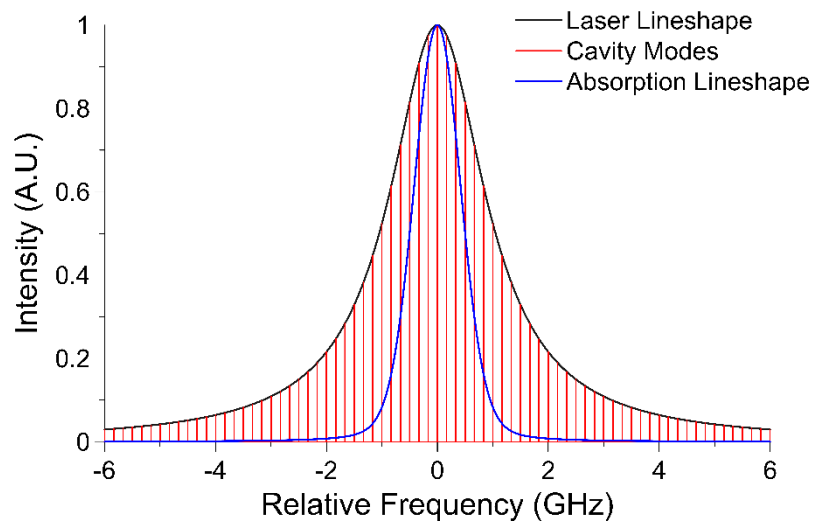


Figure 5. Schematic of the N_2 absorption line profile at $T=300$ K and $P=22$ Torr, with FWHM of 920 MHz dominated by the Doppler broadening; laser line profile, assumed to be Lorentzian with the measured FWHM linewidth of 2100 MHz; and coupled cavity modes.

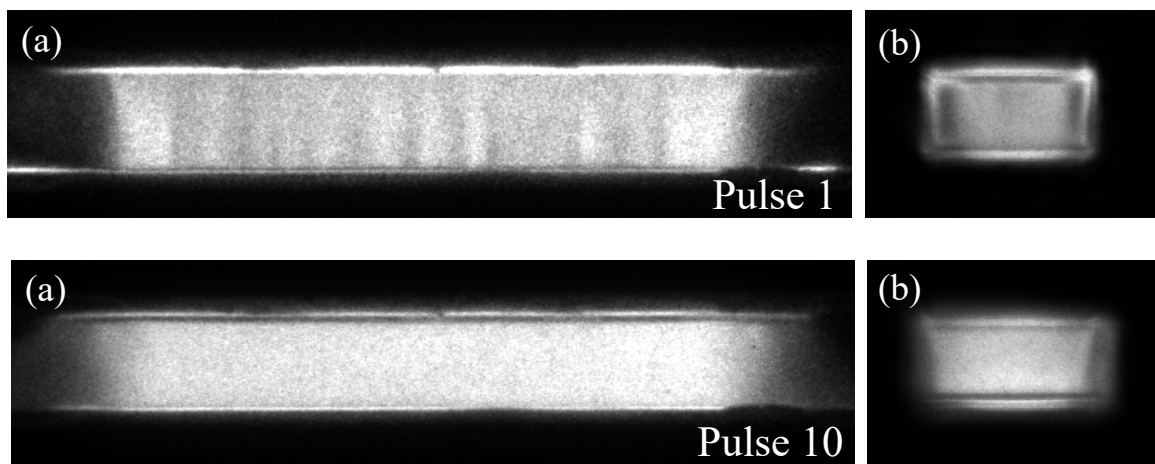


Figure 6. Single-shot, broadband nitrogen plasma emission images taken during a 10-pulse ns discharge burst, for pulses #1 and #10: (a) side view, (b) end view. $P=20$ Torr, camera gate 300 ns.

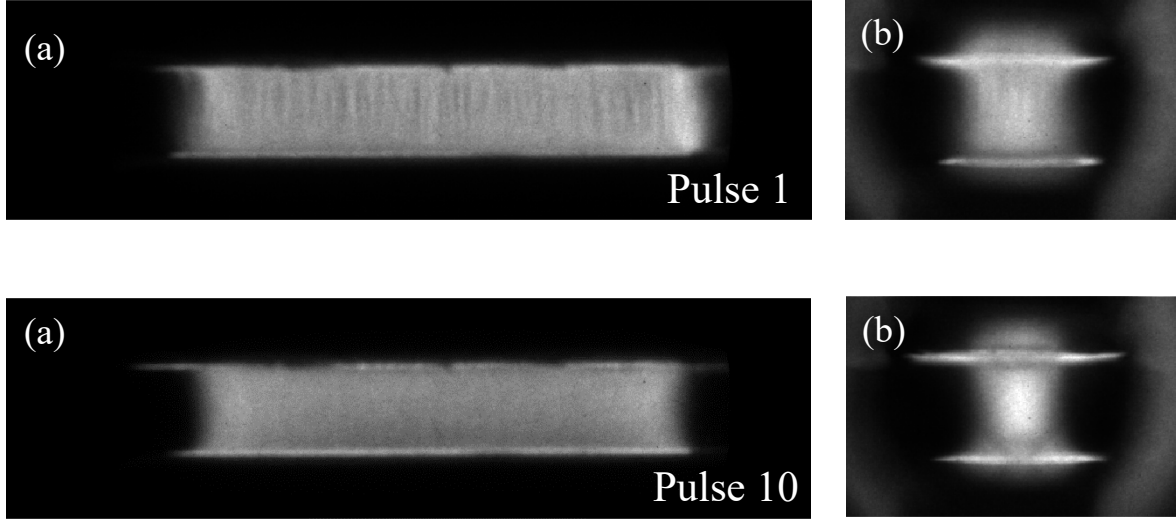


Figure 7. Single-shot, broadband nitrogen plasma emission images taken during a 10-pulse ns discharge burst, for pulses #1 and #10: (a) side view, (b) end view. $P=132$ Torr, camera gate 200 ns.

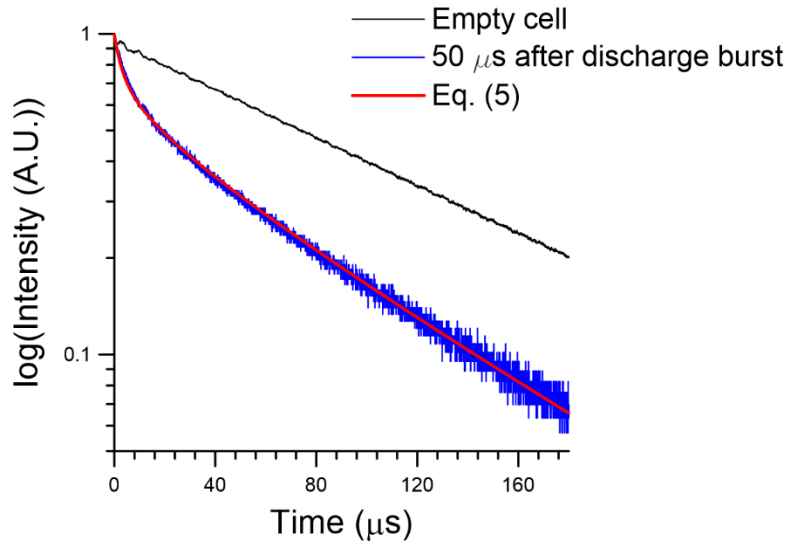


Figure 8. Typical cavity ring down traces for an empty cell and a 10-pulse ns discharge afterglow at $P=22$ Torr, $50 \mu\text{s}$ after the last discharge pulse. The ring down trace obtained from the data reduction (Eq. (5)), for the inferred value of the line-integrated absorption coefficient, is also shown by the red line.

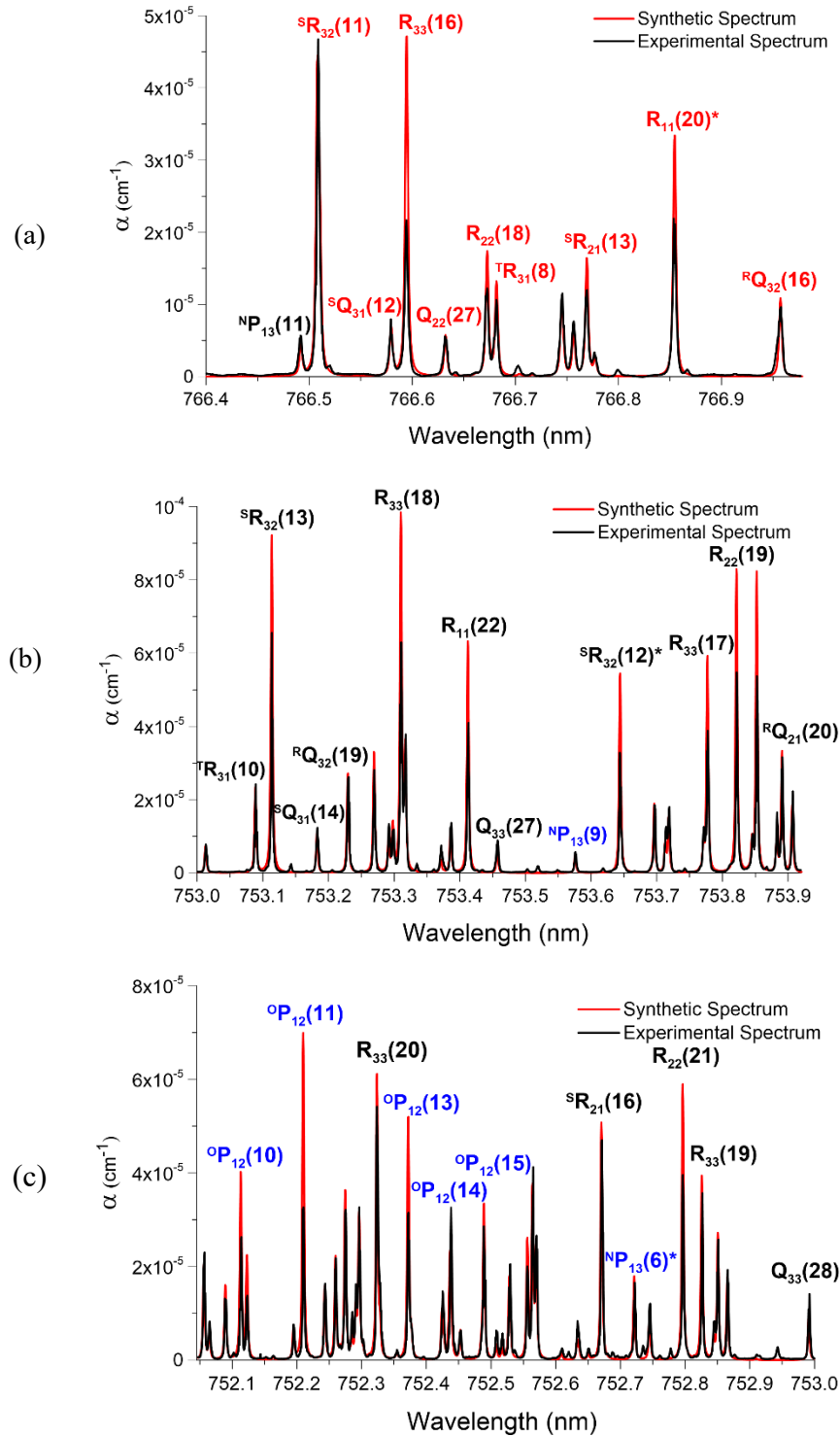


Figure 9. $N_2(A^3\Sigma_u^+)$ CRDS spectra taken 50 μs after a 10-pulse ns discharge burst at P=22 Torr: (a) $N_2(B^3\Pi_g, v=2 \leftarrow A^3\Sigma_u, v=0)$, (b) $N_2(B^3\Pi_g, v=3 \leftarrow A^3\Sigma_u, v=1)$, (c) $N_2(B^3\Pi_g, v=4 \leftarrow A^3\Sigma_u, v=2)$. The absorption transitions are labeled in different colors, red for $v''=0$, black for $v''=1$, blue for $v''=2$. The lines marked with an asterisk are used for the inference of the time-resolved vibrational populations of $N_2(A^3\Sigma_u^+)$.

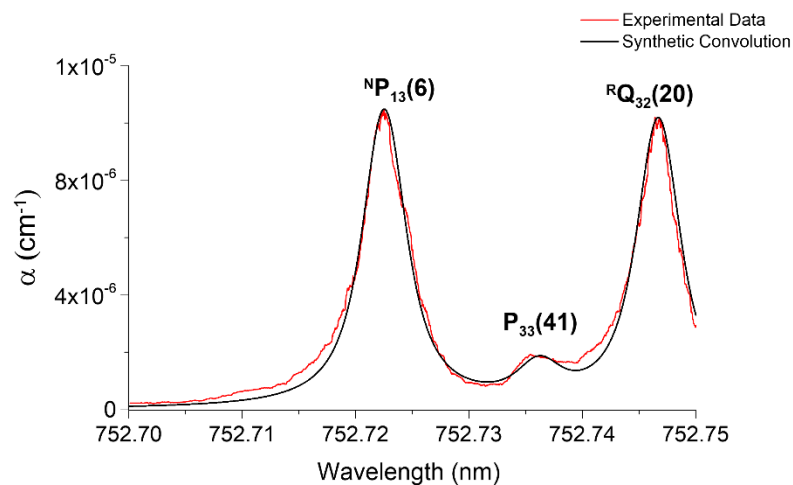


Figure 10. Comparison of the calculated convolution of the laser line shape (Lorentzian profile) and absorption line shapes (Voigt profile) with the apparent absorption line shape, at P=22 Torr.

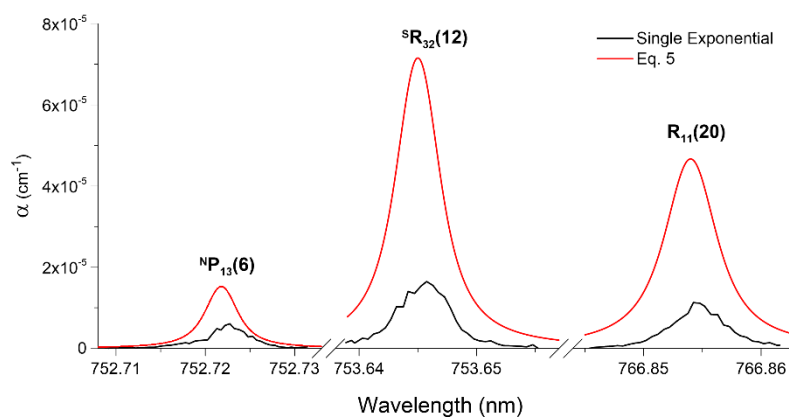


Figure 11. Comparison of the spectral absorption coefficient obtained from a single exponential fit and from Eq. (5), for three vibrational-rotational transitions used for $N_2(A^3\Sigma_u^+, v=0-2)$ vibrational population inference. P=39 Torr, 50 μ s after the discharge burst. Strong underprediction of the single exponential fit data is readily apparent.

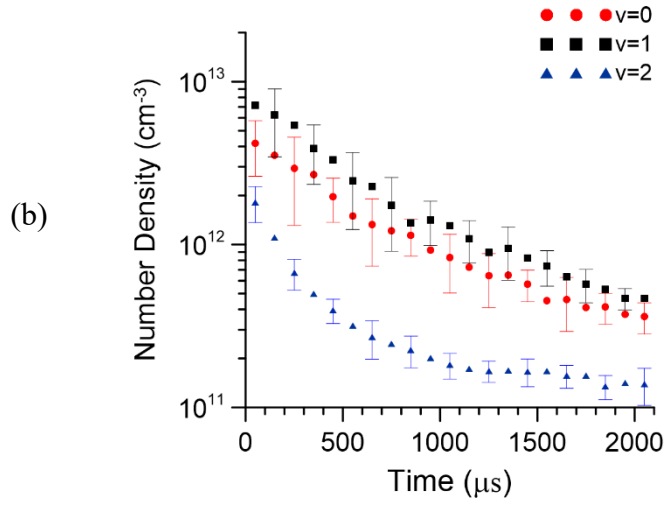
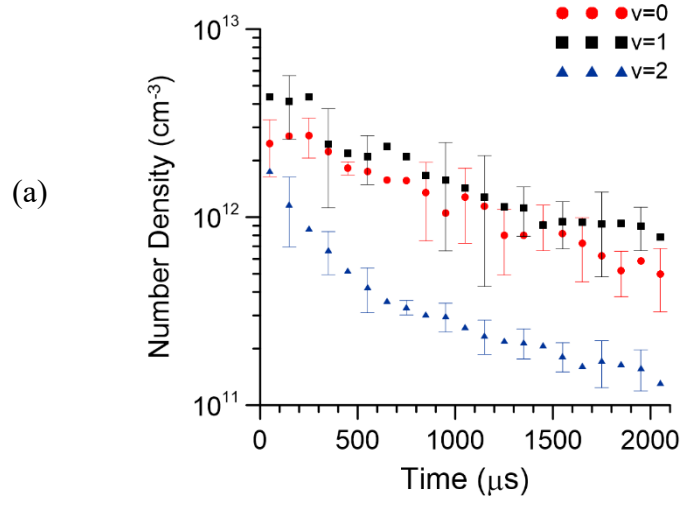


Figure 12. Time-resolved $\text{N}_2(\text{A}^3\Sigma_u^+, v=0, 1, 2)$ vibrational level populations after a 10-pulse ns discharge in nitrogen: (a) $P=22$ Torr, (b) $P=39$ Torr.

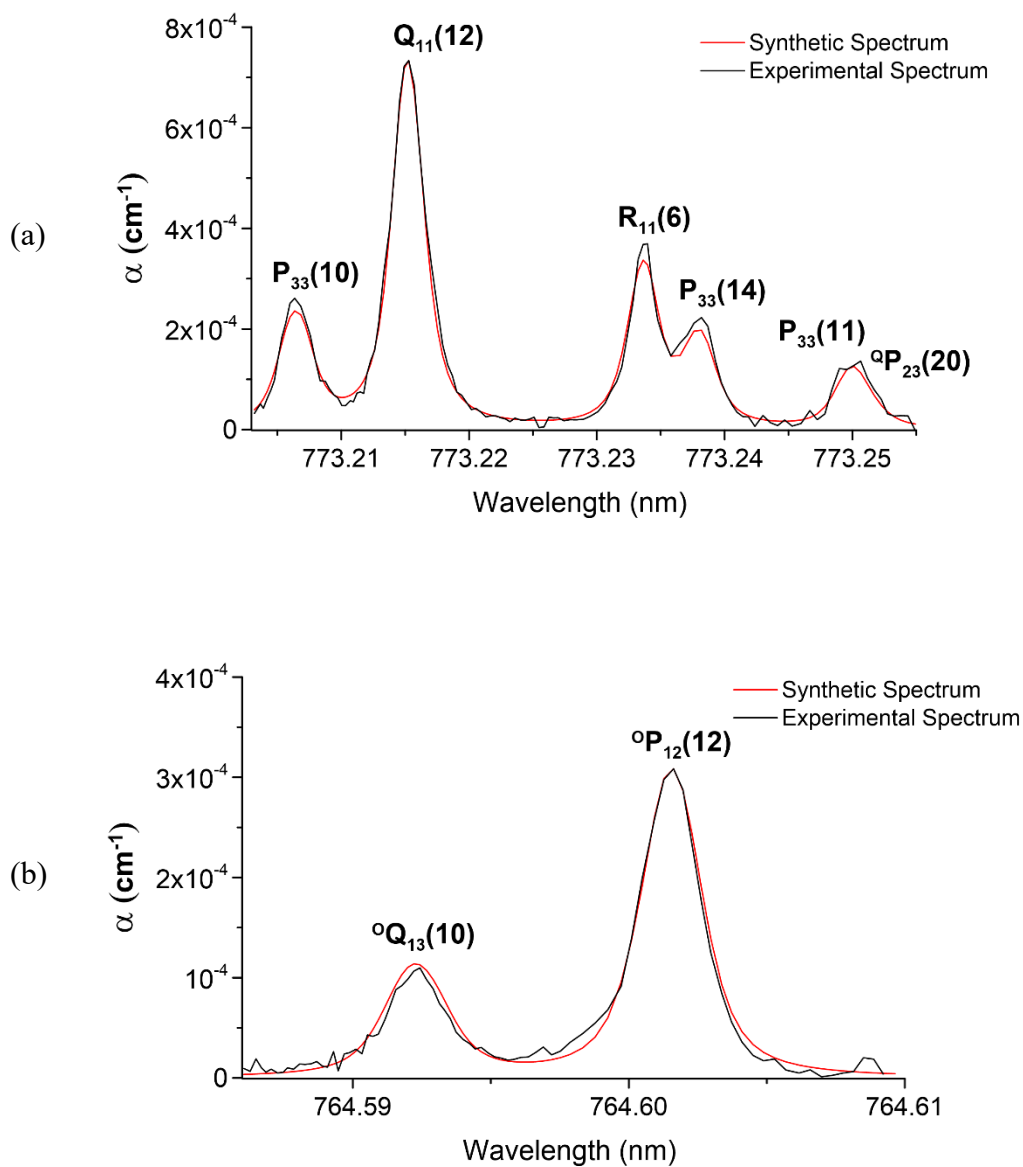


Figure 13. TDLAS scans of (a) 6 rotational lines in the N₂(B³Π_g, v = 2 ← A³Σ_u⁺, v = 0) band, and (b) 2 rotational lines in the N₂(B³Π_g, v = 3 ← A³Σ_u⁺, v = 1) band. P=132 Torr, 5-pulse ns discharge burst, 40 μs after the last pulse. Inferred rotational-translational temperature is T = 295 ± 10 K.

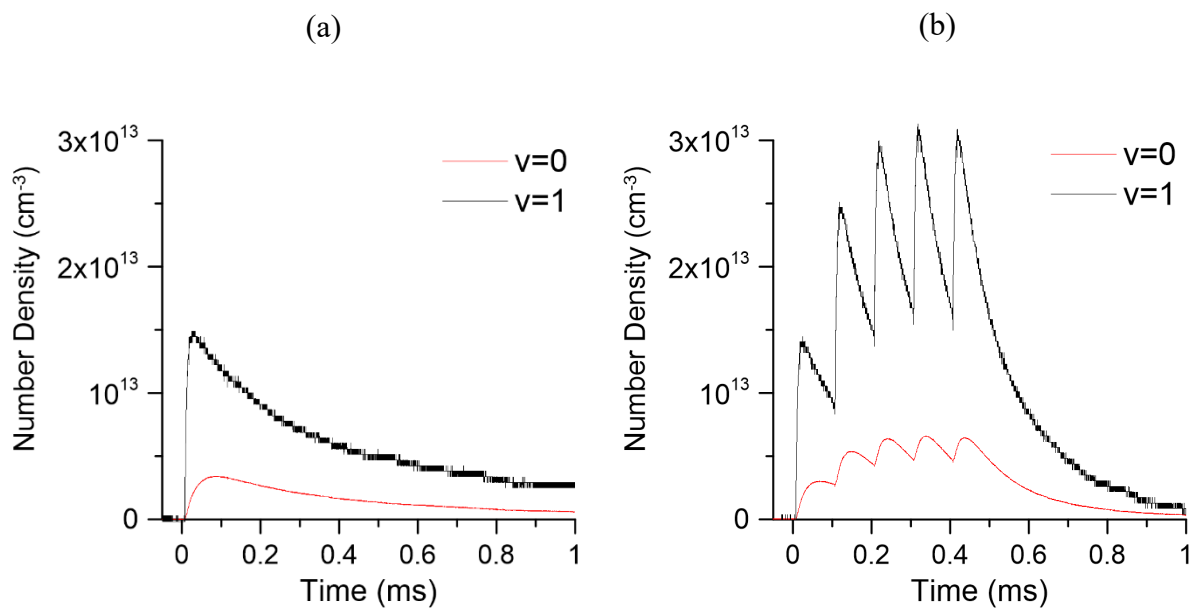
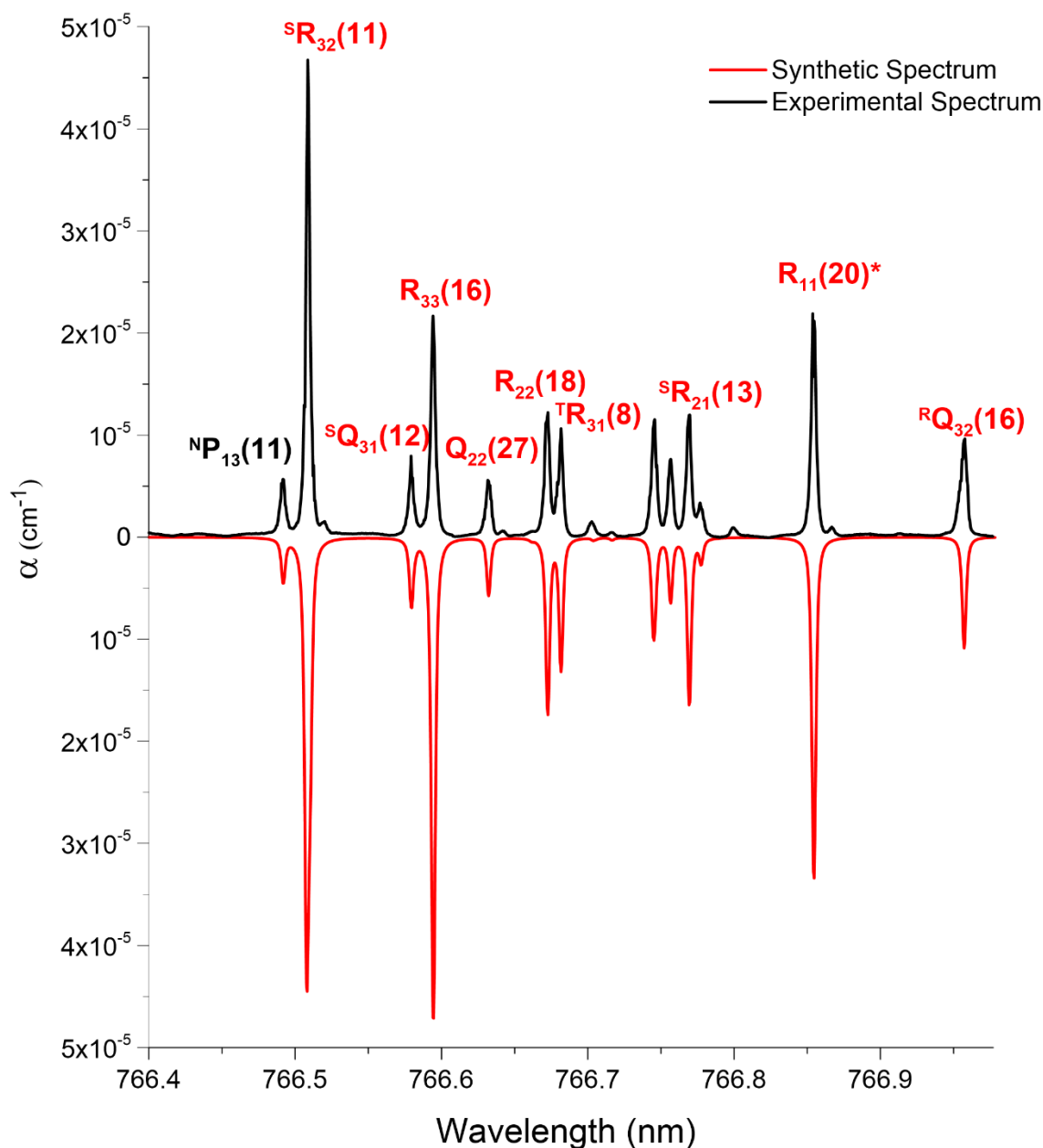
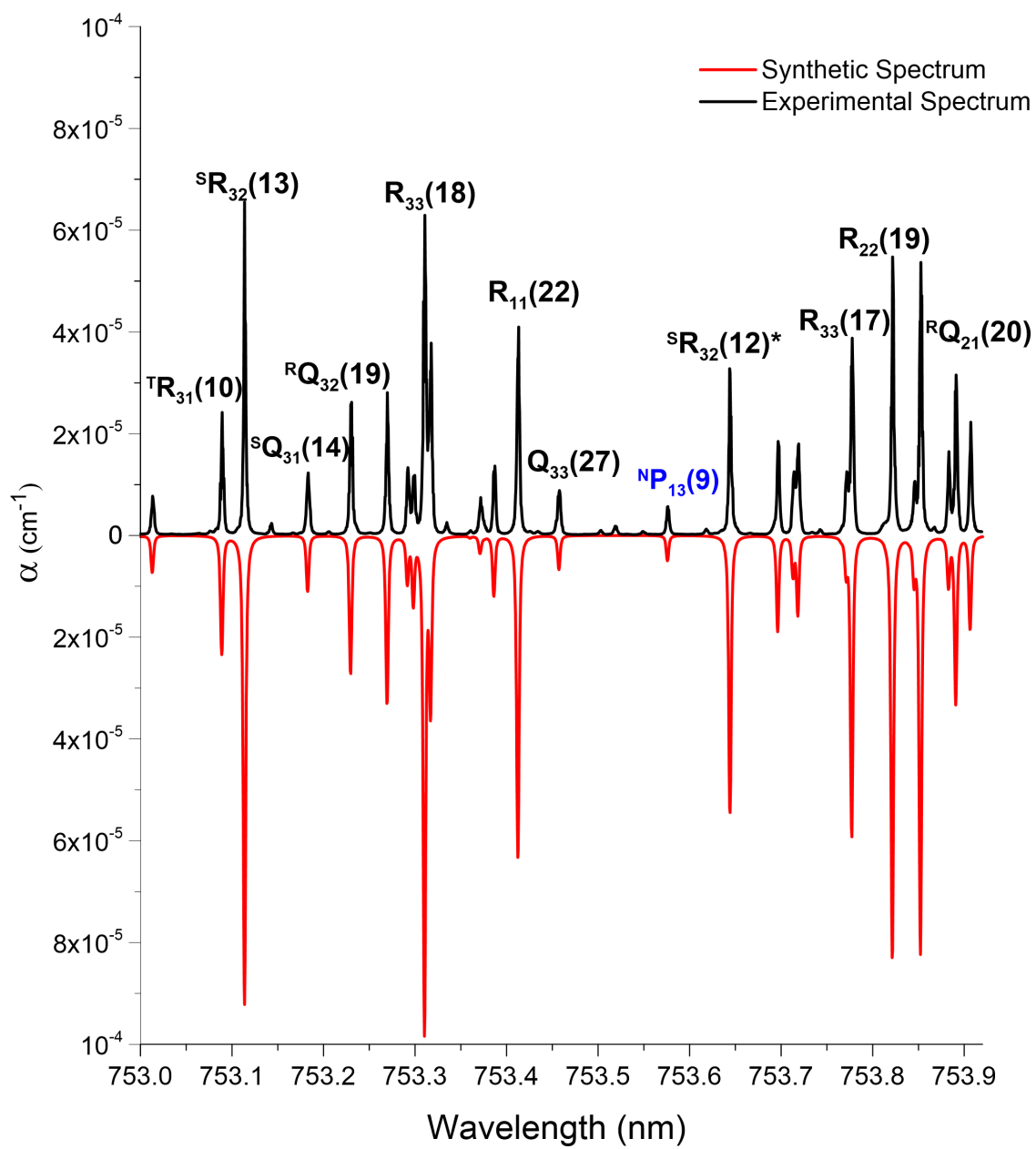


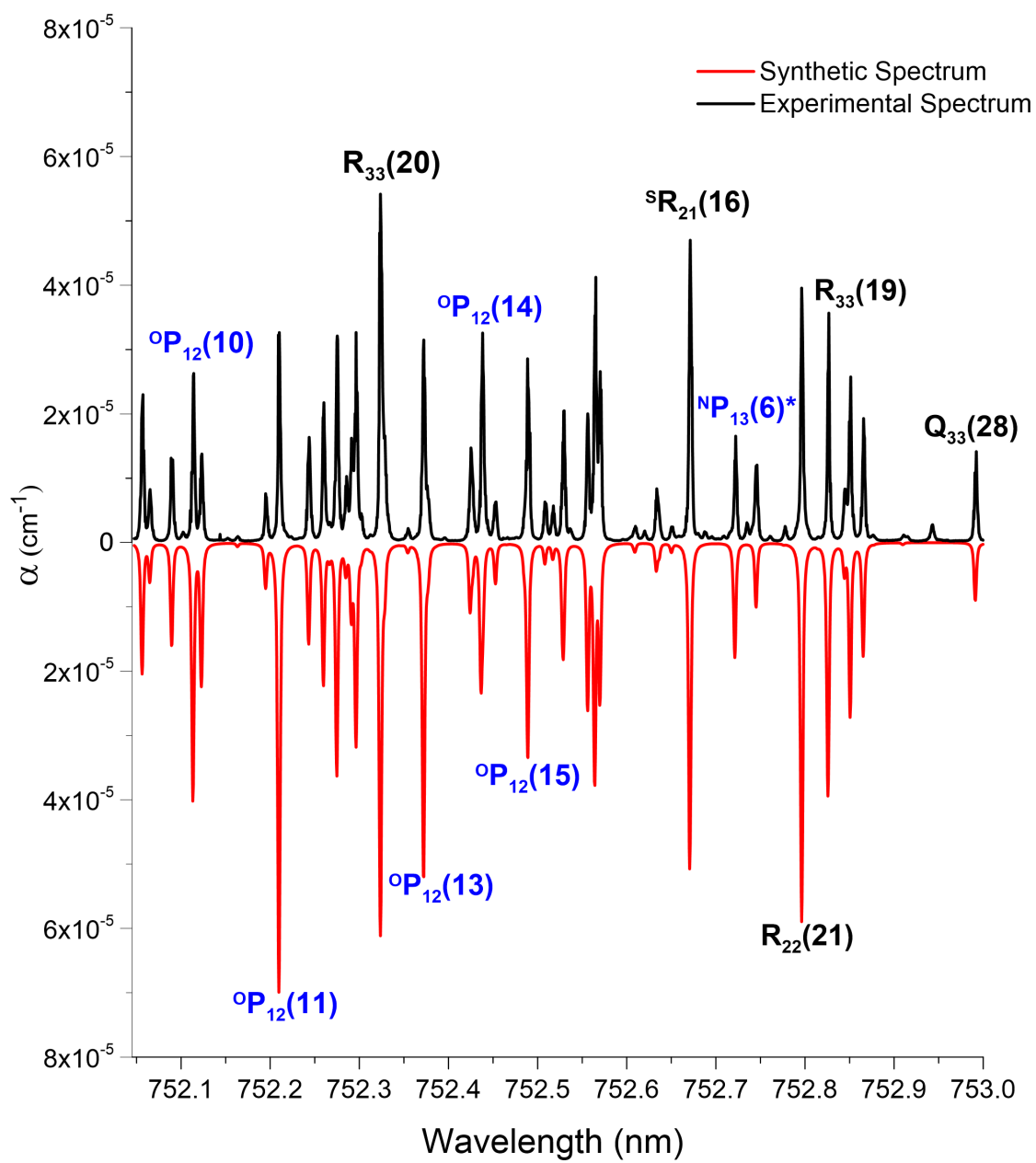
Figure 14. Time-resolved absolute populations of $N_2(A^3\Sigma_u^+, v=0,1)$ vibrational levels during the ns discharge burst and the afterglow at $P=132$ Torr, (a) for a single discharge pulse, and (b) for a 5-pulse burst.

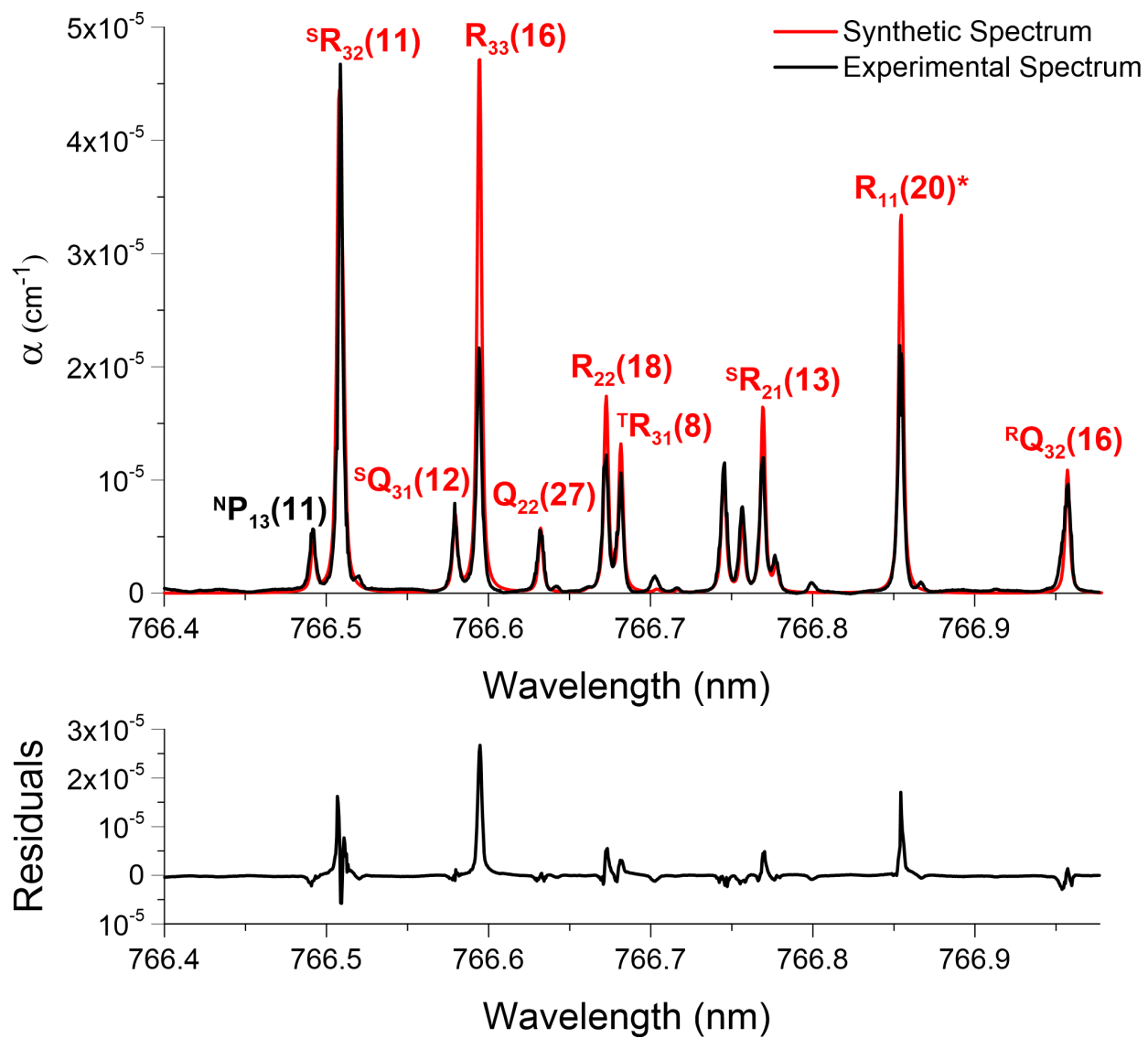
Supplemental Material

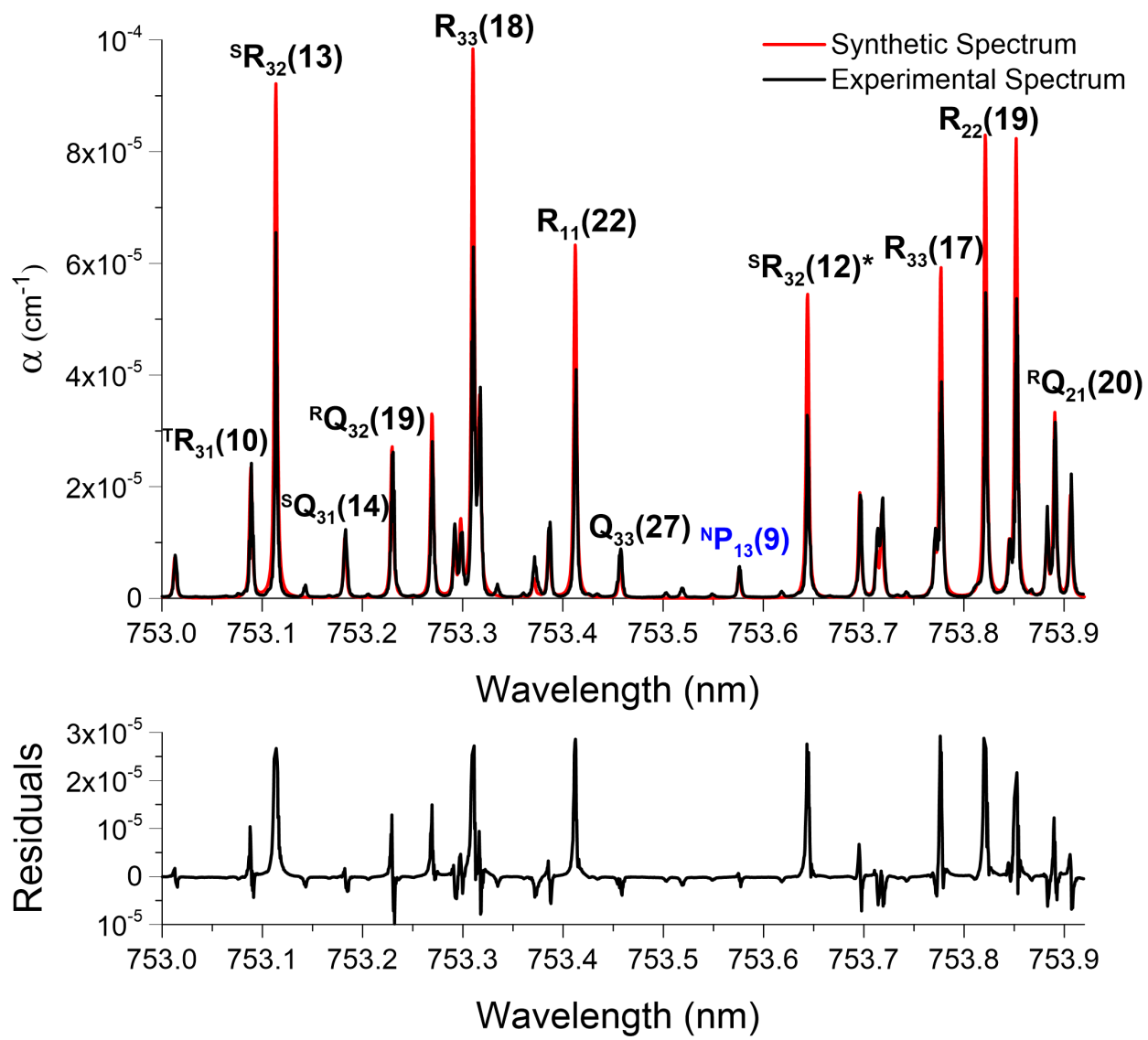
Figure S1. $N_2(A^3\Sigma_u^+)$ CRDS spectra taken 50 μ s after a 10-pulse ns discharge burst at P=22 Torr: (a,d) $N_2(B^3\Pi_g, v=2 \leftarrow A^3\Sigma_u, v=0)$, (b,e) $N_2(B^3\Pi_g, v=3 \leftarrow A^3\Sigma_u, v=1)$, (c,f) $N_2(B^3\Pi_g, v=4 \leftarrow A^3\Sigma_u, v=2)$. The absorption transitions are labeled in different colors, red for $v''=0$, black for $v''=1$, blue for $v''=2$. The lines marked with an asterisk are used for the inference of the time-resolved vibrational populations of $N_2(A^3\Sigma_u^+)$. In panels (a-c), the synthetic spectra are inverted for illustration purposes, in panels (d-f), the residuals (i.e. the difference between the experimental and synthetic spectra) are also plotted.

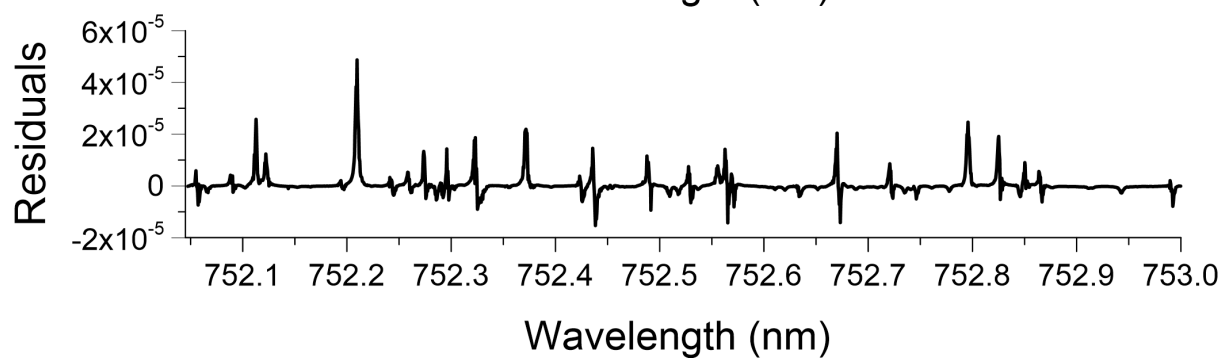
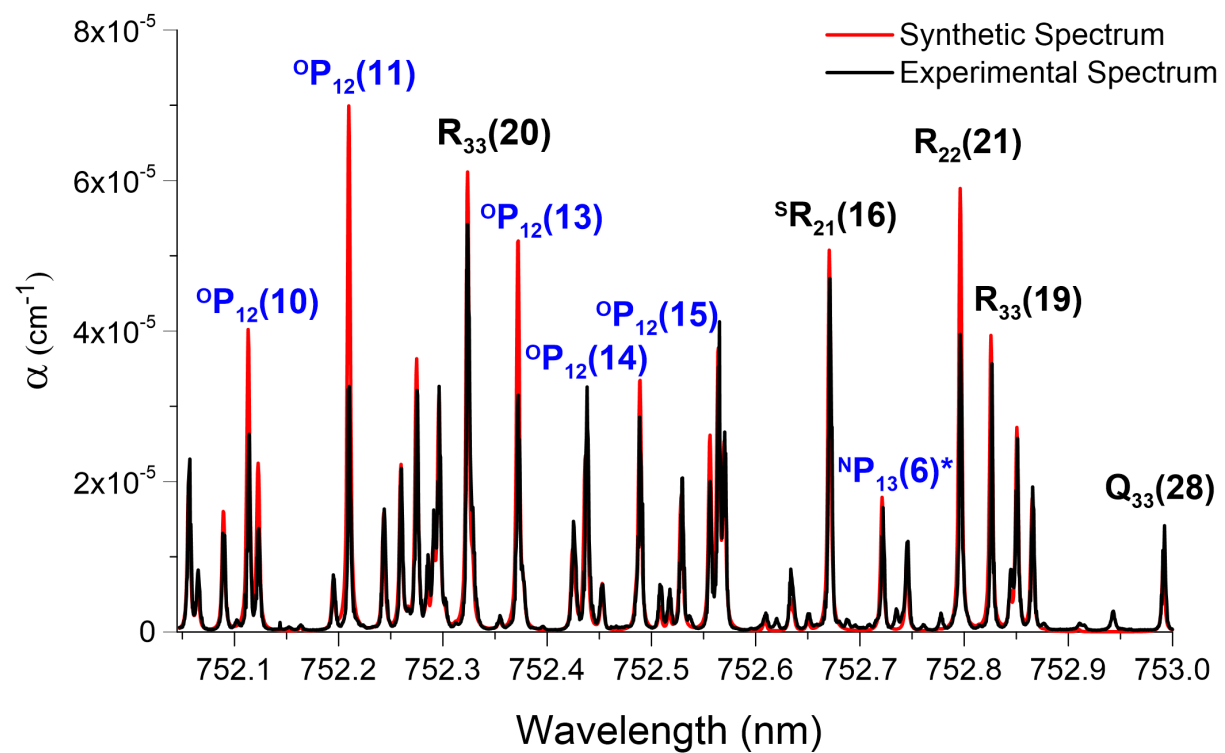












PART II.

KINETIC MECHANISMS OF $N_2(A^3\Sigma_u^+,v)$ GENERATION AND DECAY IN HIGH-PRESSURE NONEQUILIBRIUM PLASMAS ²

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 $Ar(3p^54s)$. 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,

² E.R. Jans, S. Raskar, X. Yang, and I.V. Adamovich, “Kinetics of Metastable $N_2(A^3\Sigma_u^+,v)$ Molecules in High-Pressure Nonequilibrium Plasmas”, *Plasma Sources Science and Technology* 30 (2021) 025003

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 $\frac{1}{4}$ 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 / N_2 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 $1.6 \cdot 10^{15}$ molecules/s, over 5 orders of magnitude lower compared to the flow rate, $5.3 \cdot 10^{20}$ molecules/s, such that the upper bound oxygen and water vapor impurity level is $\sim 10^{-6}$ and $\sim 10^{-7}$ 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 $N_2(A^3\Sigma_u^+,v)$ 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 $N_2(A^3\Sigma_u^+)$ 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 $\sim 10^{-3}$). Some of the TDLAS measurements have been performed using a double-pass absorption setup, 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 N_2 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. 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], $N_2(A^3\Sigma_u^+, v)$ absolute populations are inferred from the single-pass or double-pass absorption data as follows,

$$N(v'') = \frac{\alpha(v)}{f_{J''}^{v''} k_{v0} g_A(v)}, \quad (1)$$

where $\alpha(v)$ is the spectral absorption coefficient, $f_{J''}^{v''}$ 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 in Section 3. The absorption line positions and absolute line intensities are taken from the computer program Pgopher [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,

$$\frac{\alpha_1}{\alpha_2} = \frac{\Phi_1 \cdot S_1}{\Phi_2 \cdot S_2} \exp \left\{ \frac{hc}{k_B T} [E(N_2'') - E(N_1'')] \right\}, \quad (2)$$

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 Hönl-London factor for each transition. In the present TDLAS measurements, we used absorption transitions $R_{11}(6)$ and $P_{33}(14)$ in the $N_2(B^3\Pi_g, v' = 2 \leftarrow A^3\Sigma_u^+, v'' = 0)$ 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 ,

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

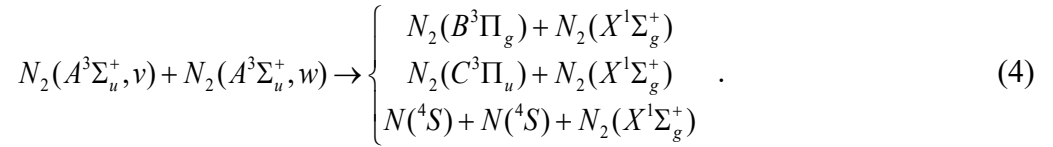
During the pressure broadening measurements, the pressure and the discharge burst duration were varied, to ensure independent variation of pressure and temperature.

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 $a'^1\Sigma_u^-$, $B^3\Pi_g$, 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 $B^3\Sigma_u^-$.

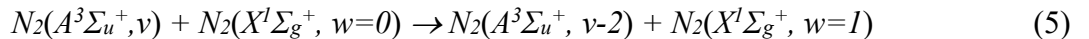
Our recent work [13] indicated that the rate of $N_2(A^3\Sigma_u^+)$ decay between the discharge pulses in nitrogen is significantly underpredicted, almost certainly due to the underprediction of the number density of N atoms generated by the electron impact dissociation from the ground electronic state 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.



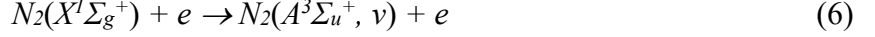
As mentioned in Ref. [24], N_2 dissociation in this process may be possible via the excitation of predissociated electronic states above the dissociation energy. Since the rate coefficient of this dissociation channel is not known, it was treated as an adjustable parameter. As will be shown in Section 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.

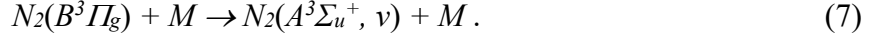
The vibrational quantum number dependence of the $N_2(A^3\Sigma_u^+, v)$ quenching rates, wherever available, is taken from Ref. [14]. The state-specific rates are one of the critical processes controlling the $N_2(A^3\Sigma_u^+, v)$ populations between the discharge pulses, the “2-by-1” vibration-vibration (V-V) energy exchange with the ground electronic state nitrogen,



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,

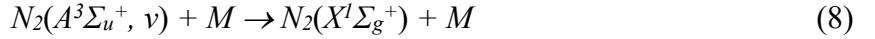


and the collisional quenching of $N_2(B^3\Pi_g)$ state,



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.



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_2H_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 $\sim 5\%$, 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 $N_2(A^3\Sigma_u^+)$ 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, $L_a = 6.0 \pm 0.5$ cm.

High resolution TDLAS $N_2(A^3\Sigma_u^+, v''=0,1)$ 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 6 and 7, plotted on the same scale, compare the experimental and synthetic TDLAS spectra for $N_2(B^3\Pi_g, v' = 2 \leftarrow A^3\Sigma_u^+, v'' = 0)$ and $N_2(B^3\Pi_g, v' = 3 \leftarrow A^3\Sigma_u^+, v'' = 1)$ 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, $T = 330 \pm 10$ K and $T = 360 \pm 20$ K, respectively, is inferred from the intensity ratio of $R_{11}(6)$ and $P_{33}(14)$ absorption transitions in the $v' = 2 \leftarrow v'' = 0$ 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, $\Delta E_{rot} = 303 \text{ cm}^{-1}$, 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 $N_2(B^3\Pi_g, v'=2 \leftarrow A^3\Sigma_u^+, v''=0)$

$Q_{11}(12)$ 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 $T=300 \pm 10$ 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 $2\gamma(T) = (4.79 \pm 0.10) \left(\frac{300}{T(K)} \right)^{0.61 \pm 0.15} \frac{\text{GHz}}{\text{atm}}$.

For the time-resolved TDLAS measurements, the diode laser wavelength is tuned to the centerline (peak absorption) of specific rotational transitions in $N_2(B, v'=2 \leftarrow A, v''=0)$, $N_2(B, v'=3 \leftarrow A, v''=1)$, $N_2(B, v'=3 \leftarrow A, v''=2)$, $N_2(B, v'=2 \leftarrow A, v''=4)$, and $N_2(B, v'=3 \leftarrow A, v''=5)$ bands, listed in Table 1.

Table 1. Absorption transitions used in TDLAS measurements and their wavelengths

Vibrational band	$v'=2 \leftarrow v''=0$	$v'=3 \leftarrow v''=1$	$v'=3 \leftarrow v''=2$	$v'=2 \leftarrow v''=4$	$v'=3 \leftarrow v''=5$
Rotational transition	$Q_{11}(12)$	${}^oP_{12}(9)$	$Q_{11}(10)$	$R_{33}(12)$	$Q_{11}(10)$
Wavelength, nm	773.215	764.291	852.120	1339.672	1300.115
k_{v0} , $\text{cm}^2 \cdot \text{Hz}$	$7.40 \cdot 10^{-6}$	$3.41 \cdot 10^{-6}$	$3.83 \cdot 10^{-6}$	$2.63 \cdot 10^{-6}$	$1.32 \cdot 10^{-6}$

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 $N_2(A^3\Sigma_u^+)$ 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 $N_2(A^3\Sigma_u^+, v=0-2)$ populations, 2-20 μs , is much longer compared to the decay time of the second positive band emission, $N_2(C^3\Pi_u, v'=0 \rightarrow B^3\Pi_g, v''=0)$ at 337 nm (~ 10 ns), and first positive band emission, $N_2(B^3\Pi_g, v'=2 \rightarrow A^3\Sigma_u^+, v''=0)$ at 770 nm (~ 100 ns). On the other hand, the rise time of $N_2(A^3\Sigma_u^+, v=4,5)$ populations is much shorter, 100-300 ns, and comparable to the first positive system emission decay time. The time-resolved $N_2(A^3\Sigma_u^+)$ 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, $v \geq 2$ (the process of Eq. (5)), following their initial population during the collisional quenching of $N_2(B^3\Pi_g)$, Eq. (7).

To determine the nascent vibrational distribution of $N_2(A^3\Sigma_u^+)$ created by the processes of Eq. (7), the model was exercised for different branching ratio for $N_2(B^3\Pi_g \rightarrow A^3\Sigma_u^+, v)$ quenching. Assuming that only $N_2(A^3\Sigma_u^+, v=6,7)$ are populated, with equal probabilities [26], resulted in a significantly longer rise time of $N_2(A^3\Sigma_u^+, v=1,2)$ 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 $N_2(A^3\Sigma_u^+, v'')$ vibrational populations are proportional to $N_2(B^3\Pi_g, v'=0) \xrightarrow{P(0 \rightarrow v'')} N_2(A^3\Sigma_u^+, v'')$ Franck-Condon factors, $k_7(v'') \sim P(0 \rightarrow$

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, $k_7(v'') \sim \sum_{v'=0-7} P(v' \rightarrow v'')$ (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 N_2 - H_2 , N_2 - O_2 , and N_2 - NO mixtures. Development of a non-empirical, state-specific model of energy transfer during $N_2(B^3\Pi_g, v' \rightarrow A^3\Sigma_u^+, v'')$ quenching would be highly desirable.

Figure 10(b) plots the predicted time-resolved $N_2(A^3\Sigma_u^+, v=0-5)$ populations after a single-pulse discharge in nitrogen at $P=250$ Torr, at the conditions of Fig. 9. It illustrates the cascade evolution of $N_2(A^3\Sigma_u^+, v)$ 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 $v=1$ and $v=0$, as discussed in Ref. [25]. Since the ratio of the V-V rate coefficients is greater than 1, $k_4(v=3 \rightarrow 1, w=0 \rightarrow 1) / k_4(v=2 \rightarrow 0, w=0 \rightarrow 1) = 5$ [25], and 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 $N_2(A^3\Sigma_u^+, v=1)$ and $N_2(A^3\Sigma_u^+, v=0)$ populations.

Figure 11 compares the experimental and predicted absolute number densities of $N_2(A^3\Sigma_u^+, v)$ during and after the discharge in nitrogen at 250 Torr, for a 20-pulse burst (a-e) and 100-pulse bursts (f-h). $N_2(A^3\Sigma_u^+, v=4,5)$ number densities, which decay rapidly after each discharge pulse, have only been measured during the 20-pulse burst. Note that panels (d,e), plotting $v=4,5$ 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 $v=0-2$ 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 N_2 , the process of Eq. (5), based on the rate coefficients suggested in Ref. [25]. Between the discharge pulses, $N_2(A^3\Sigma_u^+, v=0,1)$ 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 $N_2(A^3\Sigma_u^+)$ quenching in collisions with N atoms, the process of Eq. (8). In comparison, the $N_2(A^3\Sigma_u^+, v=2)$ population decays between the pulses considerably more rapid than $v=0$ and $v=1$ (see panel (c)), due to the V-V exchange with the ground electronic state. It can be seen that $N_2(A^3\Sigma_u^+, v=4,5)$ 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 $N_2(A^3\Sigma_u^+, v=0-2)$ populations achieved after each discharge pulse is gradually decreasing during the burst (see Fig. 11(f-h)). The reduction of $N_2(A^3\Sigma_u^+, v=4,5)$ populations over the 20-pulse burst, not plotted in Fig. 11, is comparable to those

of $v=0-2$. 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 $N_2(A^3\Sigma_u^+)$ number density in the plasma and afterglow. Therefore, comparison of the time-resolved $N_2(A^3\Sigma_u^+)$ population measurements during 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 N_2 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 $N_2(A^3\Sigma_u^+)$ 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 N_2 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 $N_2(A^3\Sigma_u^+, v=0-2)$ 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 $N_2(X^1\Sigma_g^+)$ vibrational excitation has almost no effect on the rate of $N_2(A^3\Sigma_u^+)$ 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 $1.0 \cdot 10^{14} \text{ cm}^{-3} / \text{pulse}$ (early in the burst, when the $N_2(A^3\Sigma_u^+, v)$ populations peak), to $2.5 \cdot 10^{13} \text{ cm}^{-3}$ at the end of the burst, when $N_2(A^3\Sigma_u^+)$ is quenched more rapidly by the accumulating N atoms. The N atom number density predicted at the end of a 100-pulse burst is $[N] \approx 5 \cdot 10^{15} \text{ cm}^{-3}$ (see Fig. 12). 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 $\Delta T \approx 100 \text{ K}$ (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, $\sim 10 \text{ ms}$ (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 $N_2(A^3\Sigma_u^+, v=1)$ population during the burst, as the number of pulses is increases from 20 to 100, from $9.3 \cdot 10^{13} \text{ cm}^{-3}$ to $7.4 \cdot 10^{13} \text{ cm}^{-3}$ (see Fig. 11(b,g)).

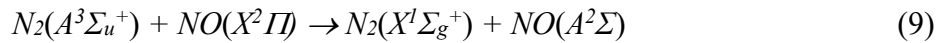
Adding hydrogen or oxygen to the gas mixture results in a dramatic reduction of $N_2(A^3\Sigma_u^+)$ populations, as summarized in Figs. 13-16. Fig. 13 plots the $N_2(A^3\Sigma_u^+, v=0-2)$ populations during a 20-pulse discharge burst in a 5% H_2/N_2 mixture at $P=150$ Torr. It is clear that the peak 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) $N_2(A^3\Sigma_u^+)$ quenching by H atoms, generated by electron impact and by the reactive quenching of the excited electronic states of N_2 , including $N_2(A^3\Sigma_u^+)$ (see Fig. 14). Accumulation of N and H atoms between the pulses also results in a gradual reduction of the peak $N_2(A^3\Sigma_u^+)$ 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 $N_2(A^3\Sigma_u^+, v=0)$ 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 $N_2(A^3\Sigma_u^+, v)$ 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



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,



which reduces the combined number density of the rapid quencher species (NO, N, and O). Finally, comparison of the measurement results in N₂-O₂ and N₂-NO provides additional evidence that the mixture composition strongly affects the N₂(A³Σ_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 N₂(A³Σ_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. N₂(A³Σ_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 0.5·10¹² cm⁻³ (double-pass absorption of 10⁻³).

The results of TDLAS measurements in nitrogen and in H₂-N₂, O₂-N₂, and NO-N₂ plasmas are compared with kinetic modeling predictions, identifying the mechanisms of N₂(A³Σ_u⁺) generation and decay during the discharge pulses and in the afterglow. It is confirmed that the dominant process of N₂(A³Σ_u⁺,v) generation during the discharge pulse is the collisional quenching of N₂(B³Π_g) electronic state, followed by the cascade population redistribution to the lower vibrational levels by the vibration-vibration exchange with N₂ in the ground electronic state. In nitrogen, the rate of N₂(A³Σ_u⁺) decay is controlled by the energy pooling (rapid decay between the discharge pulses) and by the collisional quenching by N atoms (gradual decay during the entire discharge burst). Comparison with the modeling predictions indicates that electron impact dissociation of N₂ from the ground electronic state significantly underpredicts the yield of N atoms in pure nitrogen, consistent with our previous work [13]. Since the role of N₂ 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 N₂(A³Σ_u⁺) molecules. Indeed, adding this process to the kinetic model results in a much better agreement of the modeling predictions with the time-resolved N₂(A³Σ_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 4·10⁻¹⁰ cm³ [14]. Additional evidence of the existence of this major dissociation channel in the nitrogen plasma would require absolute, time-resolved measurements of both N atoms and N₂(A³Σ_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 H₂ and O₂, the decay of N₂(A³Σ_u⁺,v) populations is significantly faster, mainly due to the collisional quenching by H atoms and O₂ molecules, respectively. Again, the present data can be used to infer the 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-N₂ mixture, it is shown that the dominant N₂(A³Σ_u⁺) decay process is the rapid energy transfer to NO, resulting in its electronic excitation and UV emission (NO γ bands). After the discharge pulse, both the time-resolved N₂(A³Σ_u⁺,v) populations and the γ 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 μs [33]. The sensitivity of the present measurements is estimated to be sufficient for the detection of N₂(A³Σ_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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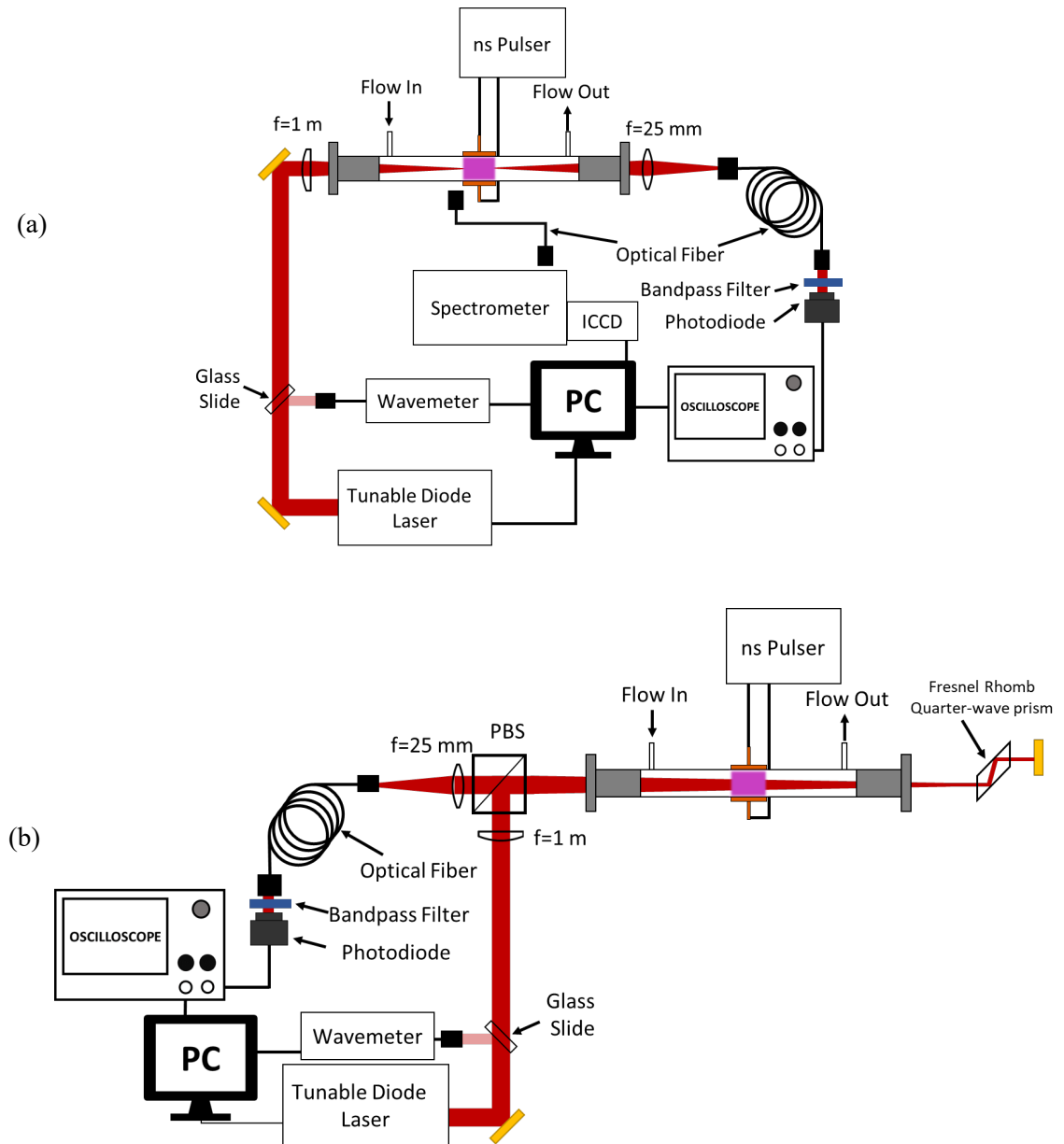


Figure 1. Schematic of the Tunable Diode Laser Absorption Spectroscopy experimental setup, (a) single-pass, and (b) double-pass.

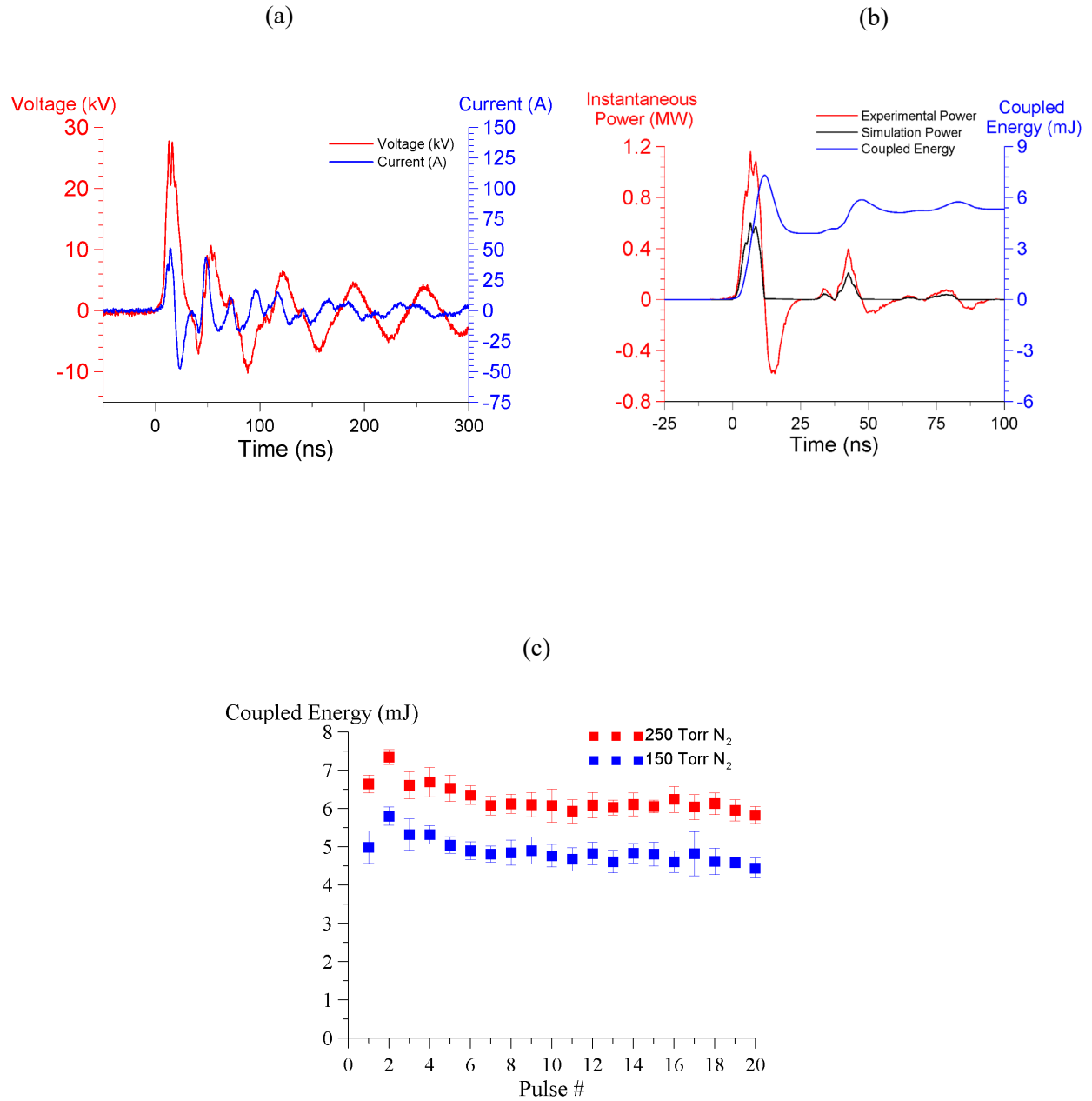


Figure 2. (a) Voltage and current waveforms, (b) instantaneous power and coupled energy waveforms in a ns pulse discharge in nitrogen at $P=250$ Torr, pulse repetition rate of 100 kHz, and burst repetition rate of 30 Hz; (c) Coupled pulse energy vs. pulse number in the train at 250 Torr and 150 Torr (error bars indicated standard deviations of multiple measurements).

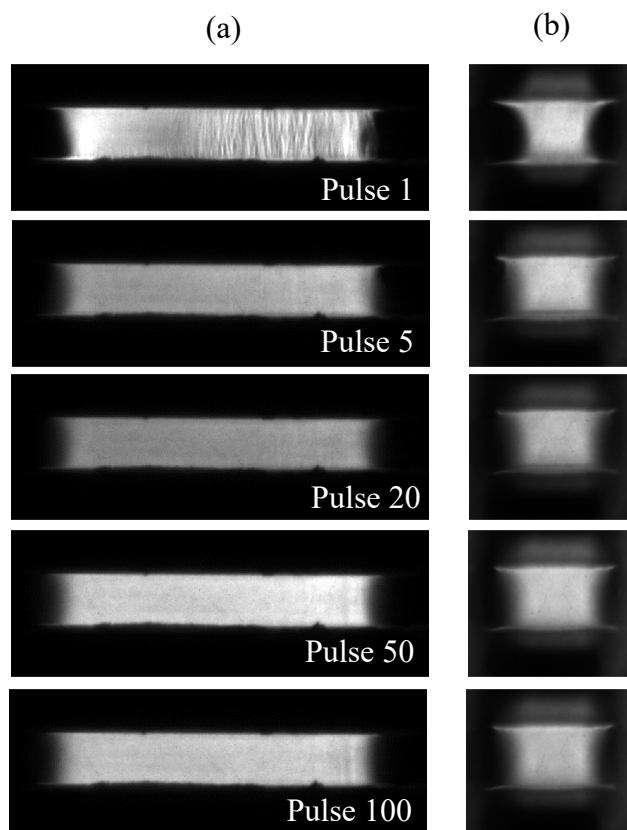


Figure 3. Single-shot, broadband plasma emission images taken during a 100-pulse discharge burst at the conditions of Fig. 2(a), (a) side view and (b) end view. Nitrogen, $P=250$ Torr, camera gate 300 ns.

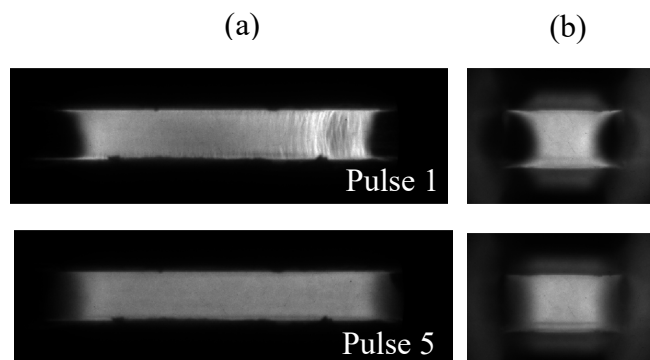


Figure 4. Single-shot, broadband nitrogen plasma emission images during a 20-pulse ns discharge burst, (a) side view and (b) end view. P=150 Torr, 5% H₂ / N₂ mixture, camera gate 300 ns.

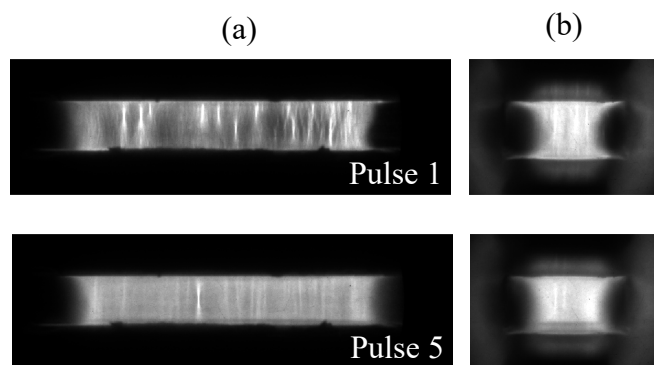


Figure 5. Single-shot, broadband nitrogen plasma emission images taken during a 10-pulse ns discharge burst, (a) side view and (b) end view. P=150 Torr, 10% air / N₂ mixture, camera gate 300 ns.

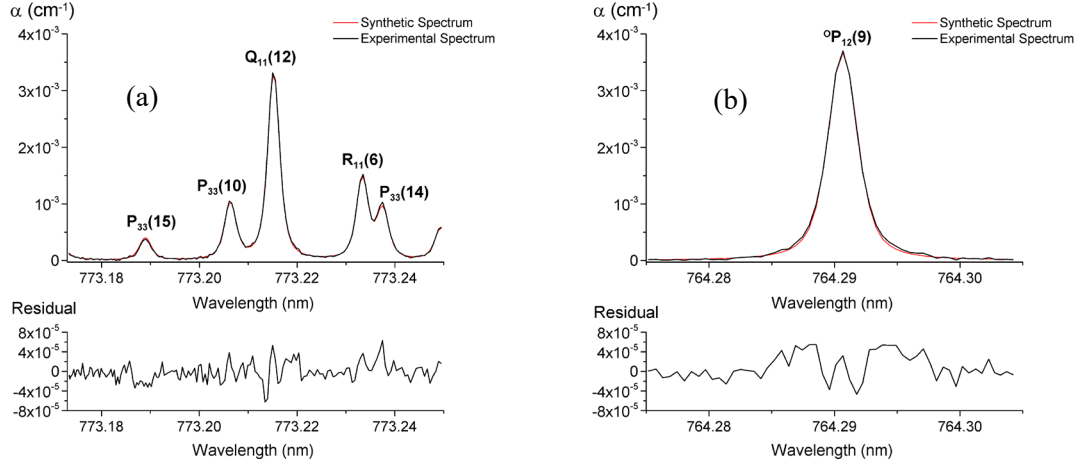


Figure 6. TDLAS scans of (a) 5 rotational lines in the $N_2(B^3\Pi_g, v' = 2 \leftarrow A^3\Sigma_u^+, v'' = 0)$ band, and (b) a single rotational line in the $N_2(B^3\Pi_g, v' = 3 \leftarrow A^3\Sigma_u^+, v'' = 1)$ band. Nitrogen, P=150 Torr, single pulse discharge, 20 μs after the pulse. Inferred rotational-translational temperature is $T = 330 \pm 10$ K.

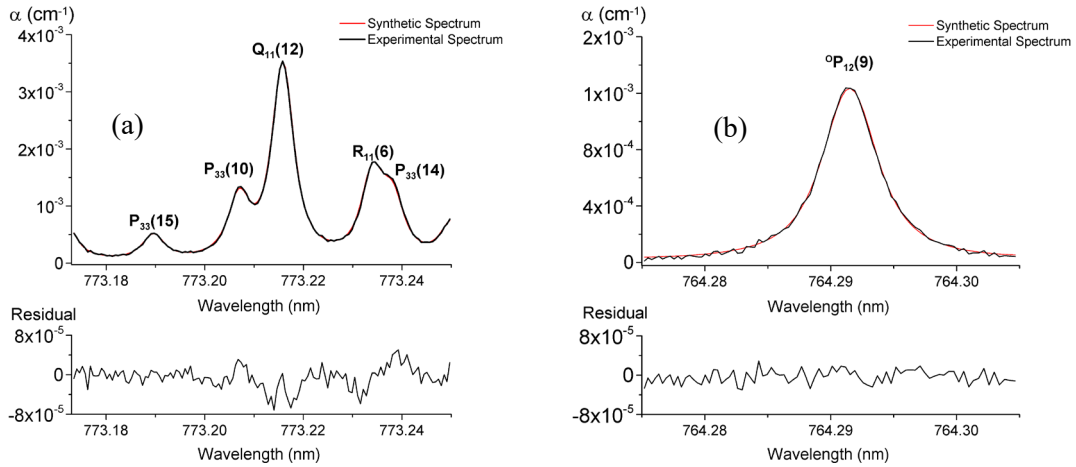


Figure 7. TDLAS scans of (a) 5 rotational lines in the $N_2(B^3\Pi_g, v' = 2 \leftarrow A^3\Sigma_u^+, v'' = 0)$ band, and (b) a single rotational lines in the $N_2(B^3\Pi_g, v' = 3 \leftarrow A^3\Sigma_u^+, v'' = 1)$ band. Nitrogen, P=412 Torr, 11-pulse discharge burst, 4 μs after the third pulse. Inferred rotational-translational temperature is $T = 360 \pm 20$ K.

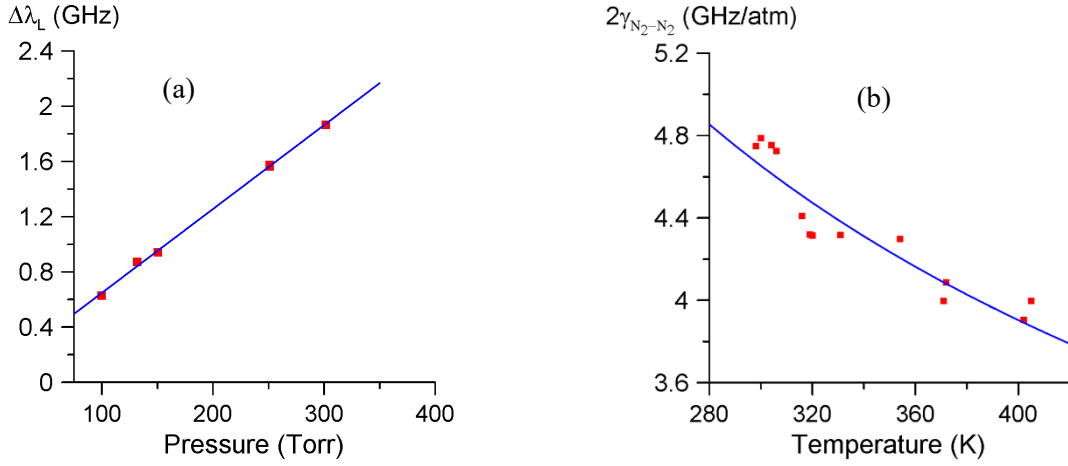


Figure 8. (a) Variation of the Lorentzian Full Width at Half Maximum (FWHM) with pressure at 300 K; (b) Pressure broadening coefficient vs. temperature for the $N_2(B^3\Pi_g, v'=2 \leftarrow A^3\Sigma_u^+, v''=0)$ $Q_{11}(12)$ spectral line. The pressure broadening coefficient inferred from the data is $2\gamma(T) = 4.79 \left(\frac{300}{T(K)} \right)^{0.61} \frac{\text{GHz}}{\text{atm}}$.

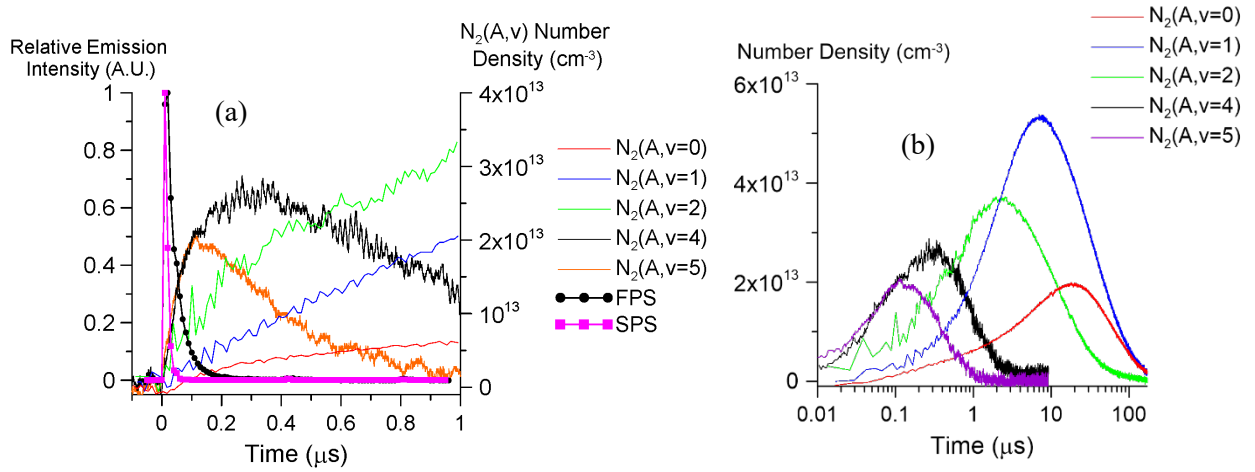


Figure 9. (a) Comparison of time-resolved Second Positive System (SPS) band, $N_2(C^3\Pi_u, v'=0 \rightarrow B^3\Pi_g, v''=0)$, and First Positive System (FPS) band, $N_2(B^3\Pi_g, v'=2 \rightarrow A^3\Sigma_u^+, v''=0)$, emission intensity with $N_2(A^3\Sigma_u^+, v)$ populations during a single pulse ns discharge. (b) $N_2(A^3\Sigma_u^+, v)$ populations during a ns pulse discharge and the afterglow. Nitrogen, P=250 Torr.

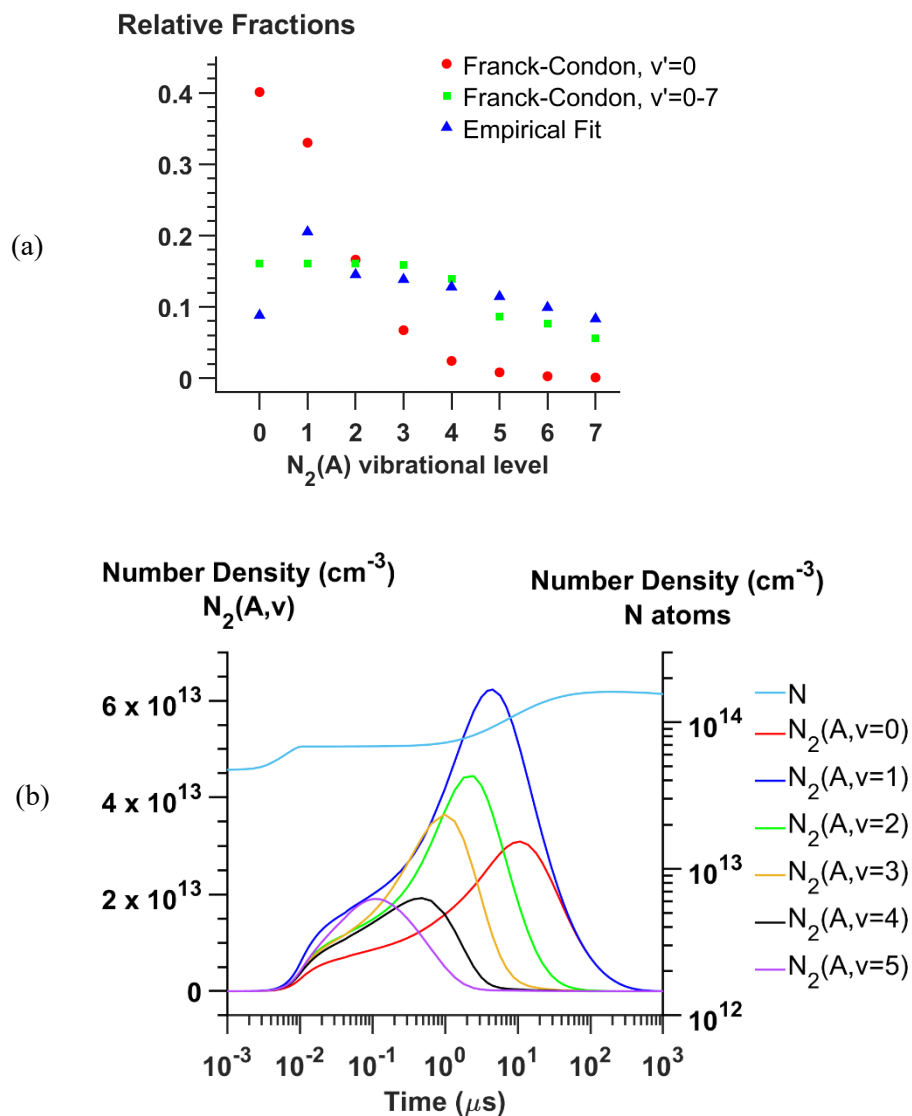


Figure 10. (a) Different $N_2(A^3\Sigma_u^+, v)$ branching ratios tested in the kinetic model; (b) Time-resolved absolute populations of $N_2(A^3\Sigma_u^+, v=0-5)$ vibrational levels and N atoms, predicted using an “empirical fit” branching ratio. Single-pulse ns discharge and the afterglow in nitrogen at P=250 Torr.

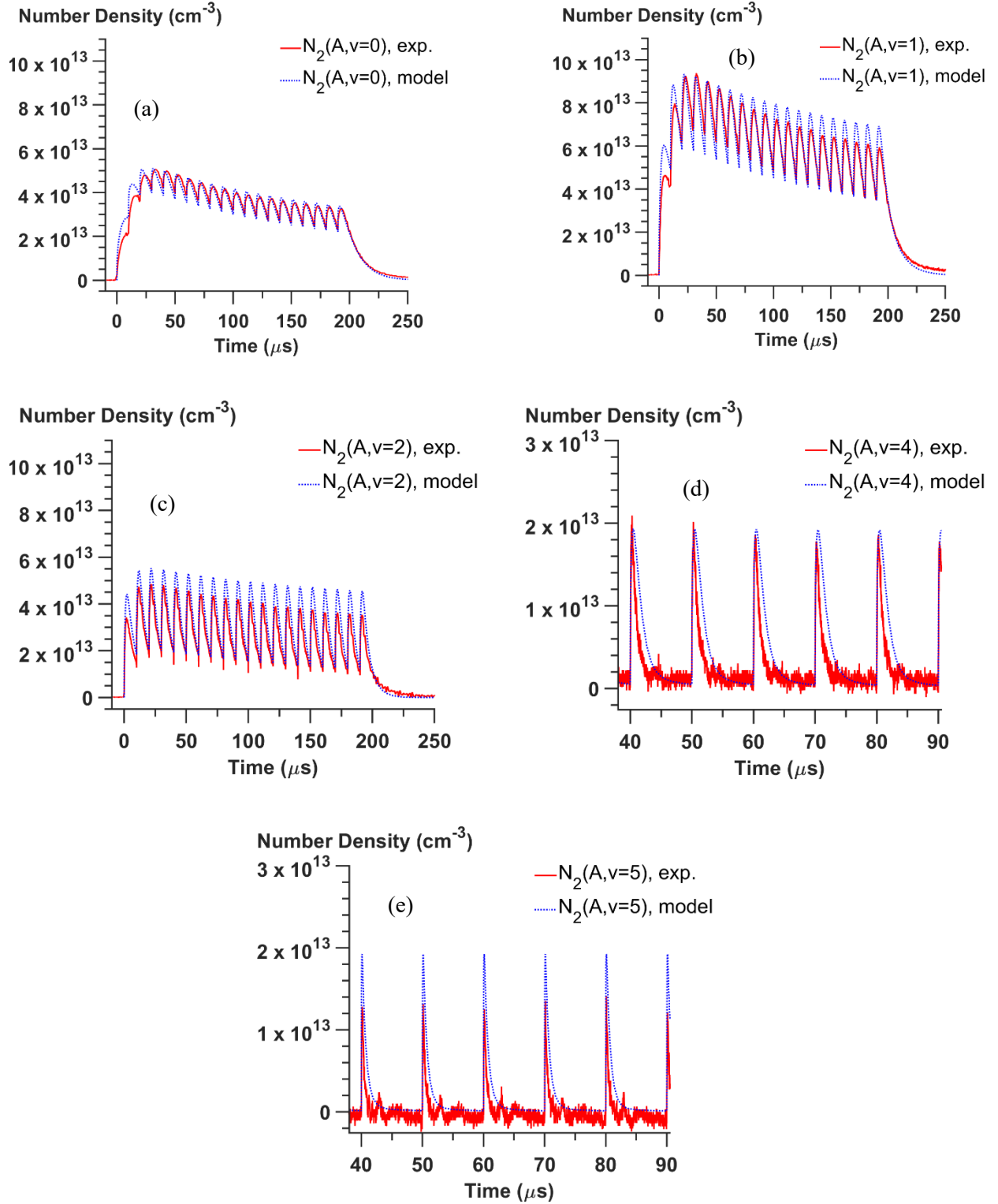


Figure 11. Time-resolved absolute $N_2(A^3\Sigma_u^+, v)$ populations during a ns discharge burst and the afterglow in nitrogen at $P=250$ Torr: (a-e) 20-pulse burst, and (f-h) 100-pulse burst.

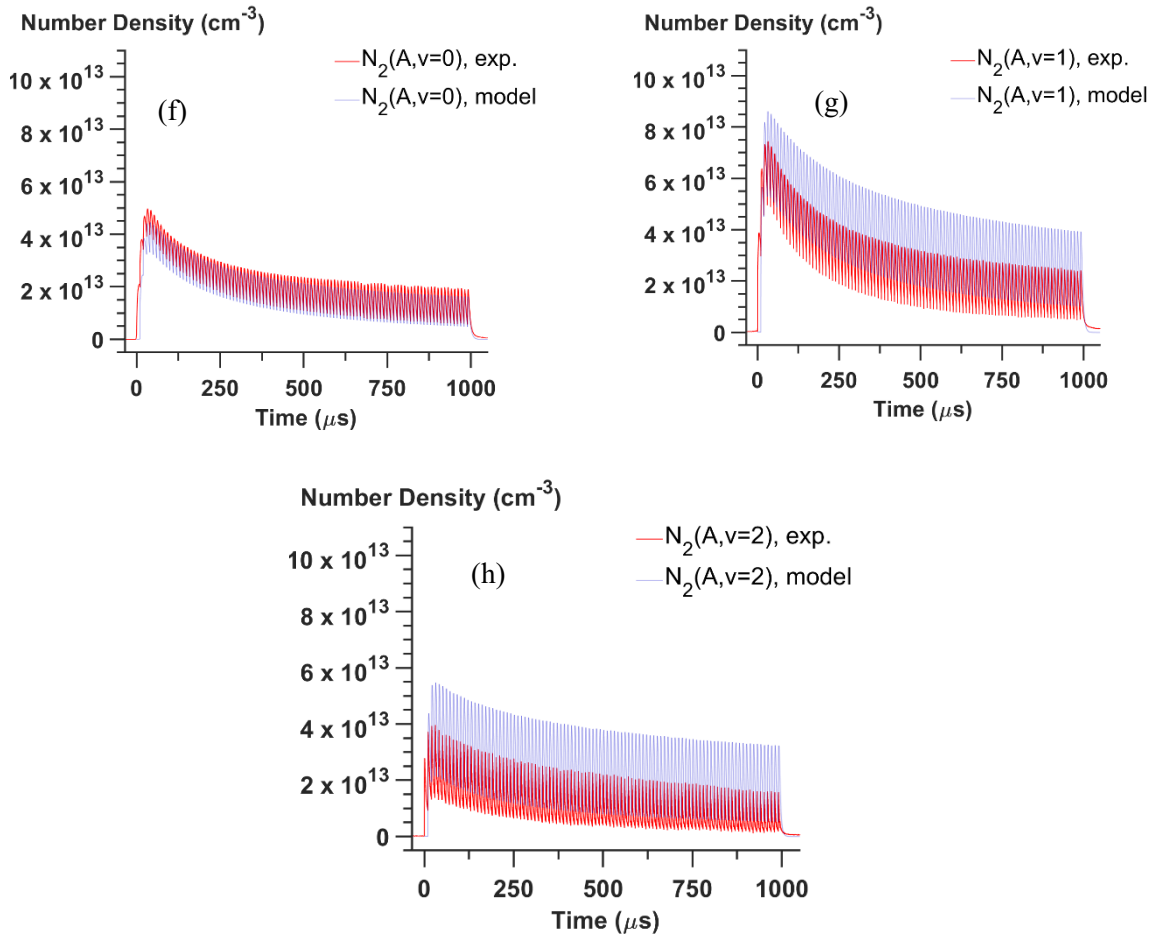


Figure 11. Time-resolved absolute $N_2(A^3\Sigma_u^+, v)$ populations during a ns discharge burst and the afterglow in nitrogen at $P=250$ Torr: (a-e) 20-pulse burst, and (f-h) 100-pulse burst.

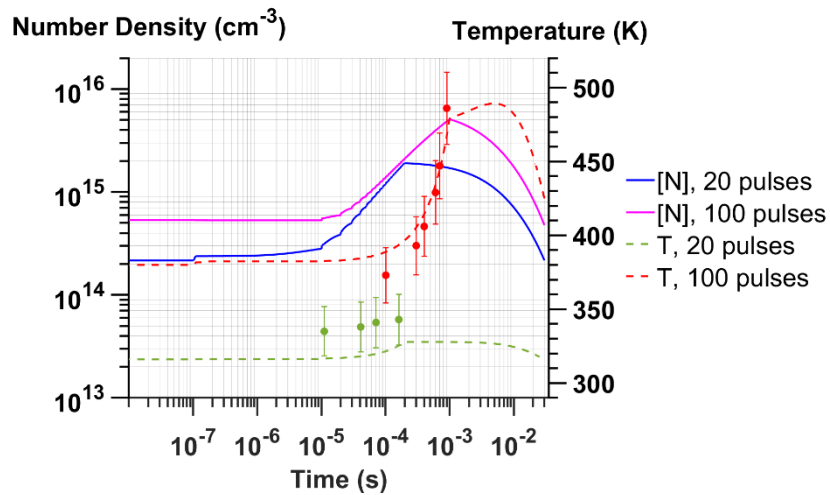


Figure 12. Time-resolved N atom number density and temperature, predicted by the model at the conditions of Fig. 11 (20-pulse and 100-pulse bursts in nitrogen at $P=250$ Torr). Lines, modeling predictions, symbols, experimental data.

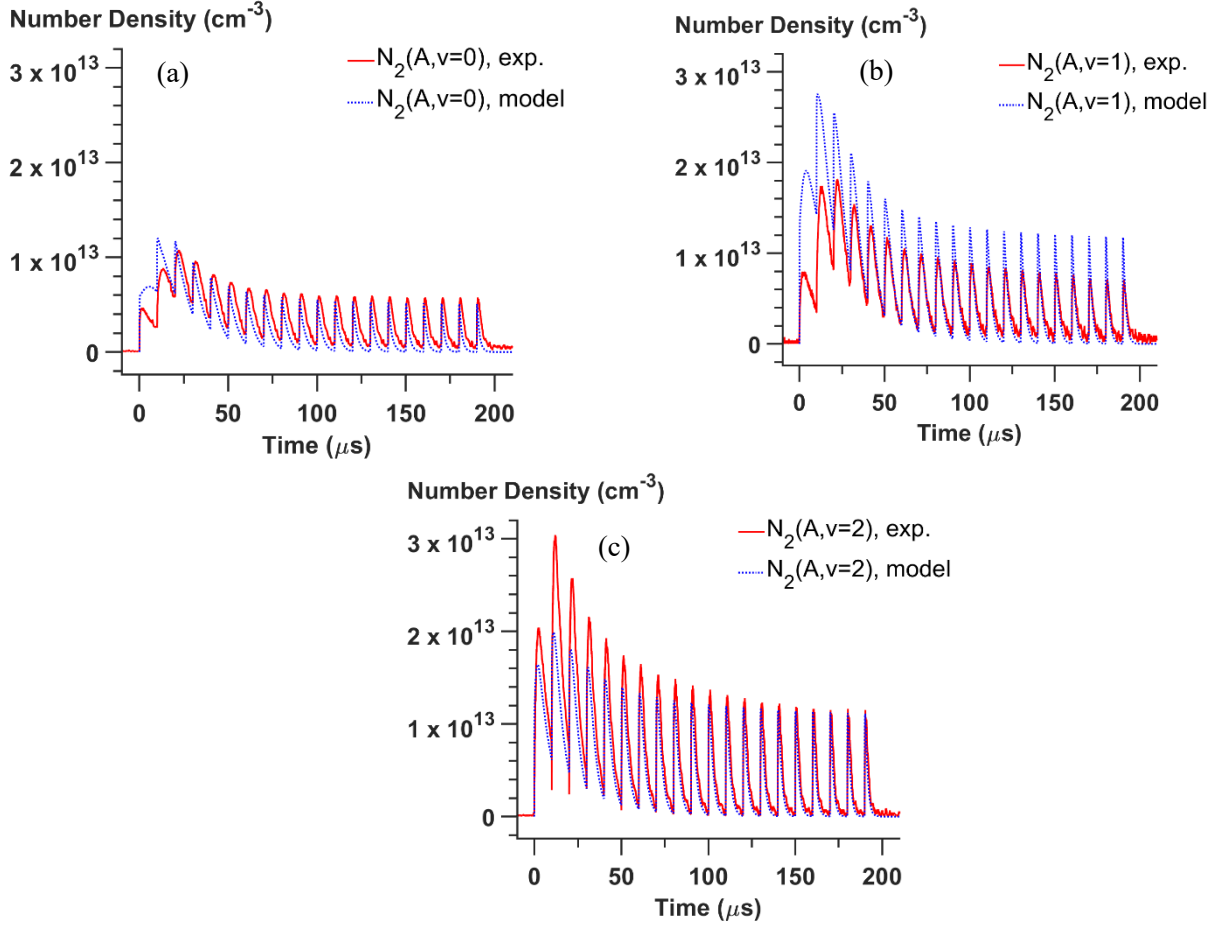


Figure 13. Time-resolved absolute $N_2(A^3\Sigma_u^+, v)$ populations during a 20-pulse discharge burst and the afterglow in 5% H_2/N_2 at $P=150$ Torr.

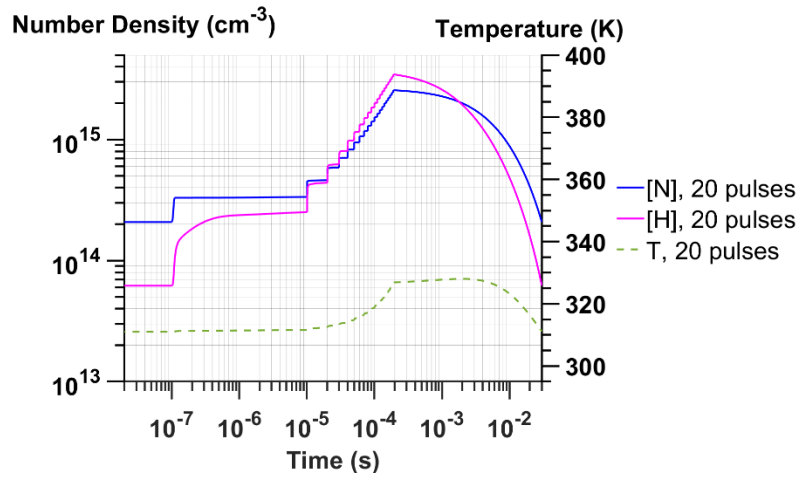


Figure 14. Time-resolved N and H atom number densities and temperature, predicted by the model at the conditions of Fig. 13 (20-pulse discharge burst in 5% H_2/N_2 at $P=150$ Torr).

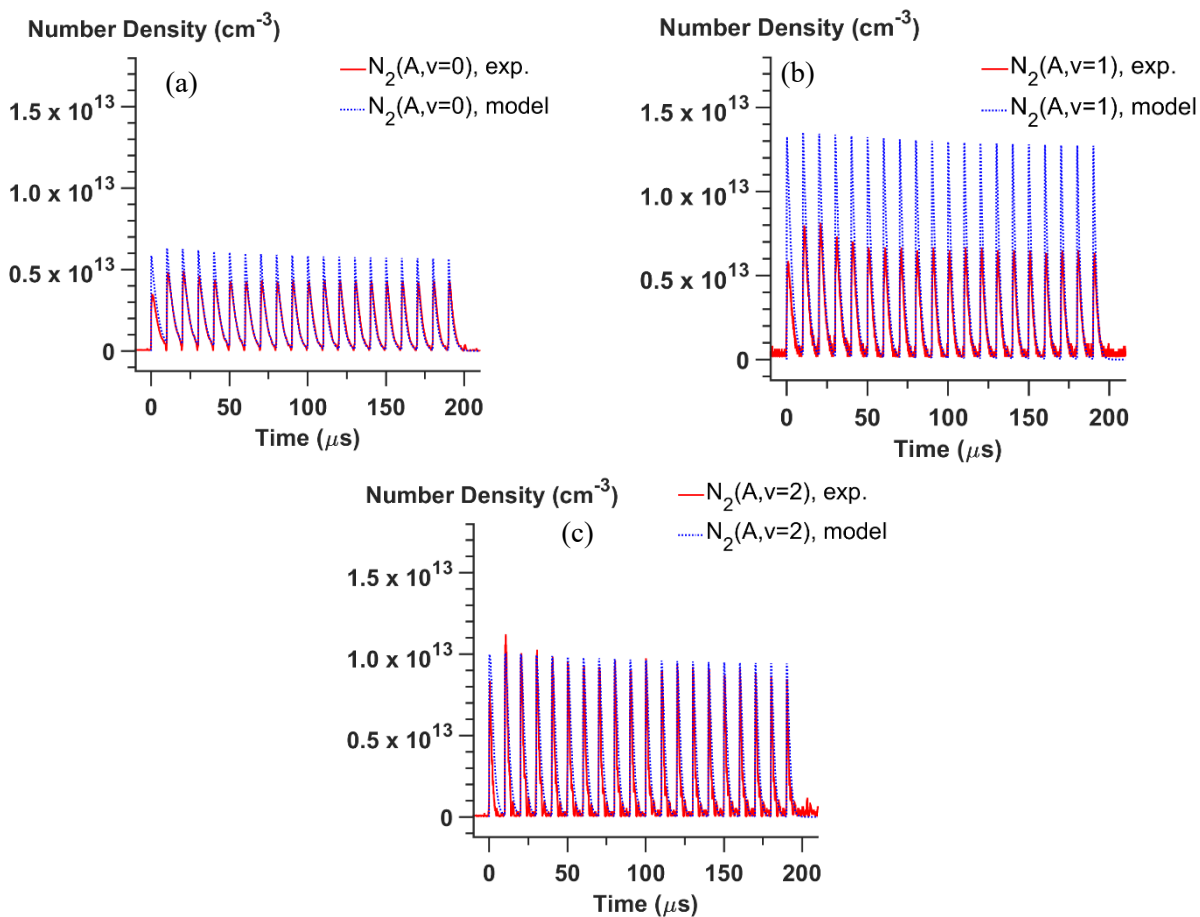


Figure 15. Time-resolved absolute $N_2(A^3\Sigma_u^+, v)$ populations during a 20-pulse discharge burst and the afterglow in a 10% dry air / N_2 mixture at $P=150$ Torr.

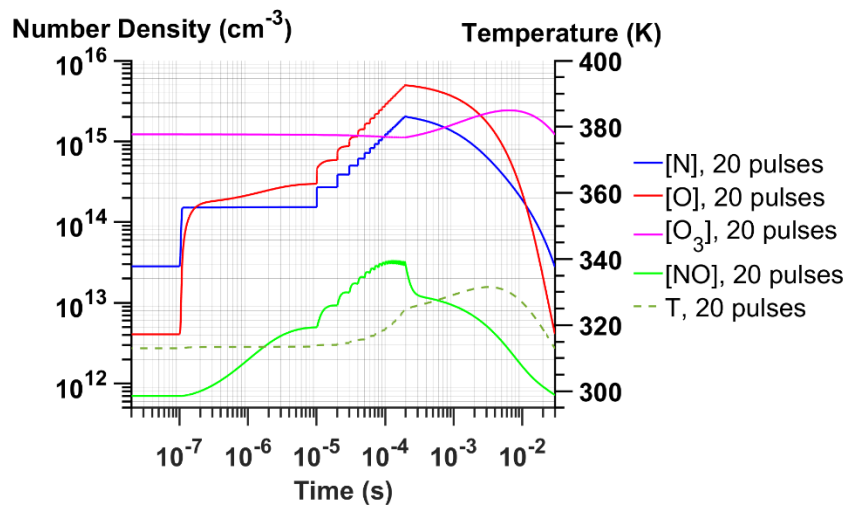


Figure 16. Time-resolved species number densities and temperature, predicted by the model at the conditions of Fig. 15 (20-pulse discharge burst in a 10% dry air / N_2 mixture at $P=150$ Torr).

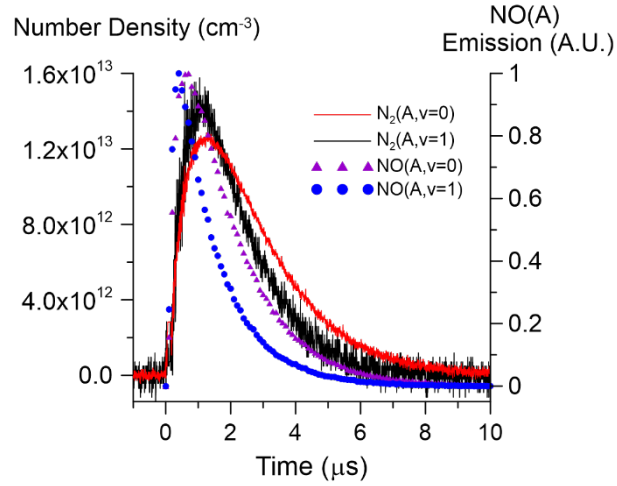


Figure 17. Comparison of $N_2(A^3\Sigma_u^+, v=0,1)$ absolute number densities and $NO(A^2\Sigma, v=0,1)$ relative emission intensities during after a single-pulse ns discharge in 1000 ppm NO/ N_2 mixture at $P=250$ Torr.

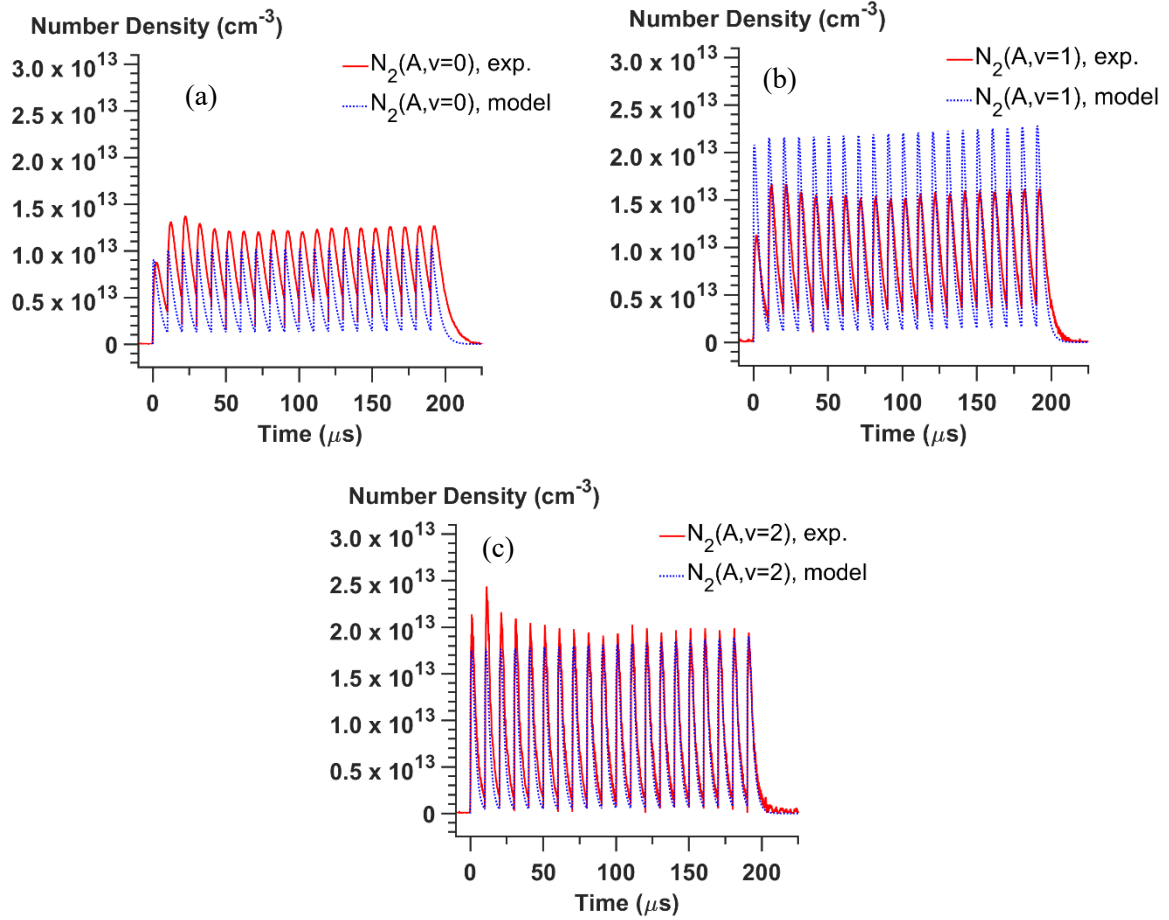


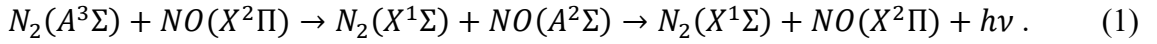
Figure 18. Time-resolved absolute $N_2(A^3\Sigma_u^+, v)$ populations during a 20-pulse discharge burst and the afterglow in a 1000 ppm NO / N_2 mixture at $P=150$ Torr.

PART III.

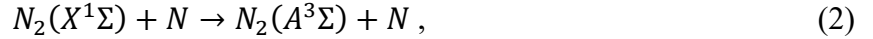
MEASUREMENTS OF METASTABLE $N_2(A^3\Sigma_u^+,v)$ MOLECULES IN NONEQUILIBRIUM SUPERSONIC FLOWS ³

1. Introduction

The lowest excited electronic state of molecular nitrogen, $N_2(A^3\Sigma_u^+)$, is believed to be a major precursor of nonequilibrium UV emission from nitric oxide in shock-heated air, due to the rapid energy transfer from $N_2(A^3\Sigma)$ to NO [1-3],



Since $N_2(A^3\Sigma)$ has never been measured in high-enthalpy nonequilibrium flows, this assumption is based solely on the kinetic modeling predictions. In Ref. [1], incorporating the energy transfer process of Eq. (1) into the vibrational relaxation / nonequilibrium air chemistry kinetic model, where $N_2(A^3\Sigma)$ behind the shock was assumed to be formed by the heavy species impact,



electron impact,



and N atom recombination,



resulted in good agreement with the time-resolved UV emission intensity (NO γ bands) measured behind a normal shock in the shock tube experiments [1], at shock velocities of 3-4 km/s (M=8-11). Kinetic modeling [1] suggested that $N_2(A)$ is generated behind the shock primarily by the heavy species excitation, Eq. (2), and N atom recombination, Eq. (4), while electron impact excitation, Eq. (3), has a negligible contribution. The critical importance of the energy transfer of Eq. (1) for the UV radiation prediction is illustrated in Fig. 1, which compares the experimental [1] and predicted [4] IR and UV emission from NO behind a 3.8 km/s normal shock in air. It can be seen that the rapid energy transfer from $N_2(A^3\Sigma)$ is responsible for the strong nonequilibrium overshoot of NO γ bands emission in the relaxation layer. In Fig. 1, the $NO(A^2\Sigma)$ number density is predicted by expanding the state-specific master equation vibrational relaxation / air chemistry kinetic model [4] to include the energy transfer processes of Eqs. (1-4), as suggested in Ref. [2]. The predictions of a more extensive collision-radiative kinetic model [3], which also included $N_2(A^3\Sigma)$ impact excitation by N_2 , O_2 , and O atoms, as well as the detailed kinetics of the excited electronic states of NO, are consistent with the NO γ bands emission intensity measured in an arc-driven shock tube [3], at shock velocities of 5-9 km/s.

³ E.R. Jans, I. Gulko, D.C.M. van den Bekerom, T.A. Miller, and I.V. Adamovich, “Measurements of Metastable $N_2(A^3\Sigma_u^+,v)$ Molecules in Nonequilibrium Supersonic Flows”, accepted for publication in *Journal of Thermophysics and Heat Transfer*, 2021

These results suggest that the dominant kinetic processes controlling NO emission in nonequilibrium hypersonic flows are understood fairly well. However, most of the rate coefficients of the energy transfer processes among the excited electronic states of N_2 and NO have been measured only at near room temperature, such that their values and vibrational quantum number dependence in the shock layer are not known. In particular, the pre-exponential factors in the rate expression for reactions (1) and (2) used in Ref. [2] considerably exceeds the gas kinetic rate, and the electronic energy transfer rates used in Ref. [3] are extrapolated from the low-temperature values. This makes the range of applicability and the predictive capability of collision-radiative kinetic models of nonequilibrium shock-heated air, and specifically the prediction of the UV emission spectra, highly uncertain.

Experimental validation of the kinetic models, such as have been developed in 1990s [3,5,6] and over the last decade [7-9], is complicated further by the difficulty of the detection of the key “dark” metastable species, $N_2(A^3\Sigma)$, in high-enthalpy pulsed test facilities, such as shock tubes and shock tunnels. Although experimental techniques for $N_2(A^3\Sigma)$ measurements in nonequilibrium low-temperature plasmas, including Cavity-Enhanced Absorption Spectroscopy (CEAS) [10], Cavity Ring Down Spectroscopy (CRDS) [11,12], and Laser-Induced Fluorescence (LIF) [13,14] are well known, their use in pulsed nonequilibrium flow facilities is challenging. In this case, the major technical issues include not only the sensitivity and uncertainty of the measurements, but also the capability to acquire the time-resolved data during a short run time, ranging from a few hundred microseconds to a few milliseconds [15]. Such capability has been demonstrated recently in CEAS measurements of electronically excited O atoms behind a reflected shock in a diluted O_2 -Ar mixture [16] and CRDS measurements of ethylene behind a reflected shock in a diluted C_2H_4 -Ar mixture [17]. Time-resolved measurements of $N_2(A^3\Sigma, v)$ vibrational populations in nonequilibrium high-enthalpy flows, along with the time-resolved NO UV emission intensity and emission spectra, would yield critical insight into the kinetics of nonequilibrium UV emission in atmospheric reentry flows and hypersonic flight.

In our recent work [18], we have developed two complementary laser diagnostic techniques, CRDS and Tunable Diode Laser Absorption Spectroscopy (TDLAS), for time-resolved, absolute measurements of $N_2(A^3\Sigma, v)$ populations in low-temperature plasmas. In the present paper, we apply these diagnostics to the measurements in a nonequilibrium flow supersonic wind tunnel, where $N_2(A^3\Sigma)$ is generated by electron impact in a pulsed electric discharge sustained in the tunnel plenum or near the nozzle throat, and transported with the flow into the test section. The objective of these experiments is two-fold. First is to show that these diagnostics are robust and applicable for the high sensitivity measurements in supersonic flows, with the results not being affected by the wind tunnel vibrations or temperature gradients in the boundary layer. The second is to demonstrate the capability for time-resolved measurements using the short duration pulse burst excitation of the flow in the plenum (for TDLAS), and single laser shot measurements in the supersonic section (for CRDS). This would demonstrate the feasibility of the use of these diagnostics in nonequilibrium flows generated at pulsed flow facilities.

2. Experimental

The photographs and a cutout view of the nonequilibrium flow blowdown wind tunnel used in the present work are shown in Fig. 2. A cross section view of the flow channel is shown in the inset in Fig. 3, which also shows a schematic of the Cavity Ring Down Spectroscopy (CRDS) and

Tunable Diode Laser Absorption Spectroscopy (TDLAS) diagnostics. In the present work, the wind tunnel is operated using nitrogen (99.999% purity) at plenum pressures of $P_0=200\text{--}300$ Torr, at steady-state flow conditions. The experiments have been done using two different wind tunnel test sections used in our previous work [19,20]. The test sections have similar designs, shown schematically in the inset of Fig. 3, but different throat heights. In both test sections, the flow expands through an aerodynamically contoured two-dimensional nozzle, with the throat height of 0.8 mm or 1.6 mm, respectively, and the area ratio of $A/A^* = 25$, designed for the exit flow of $M=5$ (nozzle exit height of 20 mm or 40 mm, respectively). The top and bottom walls of the test sections after the nozzle exit diverge at a 0.5° angle each, to provide the boundary layer relief. The static pressure in each supersonic section is measured by two MKS 925 Micro Pirani pressure transducers, using the side wall pressure taps at the end of the nozzle and the beginning of the diffuser, as shown schematically in the inset of Fig. 3. The diffuser height is 75% of the nozzle exit height. At the baseline conditions of the plenum pressure of $P_0=250$ torr, the upstream and downstream static pressures in the small test section are $P=2.8$ Torr and 4.0 Torr (quasi-one-dimensional isentropic flow Mach numbers of $M=3.6$ and 3.4), while the static pressures in the large test section are $P=0.75$ and 1.1 Torr, respectively (Mach numbers of $M=4.6$ and 4.3). In both cases, the test section Mach numbers are lower compared to the design Mach number, due to the boundary layer growth and the secondary crossflow, as discussed in our previous work [20]. As expected, these effects become more pronounced as the test section height and the plenum pressure are reduced. At $P_0=760$ Torr and $P_0=380$ Torr, the Mach number inferred from the static pressure measurements in the large test section is $M=5.0$ and 4.5, respectively [19]. Downstream of the diffuser, the flow exits into an 8 to 12 inch diameter vacuum pipe, connected to a 100 ft³ vacuum tank and a 140 cfm vacuum pump. The steady-state run time is approximately 10 s, and the runs can be repeated every few minutes.

Nonequilibrium flow in the supersonic test section is produced using two different methods. The first, used in the small test section, is a transverse ns pulse discharge sustained between two plane electrodes flush mounted in the top and bottom walls of the rectangular cross section plenum (see Figs. 2,3), using an NPG-18/100k high-voltage pulse generator (MegaImpulse Ltd, peak voltage 25 kV, pulse duration 15 ns FWHM) 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" thick, ending 10 cm upstream of the nozzle throat. The plenum test section height is 6.4 mm. The estimated flow Mach number in the discharge section is $M \approx 0.07$, with the flow residence time in the discharge of approximately 1 ms. The second approach, used in the large test section, is a transverse ns pulse discharge sustained between two cylindrical rod electrodes 1/8" in diameter, encapsulated within the 1/4" outside diameter plastic sleeves and embedded in the nozzle inserts near the throat, as shown schematically in Figs. 2,3. The distance between the electrode axes is approximately 32 mm, and the overlap between the electrode rods, facing in the opposite directions, is 32 mm. The electrodes are powered by an FPG 60-100MC4 pulse generator (FID GmbH, peak voltage 30 kV, pulse duration 10 ns FWHM) operated at a pulse repetition rate of 100 kHz. In both cases, the plasma spans nearly the entire width of the flow channel, except for the side wall boundary layers. While the first approach sustains a spatially uniform plasma in a constant cross section area flow upstream of the nozzle, the second method sustains the plasma directly in the nozzle, much closer to the supersonic test section, such that the decay of $N_2(A^3\Sigma)$ molecules generated in the plasma is greatly reduced. At these conditions, $N_2(A^3\Sigma)$ is generated by the electron impact excitation, both by the process of Eq. (3) and by the excitation of higher energy

electronic states $N_2(B^3\Pi, C^3\Pi)$, followed by their cascade quenching to $N_2(A^3\Sigma)$, as discussed in greater detail in Ref. [23].

The number density of $N_2(A^3\Sigma_u^+)$ molecules generated in the small test section discharge in the 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 (see Figs. 2,3). Broadband plasma emission images are taken through a 1.5 inch diameter fused silica window in the back (upstream) wall of the discharge section, as shown in Fig. 2. The TDLAS diagnostic is described in our previous work [18]. Briefly, a collimated output beam (≈ 1 mm diameter) of a continuous wave tunable diode laser (New Focus Velocity 6312) is focused in the center of the flow, as shown in Fig. 3. The laser wavelength is monitored by a wavemeter (High Finesse WS6). The transmitted beam is collimated again and detected by a silicon photodiode (Thorlabs DET36A), located several meters away from the wind tunnel. This allows the data acquisition to be spatially isolated from the electromagnetic noise generated by the electric discharge in the flow, which is critical for measuring weak absorption signals (path integrated absorption of $\sim 10^{-3}$ - 10^{-2}). The laser wavelength is modulated by varying the piezoelectric driver voltage using a function generator (Keysight 33220A), at the rate of up to 200 MHz/ μ s. This allows scanning across the individual absorption lines in the $N_2(B, v' \leftarrow A, v'')$ bands over approximately 10 μ s.

$N_2(A^3\Sigma_u^+)$ molecules in the supersonic test section are detected by CRDS. 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 attached to the side walls of the test section, with the total cavity length of 35.5 cm and 64 cm for the small and large wind tunnels respectively. 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 [18]. 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. 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 by a wavemeter (High Finesse WS6). The laser wavelength, corresponding to the $N_2(B, v'=2 \leftarrow A, v''=0)$ absorption band, was selected due to the excellent stability and energy output of the Rhodamine dyes used. 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 pulsed discharge with the CRDS laser system, such that each ring down trace is taken at the same time delay after the discharge pulse. For all runs, the time delay between the discharge pulse and the laser shot is varied between 107 μ s and 177 μ s for the small wind tunnel, and set to 1010 μ s after the first pulse of the discharge burst for the large wind tunnel. During each run, 50 ring down traces are acquired and saved at the laser pulse repetition rate of 10 Hz.

The present approach has several key differences from the CRDS spectrometer developed in Ref. [21], where a repetitively pulsed, non-ideally expanded, supersonic jet is exhausting from a converging-diverging nozzle into a vacuum chamber. The present approach has the flow in the wind tunnel operated at the steady state conditions and not affected by the conditions in the vacuum system, until the oblique shock system enters the test section at the end of the run. The steady-state

run time is extended significantly by the diffuser downstream of the test section. The boundary layer growth in the wind tunnel has been predicted by 3-D compressible Navier-Stokes CFD modeling in our previous work [19,20]. Based on the CFD predictions, the discharge electrode geometry can be chosen to limit the extent of the plasma to the inviscid core, and to prevent the excited species generation in the boundary layers, where the temperature and velocity gradients are significant. Finally, the present approach does not require locking the CRDS cavity to the laser system, such that the measurements are not susceptible to the wind tunnel and cavity arms vibrations.

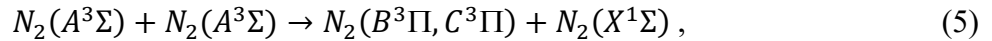
3. Results and Discussion

Figure 4(a,b) plots the time-resolved pressure traces measured in the nitrogen flow in the wind tunnel plenum and in the supersonic test sections, at the plenum pressure of $P_0=250$ Torr. The static pressure is measured at the end of the nozzle and the beginning of the diffuser, as shown schematically in the inset of Fig. 3. Although the nozzle area ratio in both test sections 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, $M=3.6$ and $M=4.6$ in small and large test sections, respectively. This is likely due to the interaction of the side wall boundary layers with the oblique shocks in the diffuser [20]. As expected, this effect diminishes considerably in the large test section, and it can be reduced further if the wind tunnel is operated at higher plenum pressures, $P_0=500-760$ Torr [19]. The test section pressure remains nearly constant for approximately 10 s (see Fig. 4). A sudden pressure jump at the end of the run is typical of the oblique shock system entering the test section from the diffuser. It can be seen that in the large test section, the steady state flow conditions are maintained until the vacuum system pressure exceeds the test section pressure by about a factor of 9 (see Fig. 4(b)). During a typical wind tunnel run, the data are acquired over a 5 s period.

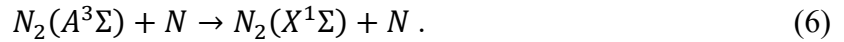
Figure 5 plots the typical discharge pulse waveforms taken in nitrogen at the plenum pressure of $P_0=227$ Torr and the pulse repetition rate of 100 kHz, using the MegaImpulse (small test section). The voltage and current waveforms are repeatable pulse-to-pulse, with the coupled energy variation during the burst of approximately 8%. The plasma emission images are taken through the optical access window in the back wall of the plenum (small and large test sections, Fig. 6(a,b)), and through the channel side wall (large test section, Fig. 6(b)). The images demonstrate that the plasma is diffuse, with no sign of filamentation. In both cases, it is evident that the plasma fills nearly the entire cross section of the flow, except for the side wall regions, to reduce the excited species generated in the side wall boundary layers. This is critical for the accuracy of line-of-sight measurements such as absorption spectroscopy, which require the knowledge of the absorption path length (determined from the span of the plasma) and a uniform distribution of the probed species number density along the beam path. If the plasma is generated in the boundary layers, with significant gradients of temperature and velocity, this assumption may well be inaccurate. It can be seen that in the large test section, when the discharge is sustained using the electrodes placed near the nozzle throat, the plasma is generated both upstream of the throat, in the high-pressure region across a small gap, and in the low-pressure supersonic flow in the diverging section of the nozzle (see Fig. 6(b)). Although in this case the decay rate of $N_2(A^3\Sigma)$ molecules is greatly reduced due to the rapid expansion in the nozzle, the axial distribution of $N_2(A^3\Sigma)$ number density is likely to be nonuniform, unlike in the plasma sustained in the plenum.

To quantify the $N_2(A^3\Sigma_u^+)$ number density generated in the discharge in the wind tunnel plenum, 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 Fig. 3. The TDLAS data are taken at two different discharge pulse repetition rates, 4 kHz and 100 kHz. Figure 7 shows a typical TDLAS scan across two overlapping rotational transitions in the $N_2(B^3\Pi_g, v'=2 \leftarrow A^3\Sigma_u^+, v''=0)$ band, $Q_{11}(18)$ and $Q_{33}(8)$. The absorption line profile in Fig. 7 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 $0.122 \cdot 10^{-3}$ nm/ms. Therefore, different parts of the composite scan in Fig. 7 are taken during different discharge pulses, for a total period of 125 ms, and all the data points are single-pulse data. The synthetic line profile in Fig. 7 is calculated for $T=300$ K and $P=227$ Torr, using the line positions and strengths obtained from PGOPHER software [22] and the pressure broadening coefficient inferred from the spectra measured in the slow flow discharge cell at different pressures [23].

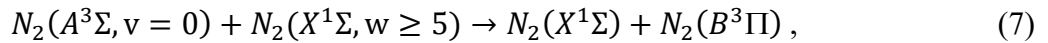
Figure 8 plots the time-resolved $N_2(A^3\Sigma_u^+, v=0)$ number densities in the wind tunnel plenum, measured with the diode laser parked at the center of the overlapping $Q_{11}(18)$ and $Q_{33}(8)$ transitions. As expected, at the relatively low discharge pulse repetition rate of 4 kHz, the $N_2(A^3\Sigma_u^+, v=0)$ population nearly fully decays between the pulses (see Fig. 8(a)). Since the quenching of $N_2(A^3\Sigma)$ by N_2 molecules is extremely slow [24], the decay is due to the energy pooling process



and quenching by N atoms,



Note that the quenching process of Eq. (6) is the reverse process of Eq. (2), which is believed to be one of the dominant processes of $N_2(A^3\Sigma)$ excitation behind the strong shocks in air. At the higher pulse repetition rate of 100 kHz, the $N_2(A^3\Sigma_u^+, v=0)$ population no longer fully decays between the discharge excitation pulses (see Fig. 8(b)), and exhibits a transient overshoot followed by a gradual reduction of the peak population during the 100-pulse discharge burst 1 ms long. It is readily apparent that the rate of the $N_2(A^3\Sigma_u^+, v=0)$ population decay between the discharge pulses also accelerates during the burst, resulting in the more pronounced minima between the peaks produced by the pulsed excitation. Since the discharge pulse energy remains nearly the same during the entire discharge burst (within 8%), this behavior indicates the gradual accumulation of a rapid $N_2(A^3\Sigma)$ quencher, most likely N atoms. Although vibrationally excited molecules in the ground electronic state, $N_2(X^1\Sigma_g^+, w)$, depopulate the $N_2(A^3\Sigma_u^+)$ molecules by the electronic-electronic energy transfer [25],



significant N_2 vibrational excitation in a repetitive ns pulse discharge is unlikely [26]. These results show that the characteristic time for the $N_2(A^3\Sigma_u^+, v=0)$ population decay in the plenum varies from ~ 100 μ s (at 4 kHz) to ~ 10 μ 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 small supersonic test section, 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 accumulation of the quenching species in the flow. As discussed in Section 2, the

CRDS laser pulses are delayed relative to the discharge pulses by 107-177 μs , 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. 9(a), the results do not exhibit a detectable difference. In both cases, the empty cavity ring down time inferred from the ring down traces is $\tau = 34 \mu\text{s}$. Figure 9(b) compares the ring down traces taken with the discharge in the plenum operating at 4 kHz, with the laser tuned to the center of the $Q_{11}(8)$ absorption transition in the $N_2(B^3\Pi_g, v' = 2 \leftarrow A^3\Sigma_u^+, v'' = 0)$ 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. Finally, Fig. 9(c) compares the ring down traces taken with the discharge in the nozzle throat operating at 100 kHz, with the laser tuned to the center of the $^PQ_{23}(4)$ absorption transition in the $N_2(B^3\Pi_g, v' = 2 \leftarrow A^3\Sigma_u^+, v'' = 0)$ band and between the absorption transitions, respectively. At these conditions, the absorption on the line center is much stronger, since the flow is excited near the throat rather than in the plenum, such that the $N_2(A)$ molecules have less time to decay before entering the supersonic test section. In this case, the ring down trace taken on the line center also exhibits the deviation from a single exponential decay (see Fig. 9(c)), since the laser linewidth is larger than the absorption linewidth and the light is coupled to the cavity on multiple modes. This effect, discussed in detail in our previous work [18], is taken into account in the CRDS data reduction.

Figure 10 summarizes the CRDS data taken in the nonequilibrium flow of nitrogen in the small 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 (black symbols) and on (blue symbols) are shown for 4 different absorption transitions. Two transitions in the $N_2(B^3\Pi_g, v'=2 \leftarrow A^3\Sigma_u, v''=0)$ band, $^PQ_{23}(4)$ and $Q_{11}(8)$, and two transitions in the $N_2(B^3\Pi_g, v'=3 \leftarrow A^3\Sigma_u, v''=1)$ band, $Q_{11}(4)$ and $Q_{11}(6)$, are used for the inference of $N_2(A^3\Sigma_u^+, v=0)$ and $N_2(A^3\Sigma_u^+, v=1)$ populations, respectively. These rotational transitions were selected because they are spectrally isolated from other rotational lines. This makes the data analysis (in particular reproducing a multi-exponential ringdown decay) considerably simpler, as discussed in detail in Ref. [18]. In addition, the intensity ratios of 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 for individual laser shots, are acquired by the data acquisition system, as discussed in Section 2. This enables monitoring the slight drift of the laser wavelength and line shape during the operation. Figure 10 also shows the synthetic apparent absorption line profiles (the convolution between the laser and absorption line shapes), calculated for the pressure of $P=2.7$ Torr and temperature of $T=70$ K, for illustration purposes. 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. 10, 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 only $\pm 1\%$. During these measurements, the empty cavity ring down time was shorter compared to that in Fig. 9, $\tau = 23$ 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 $\pm 10\text{-}15\%$ standard deviation (see Fig. 10). 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, due to the higher transition cross section. However, at these conditions the $v=0$ and $v=1$ populations are close to each other, as shown below.

Figure 11 compares the $N_2(A^3\Sigma_u^+, v=0,1)$ absolute populations inferred from the ring down data plotted in Fig. 10. Although these data were reduced taking into account the absorption on multiple cavity modes, as discussed in Ref. [18], at these conditions absorption is relatively weak (see Fig. 9(b)), such that a Single Exponential Approximation (SEA), discussed in the Appendix, yields essentially the same results. As expected, these populations, $(3.7 \pm 1.0) \cdot 10^{10} \text{ cm}^{-3}$ for $v=0$ and $(3.7 \pm 1.0) \cdot 10^{10} \text{ cm}^{-3}$ for $v=1$, respectively, are three orders of magnitude lower compared to the peak $N_2(A^3\Sigma_u^+, v=0)$ population measured in the plenum, due to both the lower number density in the supersonic test section and the rapid decay of $N_2(A^3\Sigma_u^+)$ molecules in the discharge afterglow (see Fig. 9). This illustrates the sensitivity of the present CRDS diagnostic, with the detection limit of approximately 10^{10} cm^{-3} . The most significant uncertainty in the $N_2(A^3\Sigma_u^+)$ number density inferred from the present data is the uncertainty in the flow temperature. The translational-rotational temperature is inferred from the intensity ratio of two absorption transitions,

$$\frac{\alpha_1}{\alpha_2} = \frac{\Phi_1 \cdot S_1}{\Phi_2 \cdot S_2} \exp\left(\frac{hc}{k_b T} (E(N_2'') - E(N_1''))\right), \quad (8)$$

where $\Phi = \frac{1}{3}$ (*even* N'') or $\frac{2}{3}$ (*odd* N'') is the nuclear spin statistical weight factor, $E(N'')$ is the rotational energy of the N'' state, k_b is the Boltzmann constant, h is the Planck constant, c is the speed of light, and S is the Hönl-London factor for each transition. For the rotational temperature inference from the CRDS data, we used pairs of spectrally isolated rotational lines, with (i) strong absorption at the low temperatures involved and (ii) sufficient rotational energy separation of the two lower states, $|E_1'' - E_2''|hc \sim k_b T$, which provides high sensitivity to the temperature. The spectral isolation of the lines is critical for the CRDS data reduction, which requires matching the multi-exponential decay of the ringdown signal. For $^3\Sigma \rightarrow ^3\Pi$ bands, which have 27 rotational branches, identifying such line pairs is rather challenging. Table 1 lists the rotational energy and Hönl-London factors for the transitions used for temperature inference.

Table 1: Hönl London Factor and Rotational Energies for selected rotational lines.

Transition Name	Hönl London Factor, S	Rotational Energy, $E(N'')$ (cm^{-1})
$v''=0, Q_{11}(6),$ $N''=5, J''=6,$ $\lambda_0 \text{ (nm)}=774.6001$	7.00	43.65
$v''=0, Q_{11}(8),$ $N''=7, J''=8,$ $\lambda_0 \text{ (nm)}=774.1757$	10.30	81.26
$v''=0, ^PQ_{23}(4),$ $N''=5, J''=4,$ $\lambda_0 \text{ (nm)}=773.8403$	4.71	44.04

$v''=1, Q_{11}(6),$ $N''=5, J''=6,$ $\lambda_0 \text{ (nm)}=761.9464$	6.97	42.82
$v''=1, Q_{11}(8),$ $N''=7, J''=8,$ $\lambda_0 \text{ (nm)}=761.5367$	10.24	79.94

The temperature inferred from the absorption line intensity ratio is $T=67 \pm 15$ K, which is close to the value for a quasi-one-dimensional isentropic flow at $T_0=300$ K and $M=4.6$, $T=60$ K.

Figure 12 plots the time-resolved absolute population of $N_2(A^3\Sigma_u^+, v=0)$ measured by TDLAS in the large supersonic test section at the plenum pressure of $P_0=250$ Torr, with the flow excited by a 100-pulse, 100 kHz ns pulse discharge burst (burst duration 1 ms) near the nozzle throat (see Fig. 6(b)). In the figure, the discharge in the wind tunnel throat is initiated at $t=0$, indicating the flow transit time from the plasma region to the TDLAS laser beam location of approximately 200 μs . For TDLAS data, the rotational temperature was inferred using three different rotational lines (i.e. two different line pairs), yielding consistent results. The data plotted in Fig. 12 are obtained using three absorption transitions in the $N_2(B^3\Pi_g, v'=2 \leftarrow A^3\Sigma_u, v''=0)$ band in different wind tunnel runs, yielding $[N_2(A^3\Sigma_u^+, v=0)] = (1.8 \pm 0.1) \cdot 10^{11} \text{ cm}^{-3}$ at the static temperature of $T = 67 \pm 8$ K, and illustrating the reproducibility and consistency of the data. The detection limit of the single-pass TDLAS measurements in the supersonic test section is comparable to that of the CRDS measurements, $\approx 10^{10} \text{ cm}^{-3}$. Note that these data do not exhibit the periodic variation observed in the TDLAS measurements in the wind tunnel plenum (see Fig. 8), most likely due to the shorter flow residence time in the plasma near the nozzle throat, and the rapid flow expansion downstream of the discharge, which slows down the collisional quenching of $N_2(A^3\Sigma)$.

Figure 13 shows six composite CRDS absorption line scans, each plotting two rotational lines in three different vibrational bands of $N_2(A^3\Sigma_u^+, v=0-2)$, measured at the same conditions as the TDLAS data shown in Fig. 12. Each absorption scan is done over several wind tunnel runs, with the laser tuned to different wavelengths for each run. To generate the composite scan, the single-shot ring down time data (50 shots taken during each run) were placed into the bins 0.3 pm wide (≈ 23 shots per bin) and averaged, with the uncertainty defined as the standard error of the mean. The synthetic absorption line shapes (a convolution of the absorption and laser line shape), are shown for comparison. The synthetic spectra generation, line broadening factors, and molecular data used by the synthetic spectrum software have been discussed in detail our previous work [18]. It can be seen that the experimental data agree well with the synthetic line shapes, for all six absorption transitions. Compared to the CRDS data taken in the small test section (see Fig. 10), the absolute shot-to-shot variation of the ring-down time remains about the same, $14 \pm 5 \mu\text{s}$ for $Q_{11}(8)$ transition in the $N_2(B^3\Pi_g, v'=3 \leftarrow A^3\Sigma_u, v''=1)$ band. However, the relative variation is now more significant, due to a much shorter ring down time indicating significantly higher $N_2(A^3\Sigma_u^+)$ number density in the large tunnel test section. The $N_2(A^3\Sigma_u^+, v=0-2)$ absolute populations are $(5.7 \pm 2.4) \cdot 10^{11} \text{ cm}^{-3}$, $(5.2 \pm 2.6) \cdot 10^{11} \text{ cm}^{-3}$, and $(3.1 \pm 1.5) \cdot 10^{11} \text{ cm}^{-3}$, respectively, at the static temperature inferred from the line pair ratios of $T = 76 \pm 15$ K.

Finally, Fig. 14 plots the $N_2(A^3\Sigma_u^+, v=0-2)$ populations inferred from CRDS data together with the $N_2(A^3\Sigma_u^+, v=0)$ population obtained from TDLAS data, at the conditions of Fig. 12-13

($P_0=250$ Torr, discharge in the nozzle throat, pulse repetition rate 100 kHz). At these conditions, absorption is strong and non-single exponential decay due to the absorption on multiple cavity modes is well pronounced (see Fig. 9(c)). Therefore, a Single Exponential Approximation is no longer applicable, and a more accurate approach, given by Eq. (A1) in the Appendix, was used. It can be seen that the $v=0$ populations measured by TDLAS and CRDS differ by approximately a factor of 3. We believe that this difference may be caused by absorption in the boundary layers, and possibly in the cavity arms, which were removed for the TDLAS measurements. The flow field in the small supersonic test section, predicted by the 3-D compressible Navier-Stokes flow code in Fig. 15 of Ref. [20] (for a Mach 4 nozzle) indicates the development of well-pronounced “bulges” in the side wall boundary layers, due to the secondary crossflow over the plane (non-contoured) walls. Although the predicted inviscid core flow still occupies approximately 80% of the wind tunnel span, about the same as the extent of the plasma generated in the plenum and near the throat (see Fig. 6), it is possible that some of the $N_2(A^3\Sigma_u^+)$ molecules generated in the plasma are present in the higher temperature boundary layers. This would affect the CRDS measurements because of the larger absorption linewidth in the boundary layers, such that the light is absorbed on additional cavity modes, resulting in a possible overprediction of the absorbing species number density. On the other hand, the number density inferred from the TDLAS measurements would be somewhat underpredicted, due to the lower absorption on the line center in the boundary layers.

The upper bound estimate of this effect, obtained using the temperature distribution in the supersonic test section predicted in Fig. 12 of Ref. [20] and assuming a uniform $N_2(A^3\Sigma_u^+)$ number density distribution along the test section span (absorption path) results in the population inferred by CRDS of approximately a factor of 2 higher compared to that obtained from TDLAS. This illustrates the critical importance of generation the excited species and radicals only in the inviscid core flow, outside the boundary layers and shear / mixing layers, such as produced when a supersonic jet is exhausting into a quiescent vacuum chamber. Using the present approach, this can be achieved by reducing the spanwise dimensions of the discharge electrodes or their spanwise overlap. In larger scale facilities, with longer absorption path across the test section, the boundary layer effects are expected to diminish significantly.

4. 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 $N_2(A^3\Sigma_u^+, v=0-2)$ vibrational levels in a nonequilibrium flow of nitrogen, excited by a repetitive ns pulse discharge in a supersonic wind tunnel. As expected, single-pass TDLAS measurements using a continuous wave diode laser are most effective in high pressure nonequilibrium flows, 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 flows, where the sensitivity of single-pass absorption techniques may not be sufficient. Therefore the two diagnostic techniques are complementary and can be used for the characterization of nonequilibrium high-speed flows over a wide range of pressures, from below 1 Torr to atmospheric pressure.

The results of TDLAS measurements in the wind tunnel plenum indicate the gradual accumulation of a rapid $N_2(A^3\Sigma)$ quencher species, most likely N atoms. CRDS measurements are made in the supersonic test section. It is shown that the cavity ring down time is not affected by

the supersonic flow. During each run, 50 single laser shot ring down traces are acquired, demonstrating good shot-to-shot reproducibility. The ring down time measured on several $N_2(B^3\Pi_g, v' \leftarrow A^3\Sigma_u, v'')$ absorption transitions is significantly shorter compared to the baseline value, measured when the laser is tuned off resonance. $N_2(A^3\Sigma_u^+, v=0)$ populations and the flow static temperature inferred from the single-shot CRDS data are consistent with the single-pass TDLAS measurements at the same conditions, with the difference most likely caused by the absorption in the boundary layers. The detection limit of both diagnostics at the present conditions is approximately 10^{10} cm^{-3} . To the best of our knowledge, these are the first CRDS measurements in a supersonic flow in a wind tunnel, rather than in an expansion jet.

At the present conditions, $N_2(A^3\Sigma)$ is produced by electron impact rather than by the heavy species impact excitation, as occurs behind strong shock waves in air. Therefore, the main significance of the present work is the development of laser diagnostics that can be used for $N_2(A^3\Sigma)$ measurements in high-enthalpy nonequilibrium hypersonic flows generated at pulsed flow facilities, such as shock tubes and hypervelocity expansion tubes. The present results indicate that both diagnostics used in the present work can be employed for this purpose. 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 [16]. Based on the detection limit of the present TDLAS measurements of approximately 10^{10} cm^{-3} (single-pass absorption of $\sim 10^{-4}$), single-pass absorption measurements of $N_2(A^3\Sigma_u^+)$ number density behind a strong shock in nitrogen ($T \sim 5000 \text{ K}$, $P = 1 \text{ atm}$), over an absorption path of $\sim 10 \text{ cm}$, would be feasible. The present results suggest that single laser shot CRDS measurements, with the ring down time of $\sim 10 \mu\text{s}$, are also feasible 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.

Time-resolved measurements of $N_2(A^3\Sigma)$ vibrational populations in a nonequilibrium high-enthalpy flow, combined with the time-resolved of NO number density (e.g. by mid-IR Quantum Cascade Laser absorption spectroscopy [27]), and NO UV emission spectra [28], would provide kinetic data on the mechanism of nonequilibrium UV emission in atmospheric reentry flows and hypersonic flight. These data sets would help validate the new high-fidelity DSMC calculations [29] used for the prediction of NO UV emission spectra in hypersonic ground testing facilities.

Appendix

As shown in Ref. [18], the ring down signal at the conditions when absorption in the cavity occurs on multiple models, $I(t)$, is as follows,

$$\frac{I(t)}{I_0} = \exp\left(-\frac{t}{\tau_{empty}}\right) \frac{1}{c_1} \sum_m g_L(v_0 - v_m) \exp\left(-\frac{nk_{v_0}L_{abs}cg_A(v_0 - v_m)t}{L_{cavity}}\right), \quad (A1)$$

where I_0 is the incident light intensity, c is the speed of light, t is time, τ_{empty} is the empty cavity ringdown, $g_L(v_0 - v_m)$ is the laser source line shape, $g_A(v_0 - v_m)$ is the absorption line shape, n is the number density of the absorbing species, k_{v_0} is the absorption cross section, L_{abs} is the absorption path length, and L_{cavity} is the cavity length. The normalization constant, c_1 , is given as

$$c_1 = \sum_m g_L(\nu_0 - \nu_m) \quad (A2)$$

where ν_0 is the center wavelength of the laser beam, ν_m is the cavity mode frequency, and the summation is over all cavity modes within the absorption line shape. The cavity mode spacing is controlled by the cavity length,

$$\Delta\nu_m = \frac{c}{2L_{cavity}}. \quad (A3)$$

The empty cavity ringdown time is controlled by the cavity length and the reflectivity of the mirrors,

$$\tau_{empty} = \frac{L_{cavity}}{(1-R)c}. \quad (A4)$$

Using the notations $x \equiv \frac{t}{\tau_{empty}}$ and $\beta_m \equiv \frac{nk_{\nu_0}L_{abs}}{(1-R)}g_A(\nu_0 - \nu_m)$, Eq. (A1) can be simplified as follows,

$$\frac{I}{I_0} = \frac{1}{c_1} \sum_m g_L(\nu_0 - \nu_m) \exp[-(1 + \beta_m)x] \quad (A5)$$

Assuming $(1 + \beta_m)x \ll 1$ and linearizing, obtain

$$\frac{I}{I_0} \approx \frac{1}{c_1} \sum_m g_L(\nu_0 - \nu_m) [1 - (1 + \beta_m)x] = 1 - \left(1 + \frac{1}{c_1} \sum_m g_L(\nu_0 - \nu_m) \beta_m\right) x, \quad (A6)$$

which can be approximated as a single exponential form,

$$\frac{I}{I_0} \approx \exp \left[- \left(1 + \frac{1}{c_1} \sum_m g_L(\nu_0 - \nu_m) \beta_m\right) x \right] = \exp \left(- \frac{t}{\tau_{SEA}} \right). \quad (A7)$$

In Eq. (A7), the Single Exponential Approximation (SEA) ring down time, τ_{SEA} , is

$$\frac{1}{\tau_{SEA}} = \frac{1}{\tau_{empty}} \left(1 + \frac{nk_{\nu_0}L_{abs}}{(1-R)} \frac{1}{c_1} \sum_m g_L(\nu_0 - \nu_m) g_A(\nu_0 - \nu_m) \right) \quad (A8)$$

Use of Eqs. (A7, A8) allows for a single exponential fit of multi-exponential decays observed in cavity ringdown experiments. The Single Exponential Approximation is valid for early times in a strong absorption ringdown decay ($t \ll \tau_{empty}$), or in the weak absorption regime, $\frac{nk_{\nu_0}L_{abs}}{(1-R)}g_A(\nu_0 - \nu_m) \ll 1$, when the deviation from a single exponential decay is relatively small. At these conditions, the absorbing species number density is determined as follows,

$$n = \left(\frac{1}{\tau_{SEA}} - \frac{1}{\tau_{empty}} \right) \frac{L_{cavity}}{ck_{\nu_0} L_{abs}} \frac{c_1}{\sum_m g_L(\nu_0 - \nu_m) g_A(\nu_0 - \nu_m)} . \quad (A9)$$

As expected, when the laser line shape is much smaller than the absorption line shape, this equation is reduced to the well-known limit,

$$n = \left(\frac{1}{\tau_{SEA}} - \frac{1}{\tau_{empty}} \right) \frac{1}{ck_{\nu_0} g_A(\nu_0)} \frac{L_{cavity}}{L_{abs}} . \quad (A10)$$

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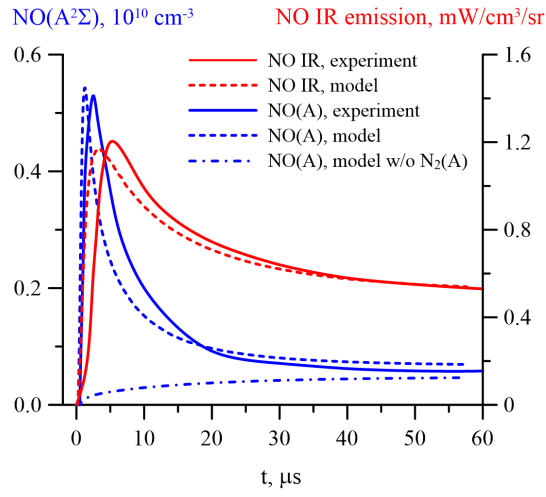


Figure 1. Comparison between experimental [1] and predicted NO infrared emission intensity and $\text{NO}(\text{A}^2\Sigma)$ number density controlling NO γ band UV emission behind a normal shock in air. $\text{NO}(\text{A}^2\Sigma)$ number density predicted without the energy transfer from $\text{N}_2(\text{A}^3\Sigma)$ is plotted for comparison. Modeling predictions are based on the kinetic model of coupled vibrational relaxation and nonequilibrium chemical reactions in air [4], extended to include electronic excitation and UV emission processes.

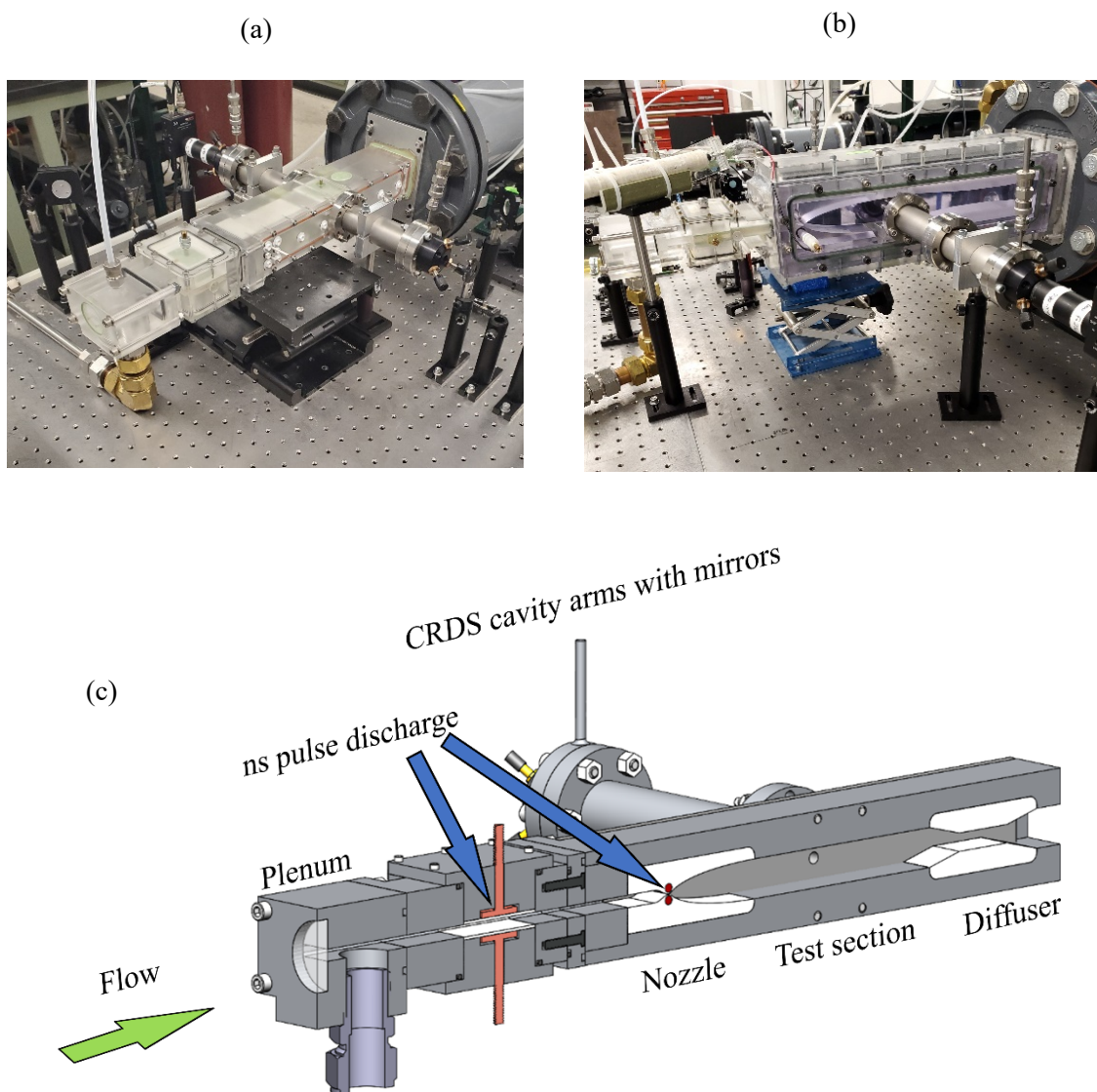


Figure 2. Photographs of the (a) small and (b) large wind tunnel sections; (c) cutout view of the flow channel, the electric discharge electrodes, and the CRDS cavity. In the cutout view, the electrodes in the small test section (a) are shown in orange and the electrodes in the large test section (b) are shown in red.

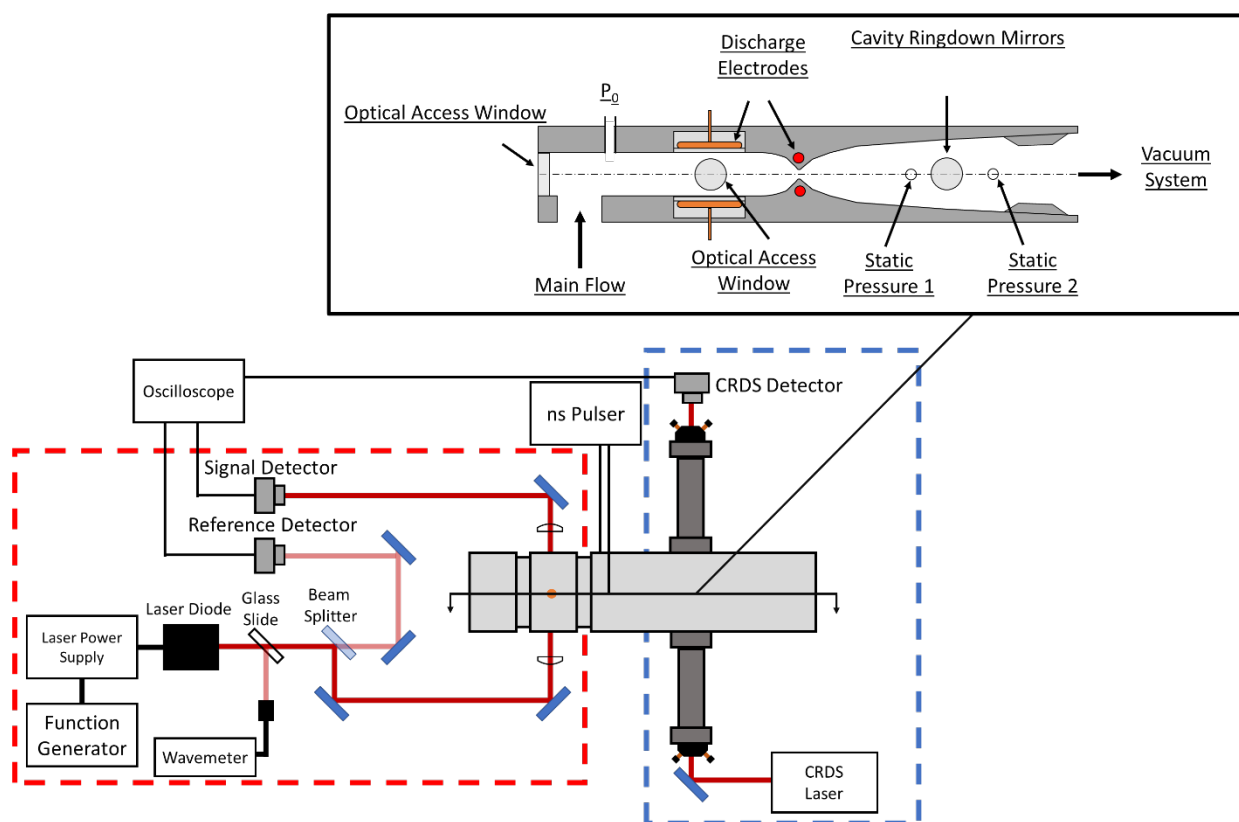


Figure 3. Schematic of the nonequilibrium flow wind tunnel, Cavity Ring Down Spectroscopy (CRDS), and Tunable Diode Laser Absorption Spectroscopy (TDLAS) experimental setup. A cross section view of the wind tunnel is shown in the inset, with the orange electrodes used in the small wind tunnel and the red electrodes used in the large wind tunnel.

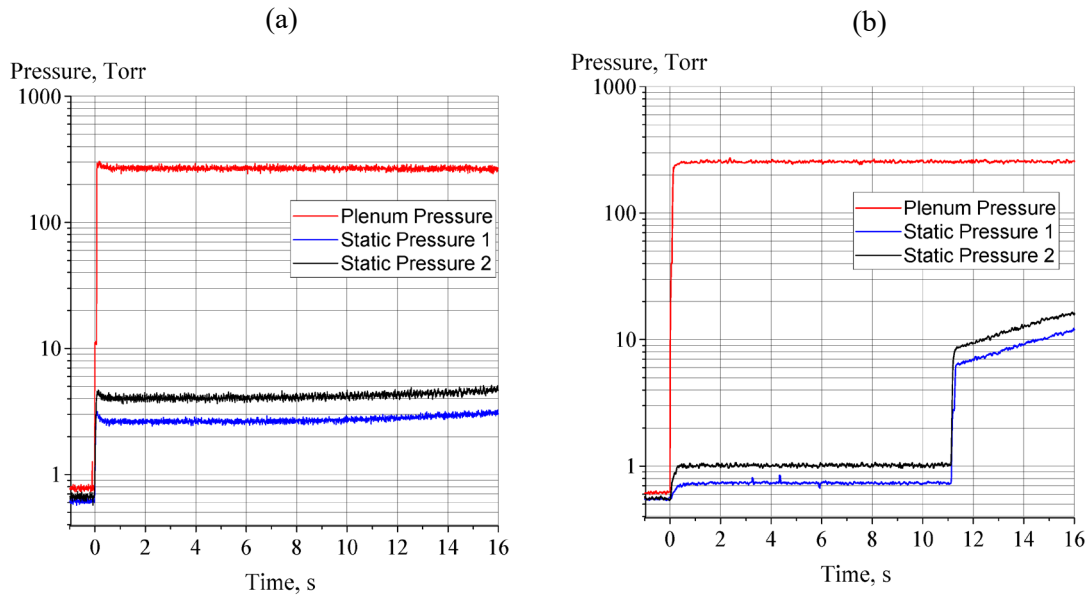


Figure 4. Plenum pressure and test section static pressure traces during the operation, (a) small wind tunnel, (b) large wind tunnel. Locations of the wall static pressure taps are shown in Fig. 3.

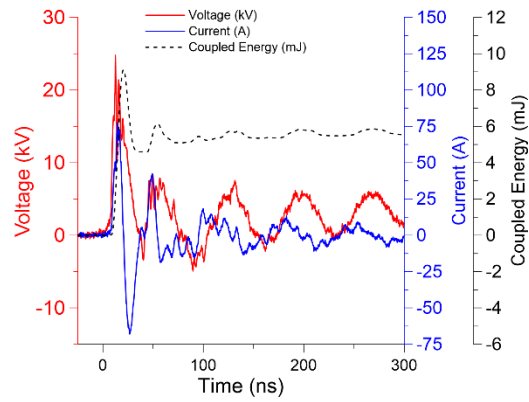


Figure 5. ns pulse discharge voltage, current, and coupled energy waveforms: (a) discharge in plenum (MegaImpulse plasma generator).

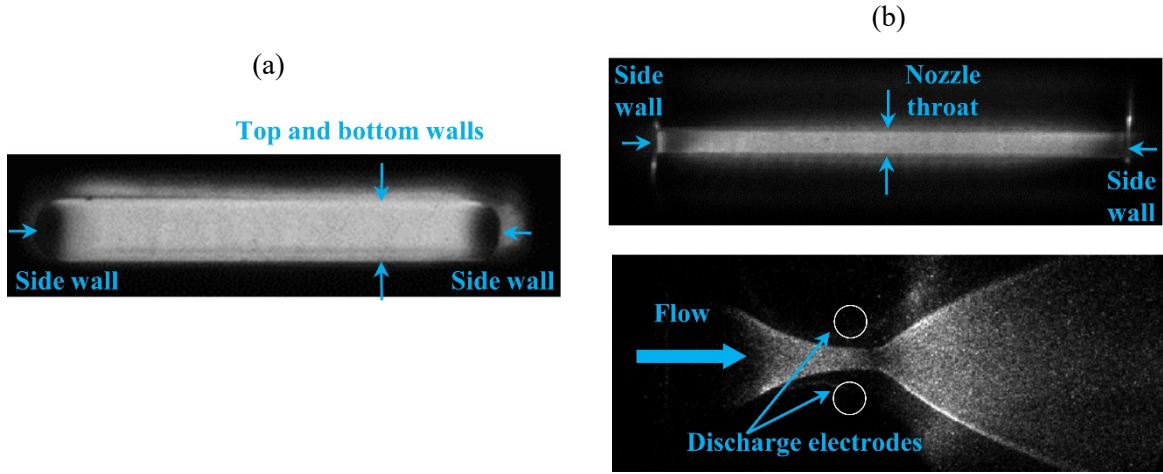


Figure 6. Single-shot, broadband plasma emission images: (a) Small test section, $P_0=230$ Torr, discharge in plenum, view through the optical access window in the back wall of the plenum (see Fig. 2(c)); (b) Large test section, $P_0=250$ Torr, discharge in the nozzle throat, views through the window in the back wall of the plenum and through the side wall of the nozzle. Nitrogen, pulse repetition 100 kHz, camera gate 1 μ s (a) and 200 ns (b).

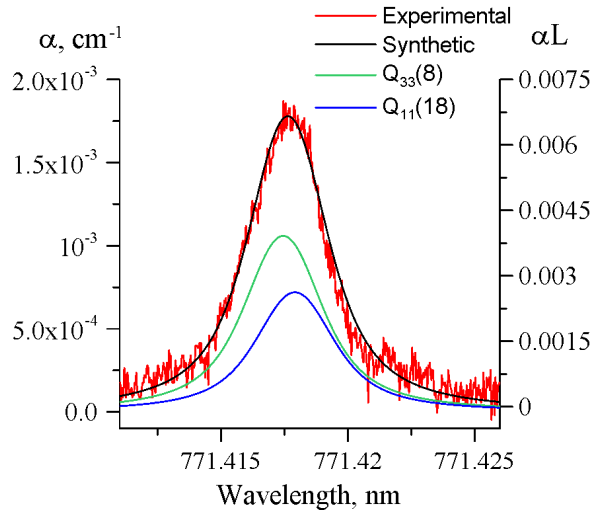


Figure 7. Composite absorption line shape of overlapping $Q_{11}(18)$ and $Q_{33}(8)$ rotational transitions in the $N_2(B^3\Pi_g, v'=2 \leftarrow A^3\Sigma_u, v''=0)$ band during a ns discharge burst in nitrogen in the small wind tunnel plenum, at $P_0=227$ Torr and pulse repetition rate of 4 kHz.

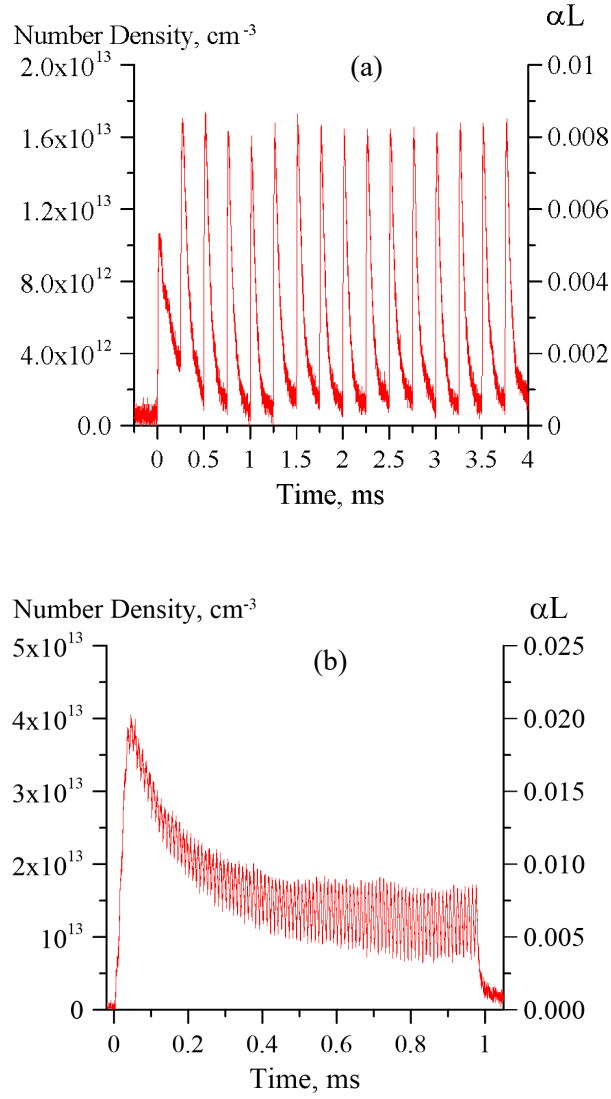


Figure 8. Time-resolved absolute population of $N_2(A^3\Sigma_u^+, v=0)$ during the ns discharge burst in nitrogen in the wind tunnel plenum at $P_0=227$ Torr, at pulse repetition rates of (a) 4 kHz and (b) 100 kHz.

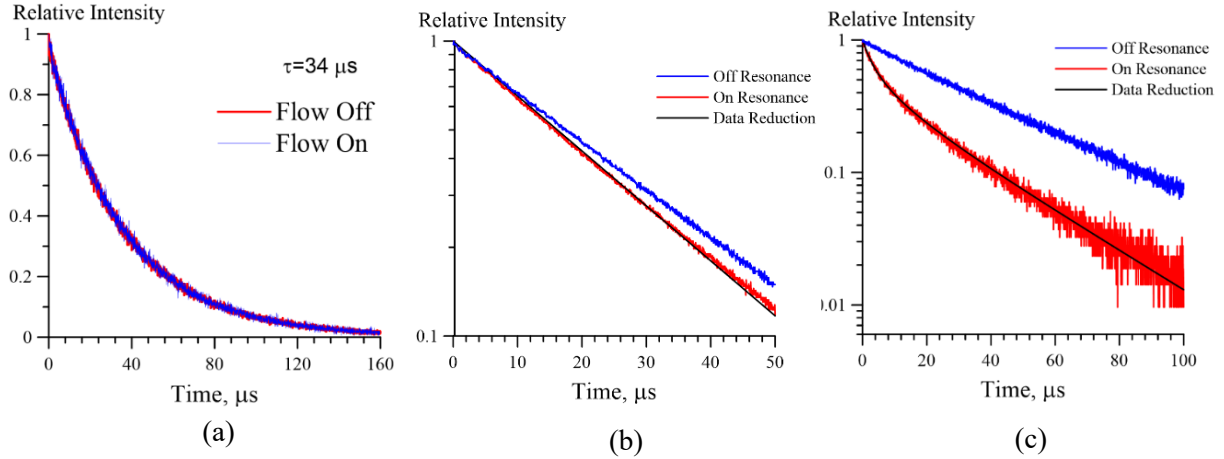


Figure 9. Typical single-shot cavity ring down traces: (a) empty cavity without flow and with $M=4.6$ flow in the cavity; (b) $M=3.6$ flow with a 4 kHz ns pulse discharge in the plenum at $P_0=250$ Torr, on and off resonance with the absorption transition $Q_{11}(8)$ in the $N_2(B^3\Pi_g, v'=2 \leftarrow A^3\Sigma_u, v''=0)$ band; (c) $M=4.6$ flow with a 100 kHz ns pulse discharge in the nozzle throat at $P_0=250$ Torr, on and off resonance with the absorption transition $^P Q_{23}(4)$ in the $N_2(B^3\Pi_g, v'=2 \leftarrow A^3\Sigma_u, v''=0)$ band.

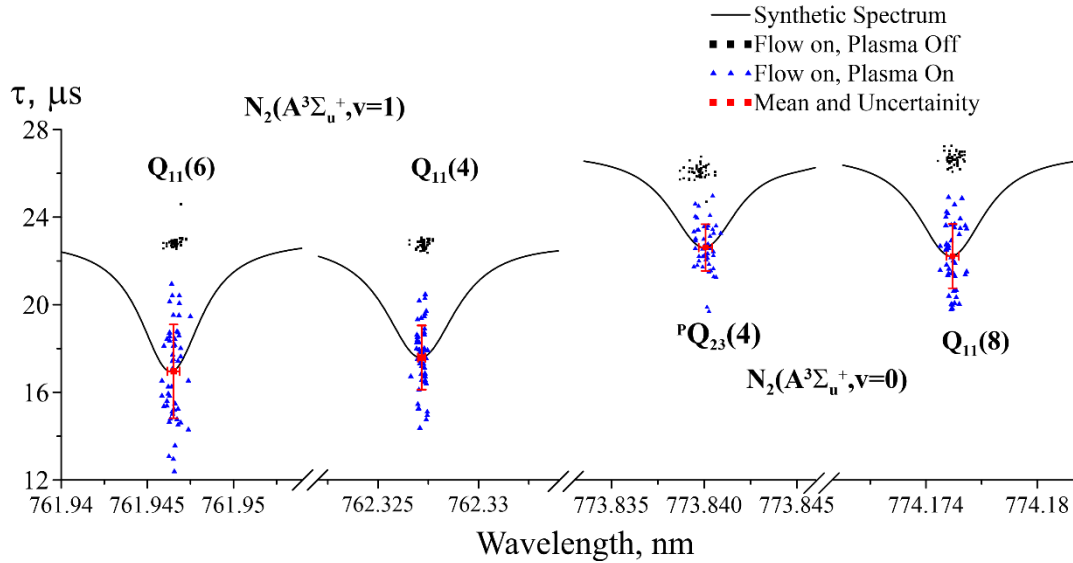


Figure 10. Comparison of single-shot ring down time measured in the $M=3.6$ flow in the small wind tunnel with the plenum discharge on and off. Data shown are for $^P Q_{23}(4)$ and $Q_{11}(8)$ absorption transitions in the $N_2(B^3\Pi_g, v'=2 \leftarrow A^3\Sigma_u, v''=0)$ band, and $Q_{11}(6)$ and $Q_{11}(4)$ transitions in the $N_2(B^3\Pi_g, v'=3 \leftarrow A^3\Sigma_u, v''=1)$ band. Synthetic absorption line shapes (convolution of the absorption and laser line shape) are also shown. $P_0=250$ Torr, discharge pulse repetition rate 4 kHz.

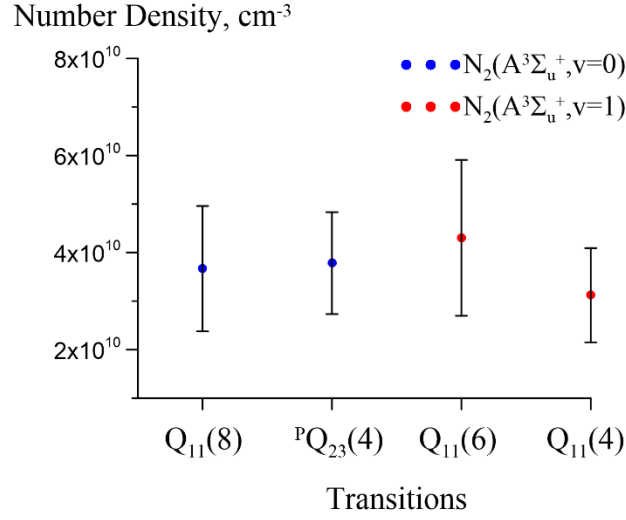


Figure 11. $N_2(A^3\Sigma_u^+, v=0)$ and $N_2(A^3\Sigma_u^+, v=1)$ populations inferred from the ring down data at the conditions of Fig. 10 ($M=3.6$ flow, $P_0=250$ Torr, discharge in plenum, pulse repetition rate 4 kHz).

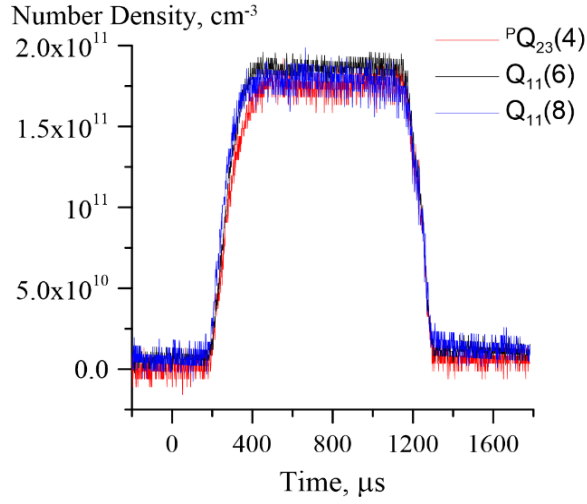


Figure 12. Time-resolved absolute population of $N_2(A^3\Sigma_u^+, v=0)$ measured in the large test section by TDLAS in the $M=4.6$ flow, using 3 different absorption transitions in the $N_2(B^3\Pi_g, v'=2 \leftarrow A^3\Sigma_u, v''=0)$ band. $P_0=227$ Torr, 100 kHz ns pulse discharge burst in the nozzle throat. The discharge in the wind tunnel throat is initiated at $t=0$. $[N_2(A^3\Sigma_u^+, v=1)] = 1.7 \pm 0.1 \cdot 10^{11} \text{ cm}^{-3}$, $T=67 \pm 15 \text{ K}$.

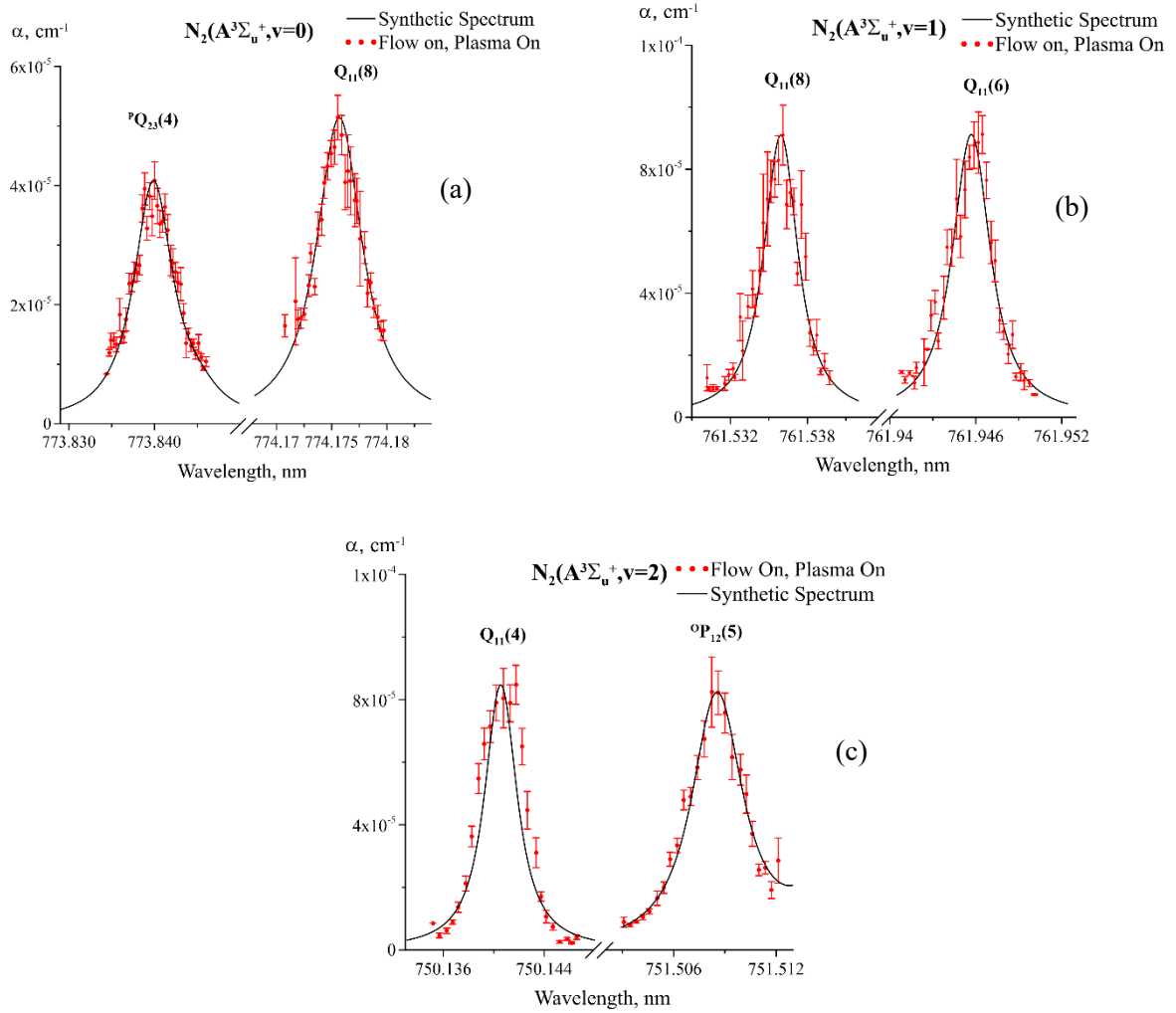


Figure 13. Comparison of CRDS data in the M=4.6 flow with the synthetic line shapes (convolution of the absorption and laser line shapes):

(a) $Q_{11}(8)$ and $^PQ_{23}(4)$ transitions, $N_2(B^3\Pi_g, v'=2 \leftarrow A^3\Sigma_u, v''=0)$,

(b) $Q_{11}(8)$ and $Q_{11}(6)$ transitions, $N_2(B^3\Pi_g, v'=3 \leftarrow A^3\Sigma_u, v''=1)$,

(c) $Q_{11}(5)$ and $^OP_{12}(5)$ transitions, $N_2(B^3\Pi_g, v'=4 \leftarrow A^3\Sigma_u, v''=2)$.

Each data point is an average of ~ 25 CRDS traces, uncertainty bars indicate standard error of the mean. $P_0=250$ Torr, discharge pulse repetition rate 100 kHz.

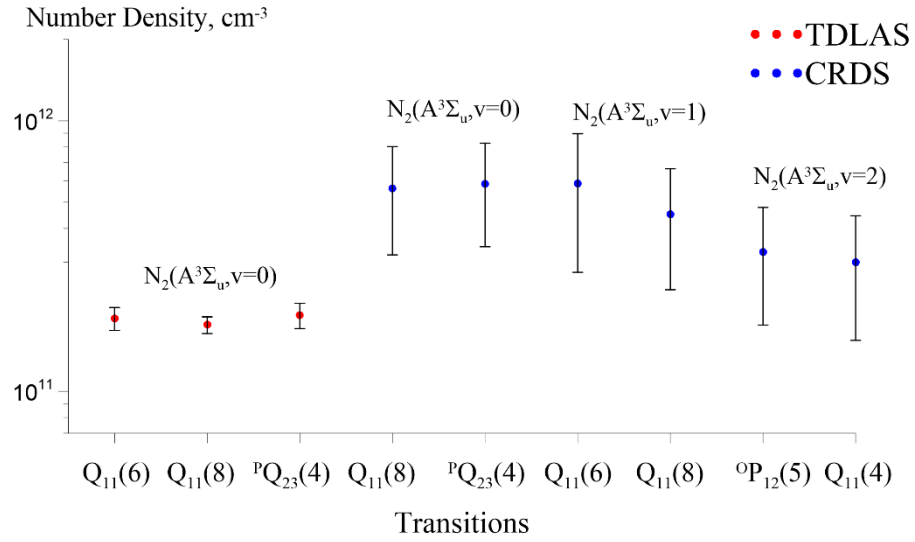


Figure 14. N₂(A³Σ_u⁺, v=0) and N₂(A³Σ_u⁺, v=0-2) populations inferred from the CRDS and TDLAS data at the conditions of Figs. 12,13 (M=4.6, P₀=250 Torr, discharge in the nozzle throat, pulse repetition rate 100 kHz). See discussion in the text.

PART IV.

MEASUREMENTS OF VIBRATIONALLY EXCITED $O_2(X^3\Sigma_g^-, v)$ MOLECULES GENERATED IN RECOMBINING O-O₂-AR FLOWS ⁴

1. Introduction

The critical role of vibrational excitation of oxygen and nitrogen during their dissociation in nonequilibrium high-enthalpy flows (primarily behind the hypersonic shock waves), has been recognized for a long time [1]. However, accurate experimental quantification of this effect is difficult. Although significant O₂ vibrational populations and O atom number density can be generated at pulsed hypersonic flow facilities, such as shock tubes [2-6], nonequilibrium dissociation measurements necessitate acquiring the state-specific data during a single shot experiment, on ~1-100 μ s time scale. In spite of the remarkable recent progress in laser diagnostics, paving the way to the low-uncertainty measurements of the nonequilibrium dissociation factor in shock tubes [4-6], state-specific measurements of molecular dissociation from high vibrational levels remain extremely challenging.

In the present work, we use a different approach, where the vibrational levels of molecular oxygen in the ground electronic state, $O_2(X^3\Sigma_g^-, v)$, populated during the recombination of O atoms, are monitored in an O₂-Ar mixture partially dissociated by a ns pulse discharge burst in a flow reactor. Comparison of the experimental data with the predictions of a kinetic model, incorporating the state-specific rate coefficients of O atom recombination,



as well as the rates of vibrational-translational (V-T) and vibrational-vibrational (V-V) relaxation [7-10], is expected to yield insight into the kinetics of vibrationally-enhanced O₂ dissociation, since the recombination rates, $k_r(\rightarrow v)$, are related to the dissociation rate, $k_d(v \rightarrow)$, via the detailed balance,

$$k_d(v \rightarrow, T) = k_r(\rightarrow v, T) \cdot \frac{n_O^2(T)}{n_{O_2(v)}(T)}. \quad (2)$$

In Eq. (2), $n_O(T)$ and $n_{O_2(v)}(T)$ are the number densities of O(³P) atoms and $O_2(X^3\Sigma_g^-, v)$ molecules in thermal equilibrium. This approach can be used if the reactants (O atoms) are generated in significant amounts at well-characterized conditions, and if the number densities of the reactants and the products (e.g. O atoms and $O_2(X, v)$ molecules, respectively), as well as the gas temperature, are measured at the same time. Figure 1 plots the kinetic modeling predictions of $O_2(X, v)$ vibrational populations in a recombining O-O₂-Ar mixture at T = 500 K and P = 100 Torr,

⁴ D.C.M. van den Bekerom, E. Jans, X. Yang, A. Paul, D. Andrienko, and I.V. Adamovich, "Measurements of Vibrationally Excited Oxygen Produced in Recombining O-O₂-Ar Mixtures", AIAA Paper 2021-1145, AIAA Aerospace Sciences Meeting (SciTech 2021), 11-15 & 19-21 January 2021

illustrating the formation of a quasi-steady-state “tail” in the O₂ vibrational distribution function, produced by the O atom recombination.

In the present experiments, oxygen atoms are produced in a repetitive ns pulse discharge in an O₂-Ar mixture, which generates a diffuse, spatially uniform plasma at high pressures and high reduced electric fields [11]. This is critical for the efficient O₂ dissociation by electron impact, and by quenching of excited electronic states of Ar atoms. O atom recombination is monitored on a long time scale after the discharge burst, up to of several milliseconds, much longer compared to the time scales for O₂ vibrational relaxation and collisional quenching of excited electronic states of O₂, O, and Ar generated in the discharge. At these conditions, oxygen recombination is dominated by the reactions of O atoms in the ground electronic state. Although the present measurements are done at relatively low temperatures $T = 380\text{--}650\text{ K}$, this approach can be also extended to higher temperatures, up to $T \sim 1500\text{ K}$, such that the predictive capability of the kinetic model may be assessed over a wide temperature range.

2. Experimental

A schematic of the experimental apparatus is shown in Fig. 2. The electric discharge cell is a 22 mm x 10 mm rectangular cross section, 20 cm long quartz channel fused to 1 inch diameter quartz tubes, attached to 1 inch diameter quartz endpieces with Brewster’s angle optical access windows made of fused silica, using Ultra-Torr vacuum fittings. The total length of the cell is 60 cm. A 20% O₂ / 80% Ar mixture flows through the cell at the flow rate of 2 SLM, through the ¼ inch diameter inlet port and 1 inch diameter exit port, connected to the gas delivery and exhaust lines by the Ultra-Torr fittings. The mixture components are pre-mixed and delivered from a single gas cylinder. The flow rates of the mixture components are regulated and monitored by the mass flow controllers (MKS1179A). The pressure in the cell is maintained at 100 Torr by throttling the flow in the vacuum exhaust line. The flow is preheated several cm upstream of the discharge electrodes, using a heating tape wrapped around the flow channel and insulated on the outside by fiberglass wrapping sleeves around the heating tape (see Fig. 2). Preheating the flow serves both to improve the discharge plasma uniformity and to suppress ozone formation during the O atom recombination in the flow dissociated by the electric discharge. The temperature of the heating tape, up to $T = 270\text{ }^{\circ}\text{C}$, is measured by a thermocouple placed between the cell and heating tape.

The flow in the cell is excited by a diffuse double dielectric barrier, ns pulse discharge between two parallel rectangular plate copper electrodes 60 mm long and 14 mm wide, mounted to the top and bottom walls in the middle of the quartz channel, as shown in Fig. 2. The electrodes are held in place by ceramic brackets and screws, and are embedded in RTV high temperature silicone sealant. The discharge is sustained by a positive polarity MegaImpulse NPG-18/100k high-voltage pulse generator, with the pulse peak voltage up to 16.7 kV and pulse duration of approximately 14 ns FWHM. The pulse generator is operated in burst mode, at a pulse repetition rate of 100 kHz, burst duration of 100 pulses (1 ms), and burst repetition rate of 10 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 [12]. No corona discharge was detected on the electrodes at the present conditions. After the pulse burst, O atoms generated by the electron impact dissociation of O₂, and by the reactive quenching of electronically excited Ar atoms by O₂ recombine to form the vibrationally excited O₂ molecules. The discharge bursts are repeated at 10 Hz, allowing the O atom recombination between the bursts, and the data are integrated over multiple bursts.

Time resolved populations of vibrational levels of molecular oxygen in the ground electronic state, $O_2(X^3\Sigma_g^-,v)$ and ground state O atoms, $O(^3P)$, are measured in the recombining O_2 -O-Ar flow by ps single-photon Laser Induced Fluorescence (LIF) and ps Two-photon Absorption LIF (TALIF), respectively. For both of these diagnostics, we use a ps Optical Parametric Oscillator (OPO, Ekspla PG401), pumped by the 3rd harmonic of a 10 Hz ps Nd:YAG laser (Ekspla PL2143A, nominal pulse duration 30 ps), at the pulse energy of 5 mJ at 355 nm. In the present work, the OPO produces output at 225-450 nm, with the pulse energy of 15-190 μ J and the linewidth of 2.0-3.5 cm^{-1} , tunable in 0.05 nm increments below 420 nm, and 0.1 nm increments above 420 nm. The OPO output beam is focused into the center of the discharge cell by a plano-convex lens with the focal distance of 50 cm. A beam reflection off a fused silica plane window is used to monitor the OPO output pulse energy, using a photodiode (see Fig. 2). The OPO output linewidth is measured by an Acton SpectraPro-500i 0.5 m spectrometer with a 2400 lines/mm grating and a Princeton Instruments PI-Max ICCD camera as a detector, using a beam reflection from another fused silica plane window (see Fig. 2). Where possible, spectra from higher orders of the grating were recorded, to maximize the spectral resolution. Line shapes up to 230 nm were measured in the 3rd order, between 230 nm and 330 nm in the 2nd order, and above 330 nm in the 1st order. The fluorescence signal is collected by a 2 inch diameter, 10 cm focal distance fused silica lens and detected by a gated PMT (Hamamatsu R3896), to isolate the signal from the plasma emission, as shown in Fig. 2. A narrow bandpass filter (12 nm FWHM, centered at 340 nm) placed in front of the PMT is used to isolate one of the fluorescence transition bands, and to block laser scattering and plasma emission.

Vibrational level populations of molecular oxygen, $O_2(X^3\Sigma_g^-,v)$, formed during the recombination of O atoms in the recombining flow, are monitored by LIF on the $O_2(B^3\Sigma_u^-, v' \leftarrow X^3\Sigma_g^-, v'')$ Schumann Runge bands, as shown schematically in Fig. 3. This approach is similar to the one used in Ref. [13], where a narrow linewidth tunable dye laser was used to probe $O_2(X^3\Sigma_g^-, v=8-22)$ vibrational level populations formed by the photodissociation of ozone. During the measurements, the vibrational level of the upper state was kept the same, $v'=0$, since this resulted in the highest Franck-Condon factor for the pump transition. Because the $B^3\Sigma_u^-$ state is strongly predissociated, as shown schematically in Fig. 3, the decay of the upper state is dominated by predissociation rather than emission or collisional quenching [14], and therefore assumed to be independent of the mixture composition, pressure, and temperature. For every O_2 vibrational level probed, the overlapping rotational transitions $N'' = R7$ and $N'' = P3$ are selected, since they are close to the peak rotational level population at the relatively low temperatures in the plasma.

A portion of the synthetic excitation spectrum for the $v'=0 \leftarrow v''=13$ pump transition is shown in Fig. 4. Due to the relatively broad OPO output linewidth of 2.0-3.5 cm^{-1} , it may produce excitation on other rotational transitions in the vicinity of the target R7 and P3 transitions. This is accounted for during the data reduction. A bandpass filter in front of the PMT isolates the $v'=0 \rightarrow v''=14$ fluorescence transition band back to the $X^3\Sigma_g^-$ state, such that $v''=14$ is not accessible to present LIF measurements. Additionally, levels $v''=15$ and $v''=16$ cannot be accessed since the OPO does not produce the output in this range, near the pump laser wavelength of 355 nm.

Absolute calibration of the LIF measurements using the known $O_2(X^3\Sigma_g^-,v)$ populations at thermal equilibrium is challenging, since it needs to be done at relatively high temperatures in the reactor cell and requires the excitation transitions in vacuum UV. In the present work, we use the NO LIF signal from a reference 100 ppm NO- N_2 mixture at room temperature, following the pump transition $NO(A^2\Sigma, v'=0 \leftarrow X^2\Pi, v''=0)$ at 225-227 nm for absolute calibration. The schematic of

the pump and fluorescence transitions in O₂ and NO molecules is shown in Fig. 5. The advantage of using the NO γ bands for calibration is that the fluorescence on the $v'=0 \rightarrow v''=8$ band is entirely within the pass band of the 340 nm bandpass filter used for the O₂ fluorescence measurements. This removes the need for the comparison of the collection optics and the PMT response at two different wavelengths. The calibration has been done at the quenching-free conditions in a low-pressure NO-N₂ mixture, at $P = 10.3$ Torr, when the fluorescence is controlled by the spontaneous radiative decay of the NO($A^2\Sigma, v'=0$) state. A computer code predicting the synthetic O₂ fluorescence spectrum, based on LIFBASE [15], is used to relate the NO number density in the calibration mixture to O₂($X^3\Sigma_g^-, v$) vibrational level populations in the discharge afterglow. Figure 6 compares the synthetic NO LIF excitation spectrum (line) with the experimental NO LIF spectrum (symbols), obtained by the stepwise tuning of the OPO, showing good agreement.

The O atom number density in the recombining flow is measured using the two-photon absorption LIF transition at 225.65 nm, which corresponds to the $J''=2$ component of the triplet ground electronic state, O(^3P). The fluorescence is detected by the same PMT, using a 840 nm bandpass filter with the FWHM of 40 nm. For absolute calibration, the TALIF signal in the O₂-Ar afterglow is compared to that of xenon excited at 224.35 nm, using the calibration technique described in detail in Ref. [16]. During the measurements, the OPO is maintained within the quadratic TALIF signal range.

The temperature of the flow excited by the discharge in the cell is measured by Tunable Diode Laser Absorption Spectroscopy (TDLAS) of electronically excited Ar atoms [17]. For this, a c.w. diode laser beam (New Focus Model 6312, linewidth <300 kHz), producing tunable output from 765 nm to 781 nm, is directed along the cell, and the absorption line profile is measured on the $1s_5 \rightarrow 2p_7$ transition in the $3p^5 4s$ state of Ar. Due to the rapid quenching of excited argon atoms by oxygen, the absorption line shape is measured only at the end of the discharge burst, after pulse #100. The pressure broadening coefficient for this absorption transition is available only for pure Ar [17], so at the present conditions it is determined by measuring the absorption line shape over a range of pressures, from 20 to 120 Torr. During these measurements, the number of discharge pulses in the burst was limited to 3 to keep gas heating to a minimum. The inferred pressure broadening coefficient, $K = 22.85$ MHz/Torr, is 30% higher compared to the value reported for pure Ar. The collisional (Lorentzian) broadening linewidth, $\Delta\nu_L$, is calculated as follows, $\Delta\nu_L = K \cdot P[\text{Torr}] \left(\frac{300}{T}\right)^{0.7}$. The temperature is inferred from the best fit synthetic absorption line shape (Voigt profile).

3. Results & Discussion

Figure 7 plots the ns pulse discharge voltage, current, and coupled energy waveforms, taken in a 20% O₂-Ar mixture, initially at room temperature, at a pressure of 100 Torr. At these conditions, the coupled discharge pulse energy remains nearly the same during the burst, 1.1 mJ/pulse. The waveforms in the preheated 20% O₂-Ar mixture have not yet been measured, but measurements in a 2% H₂ - 2% O₂ - Ar mixture at similar conditions (plane-to-plane ns pulse discharge at $P=100$ Torr and $T = 300\text{-}600$ K) [18] indicate that the coupled pulse energy decreases significantly at higher temperatures, by up to a factor of 2-3 at $T = 600$ K. Figure 8 shows the plasma emission images taken at these conditions, with and without preheating. It can be seen that in a non-preheated mixture, several filaments are formed in the plasma during the discharge burst,

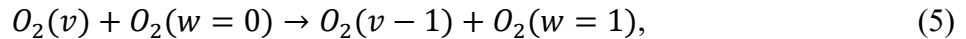
due to the ionization instability development. As expected, in a preheated mixture the plasma is diffuse, with no sign of well-defined isolated filaments. As shown in our previous work [19], preheating suppresses the ionization instability development in the plasma, most likely by enhancing the transport (ambipolar diffusion and thermal conductivity) from the incipient filaments. The plasma remains diffuse during the entire discharge pulse burst, and images taken in the preheated mixture are similar. This justifies the use of the line-of-sight averaged TDLAS temperature measurements, as well as a quasi-zero-dimensional kinetic model for the interpretation of the results.

Figure 9 compares the experimental and best fit synthetic Ar* absorption line shapes measured during the last pulse of the discharge burst in the initially room temperature and preheated O₂-Ar flows. The temperatures inferred from the synthetic line shapes at these conditions are $T = 360 \pm 30$ K and $T = 610 \pm 30$ K, respectively. Preheating the flow is essential for reducing the effect of ozone chemistry on the O atom recombination process, due to the following reactions,



Note that the reaction of Eq. (4) may also contribute to O₂ vibrational excitation [20], such that its effect needs to be reduced, to isolate that of reaction of Eq. (1). By increasing the temperature, the thermal decomposition of ozone, i.e. the reverse reaction of Eq. (3), is enhanced, such that the contribution of both reactions on the net rate of O atom recombination is reduced.

At the present conditions, two different kinetic processes contribute to the vibrational excitation of oxygen in the ground electronic state. The first process is vibrational excitation by electron impact during the discharge burst. Although the energy fraction going to vibrational excitation of molecules in dielectric barrier ns pulse discharges is low, due to very high peak reduced electric field, modest vibrational excitation of N₂ in ns pulse discharges in air and nitrogen has been measured previously [19,21]. Following the electron impact excitation, O₂(X³Σ_g⁻,v) vibrational level populations decay, both by the “downward” V-V exchange with the non-excited O₂ in the ground vibrational state, w=0 [13],



and by the rapid V-T relaxation by O atoms, which may include multi-quantum energy transfer [22],



The second process is the vibrational excitation produced during the O atom recombination, isolating which is the objective of the present work. Based on the V-V rates for O₂-O₂ measured in Ref. [13], the characteristic time for the V-V exchange at the present conditions is estimated to be approximately 20 μs. Therefore detecting the vibrationally excited molecules on a significantly longer time scale would indicate O₂ vibrational excitation generated during the O atom recombination.

In the present work, the vibrational populations are monitored after the discharge burst excitation for time delays ranging from 4 μs to 20 ms, i.e. significantly longer compared to the characteristic time for the V-V relaxation. The results are summarized in Figs. 10-13. Figure 10 plots the absolute O₂(X³Σ_g⁻,v) vibrational level populations in a 20% O₂-Ar mixture, initially at

room temperature, at different delay times after the excitation by the discharge burst. It can be seen that vibrational levels ranging from $v=8$ to $v=19$ are populated, creating an extended “plateau” in the O_2 vibrational distribution function. As discussed in Section 2, vibrational levels $v=14-16$ are not accessible to the present LIF diagnostics. It is also apparent that the $O_2(v)$ populations decay on a long time scale, over 10 ms, which exceeds considerably the characteristic time for the V-V relaxation. The results measured in the preheated mixture, also plotted in Fig. 10, are similar.

Time-resolved $O_2(X^3\Sigma_g^-,v)$ vibrational level populations after the discharge burst excitation, plotted in Figs. 11-13, provide additional insight into the kinetics of their excitation, based on the time scales of their decay. From Fig. 11, showing the data for $v=8$, it is clear that the $O_2(v)$ population before the discharge burst is near the detection limit. The initial rapid decay of $O_2(v)$ molecules excited during the discharge, due to the downward V-V exchange and V-T relaxation, is readily apparent. The apparent $O_2(v=8)$ initial decay rate coefficient inferred from the data taken at $t = 4-20 \mu s$ at room temperature, $1.3 \cdot 10^{-13} \text{ cm}^3/\text{s}$, is consistent with the O_2-O_2 V-V rate coefficient measured in Ref. [13] (in the present work, the decay rate is higher by a factor of 2). However, on a ms time scale the decay slows down considerably, clearly indicating an additional source of $O_2(v)$ generation after the discharge burst is over. Since the characteristic time scales for electron-ion recombination, electron attachment, and ion-ion recombination are much shorter, this source can be attributed only to the reactions of the neutral species, initiated by the O atom recombination. The decay of $O_2(v)$ molecules on a very long time scale, ~ 10 ms, may also be affected by the excited flow residence time between the electrodes, estimated to be 15 ms.

Comparing the data taken in non-preheated and preheated O_2 -Ar mixtures, at $T = 360 \pm 30$ K and $T = 610 \pm 30$ K, respectively, it can be seen that the $O_2(v=8)$ population during a extended “plateau” formed by the slow decay in the preheated mixture is significantly lower. This may indicate a slower recombination of O atoms at the lower total number density, but may also be due to the contribution of the reactions of Eqs. (3,4) involving ozone. These reactions accelerate the net rate of O atom decay and may enhance the rate of $O_2(v)$ formation after the discharge burst. Therefore isolating the $O_2(v)$ generation in the reaction of Eq. (1) requires taking data in the preheated O_2 -Ar mixtures.

The results for $v=13$, plotted in Fig. 12, indicate the transient rise of the $O_2(v)$ population in a non-preheated mixture on a ms time scale, following the initial rapid decay due to V-V and V-T relaxation, suggesting that the state-specific rate of O atom recombination may be higher compared to that for $v=8$. This rise becomes less pronounced in the preheated mixture, although the rate of $O_2(v)$ decay becomes significantly slower, such that it is not clear to what extent this effect may be influenced by the possible contribution of the ozone chemistry. Finally, Fig. 13 plots the results for $v=19$, which indicate the same trend as Figs. 11-12, i.e. a rapid initial decay of the $O_2(v)$ molecules generated during the discharge burst, followed by a much slower decay of $O_2(v)$ molecules produced by the chemical reactions after the excitation. The apparent $O_2(v)$ initial decay rates for $v=13$ and 19, $1.7 \cdot 10^{-13} \text{ cm}^3/\text{s}$ and $4.9 \cdot 10^{-13} \text{ cm}^3/\text{s}$, respectively, are significantly higher compared to the room temperature V-V rate coefficients for O_2-O_2 measured in Ref. [13]. This is most likely due to the contribution of the rapid V-T relaxation by O atoms.

As can be seen, in all three cases shown in Figs. 11-13, i.e. $v=8$, 13, and 19, preheating the mixture (a) results in the lower vibrational level populations during the long-term decay after the discharge burst, and (b) reduces the trend for a transient rise on a ms time scale, most pronounced at $v=8$. The data taken for other O_2 vibrational levels, $v=9-12$ and $v=17-20$, exhibit similar behavior. These results suggest a significant effect of the ozone chemistry on the mechanism of

$O_2(v)$ formation after the burst excitation at the low-temperature (non-preheated) conditions. To minimize this effect, additional measurements need to be taken at higher temperatures and higher O_2 dissociation fractions generated by the discharge burst, at the conditions where the recombination of O atoms and O_2 molecules (i.e. the reaction of Eq. (3)) would become a minor pathway.

Figure 14 plots the time-resolved, absolute O atom number density measured by ps TALIF in non-preheated and preheated 20% O_2 -Ar mixtures, after the excitation by the discharge burst. It can be seen that the O atom number densities at these conditions are comparable. As expected, preheating the mixture reduces the rate of the O atom decay, due to the lower total number density, negative temperature dependence of the recombination rate coefficient, and possibly due to more rapid thermal decomposition of ozone.

4. Summary

In the present work, partial dissociation of an O_2 -Ar mixture by a burst of ns discharge pulses in a flow reactor is used to study the kinetics of O_2 vibrational excitation during the O atom recombination. Vibrational level populations of ground electronic state molecular oxygen, $O_2(X,v=8-20)$ in the partially dissociated, recombining 20% O_2 -Ar mixture, initially at room temperature or preheated up to $T = 610$ K, is monitored by ps Laser Induced Fluorescence on the O_2 Schumann Runge bands, with absolute calibration by NO LIF in a NO- N_2 mixture with the known composition, at quenching-free conditions. O atom number density in the O_2 -Ar mixture dissociated by the discharge burst is measured by ps Two-Photon absorption LIF (TALIF). The discharge generates a diffuse volumetric plasma, without well-pronounced filaments. The temperature in the plasma is measured by Tunable Diode Laser Absorption Spectroscopy (TDLAS) of excited Ar atoms. The results indicate a rapid initial decay of the $O_2(X,v=8-20)$ molecules generated by electron impact in the discharge, on ~ 20 μs time scale, due to the V-V exchange and V-T relaxation. This decay is followed by a much slower decay, on the time scale much longer compared to the characteristic time for V-V relaxation, up to several ms. This indicates an additional process of $O_2(v)$ generation by chemical reactions initiated by the O atom recombination.

The effect is observed both in the non-preheated and preheated O_2 -Ar mixtures. However, comparison of the time-resolved $O_2(v=8-13, 17-20)$ vibrational level populations after the burst excitation of non-preheated and preheated mixtures exhibits significant differences. In the preheated mixtures, peak $O_2(v)$ populations during the slow decay following the excitation burst are significantly lower, suggesting a significant effect of O atom recombination via the reaction pathways involving ozone at near-room temperatures. Preheating the mixture likely reduces the ozone number density in the discharge afterglow. To estimate the contributions of different reaction pathways of O atom recombination into the generation of the vibrationally excited $O_2(v)$ molecules, O atom recombination in a partially dissociated O – O_2 – O_3 – Ar mixture is analyzed at $T = 380-1000$ K, using a simple zero-dimensional chemical kinetics model. The results indicate that at $T = 380$ K, over 90% of the O atoms recombine into O_2 via the reactions of Eq. (3,4), rather than via the reaction of Eq. (1). In a mixture preheated to $T = 1000$ K, this fraction is reduced to approximately 80%, but still remains very significant. This estimate indicates that additional data need to be taken in preheated mixtures with a low O_2 mole fraction, $\sim 1\%$, and at higher pressures, at the conditions when the discharge excitation results in dissociation of most of the initial O_2

molecules in the mixture, and recombination occurs on the time scale shorter than the flow residence time in the discharge cell.

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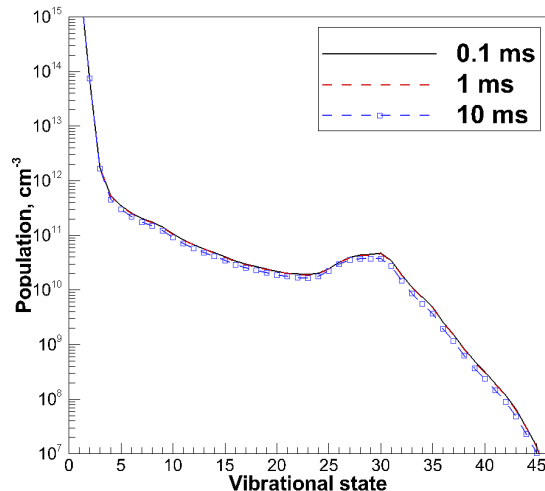


Figure 1. Kinetic modeling predictions of $O_2(X,v)$ vibrational populations in a recombining $O-O_2-Ar$ mixture, at $T = 500$ K and $P = 100$ Torr. 20% O_2-Ar mixture, complete O_2 dissociation into O atoms is assumed at $t=0$. A quasi-steady-state “tail” produced by the O atom recombination is apparent.

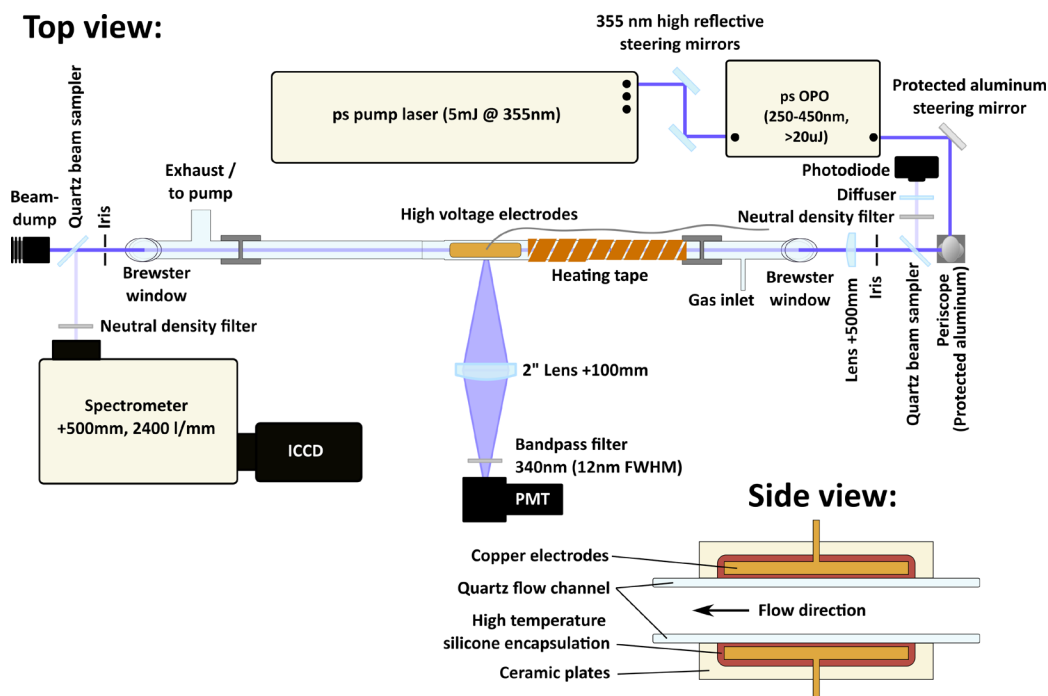


Figure 2. Schematic of the experimental setup showing excitation laser, discharge cell, and detection apparatus.

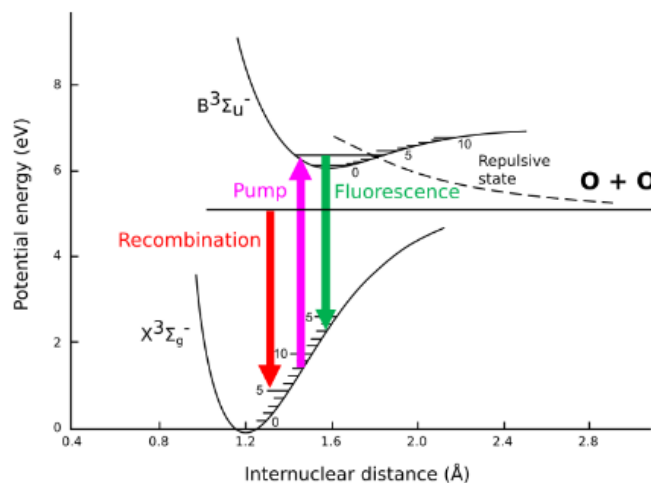


Figure 3. Schematic of LIF excitation & fluorescence transitions, and vibrational excitation due to recombination.

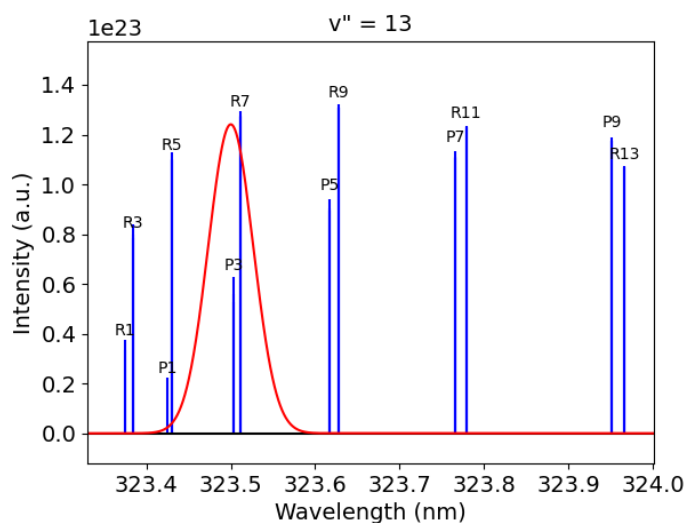


Figure 4. OPO line shape and $\text{O}_2(\text{B}^3\Sigma_u^-, v'=0, N' \leftarrow \text{X}^3\Sigma_g^-, v''=13, N'')$ pump transitions lines at $T = 300$ K. The pump transitions (blue lines) are shown as narrow peaks since the absorption linewidth is negligible compared to the OPO linewidth. The OPO line shape (Voigt profile, red line) is inferred from the line shape measured by a spectrometer.

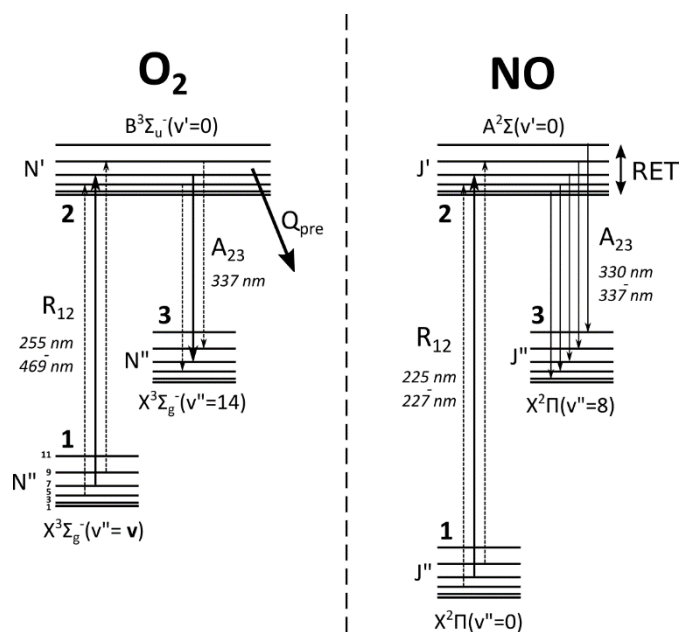


Figure 5. Schematic of O_2 and NO pump and fluorescence transitions.

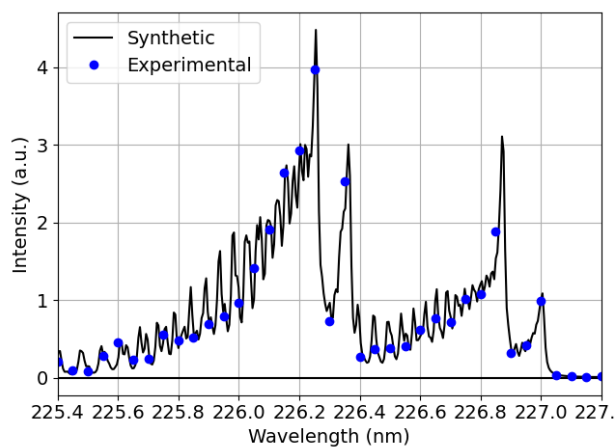


Figure 6. Comparison of the experimental $NO(A^2\Sigma, v'=0 \leftarrow X^2\Pi, v''=0)$ LIF excitation spectrum, taken in a 100 ppm $NO-N_2$ calibration mixture at room temperature at $P = 10.3$ Torr, with the synthetic spectrum.

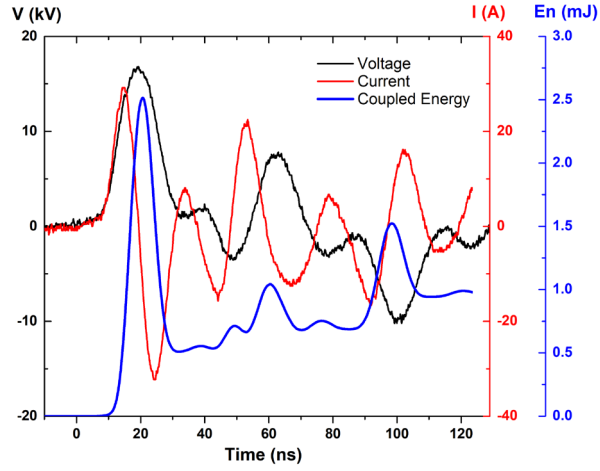


Figure 7. Discharge pulse voltage, current, and coupled energy waveforms. 20% O₂-Ar mixture, initially at room temperature, P = 100 Torr, pulse #100 in the burst.

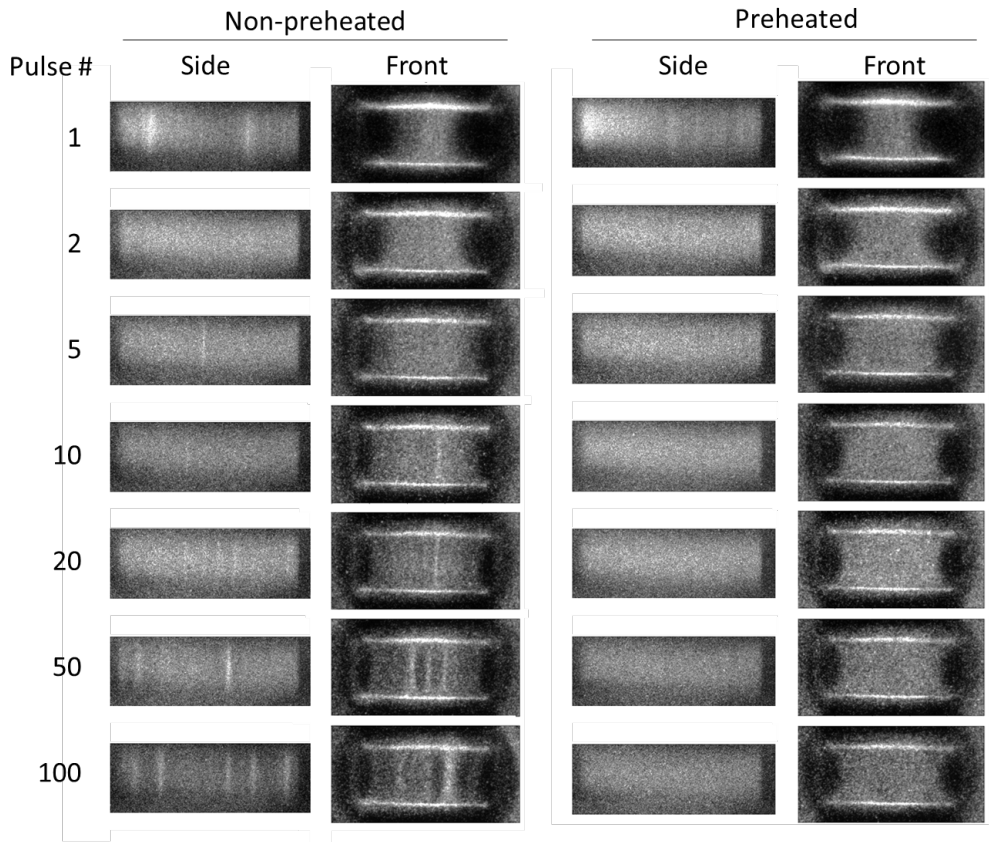


Figure 8. Single-shot, broadband plasma emission images taken during a 100-pulse discharge burst, in non-preheated (initially at room temperature) and preheated flows. 20% O₂-Ar mixture, P = 100 Torr, pulses #1-100 in the burst, camera gate 10 ns.

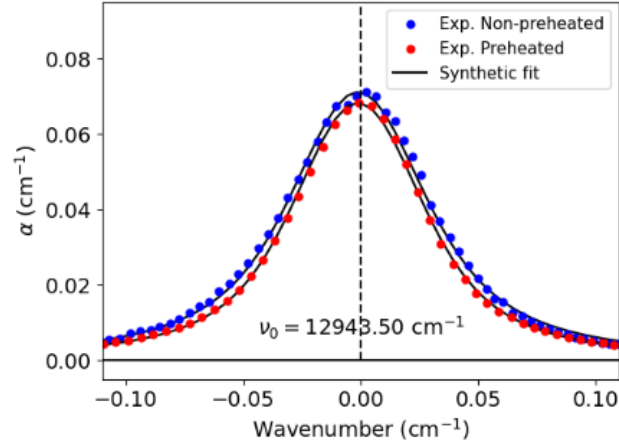


Figure 9. Experimental Ar* absorption line shapes, measured during pulse #100 of the discharge burst in a 20% O₂-Ar mixture, with and without preheating (red and blue dots, respectively). Temperatures inferred from the best synthetic fit of the line shapes (black solid curve) are $T = 360 \pm 30$ K and $T = 610 \pm 30$ K, for non-preheated and preheated flows, respectively.

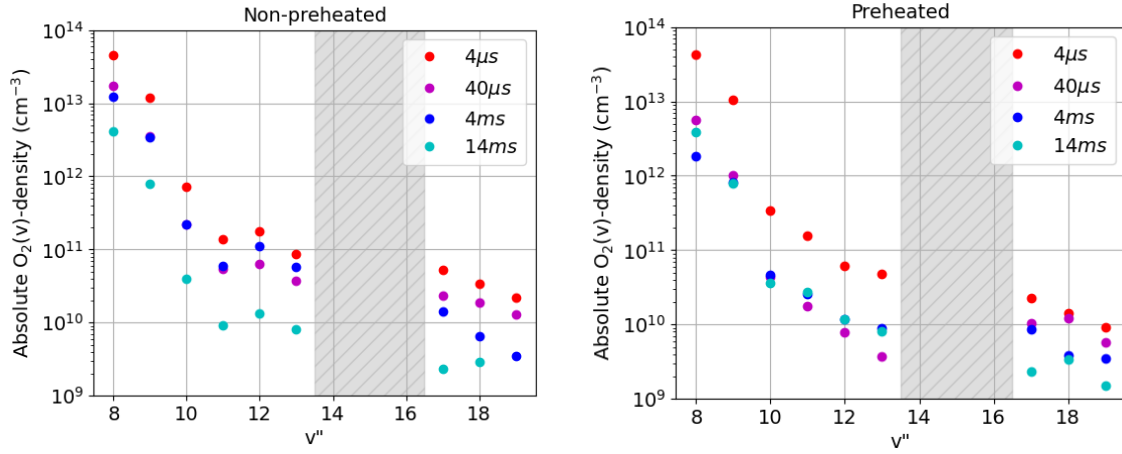


Figure 10. **Left:** O₂(X³Σ_g⁻, v=8-19) vibrational level populations in the 20% O₂-Ar mixture, initially at room temperature, at different delay times after the excitation by the discharge burst. **Right:** same data measured in the preheated 20% O₂-Ar mixture.

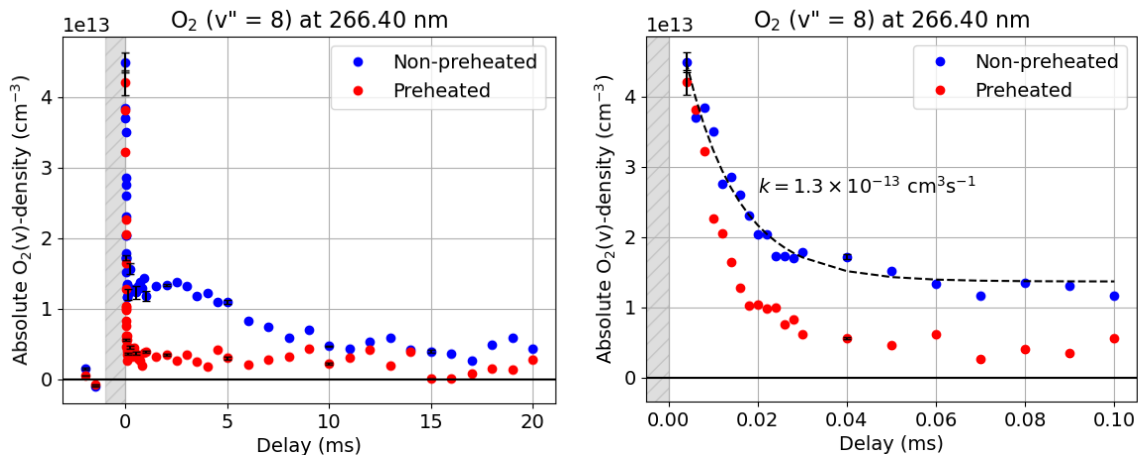


Figure 11. Time-resolved $\text{O}_2(\text{X}^3\Sigma_g^-, v=8)$ vibrational level populations in the non-preheated and preheated 20% O_2 -Ar mixtures vs. delay time after the excitation by the discharge burst, plotted on two different time scales. The shaded bar indicates the discharge burst excitation 1 ms long. The dashed black line shows an exponential fit to the data in the non-preheated flow up to 100 μs , along with the inferred decay rate coefficient.

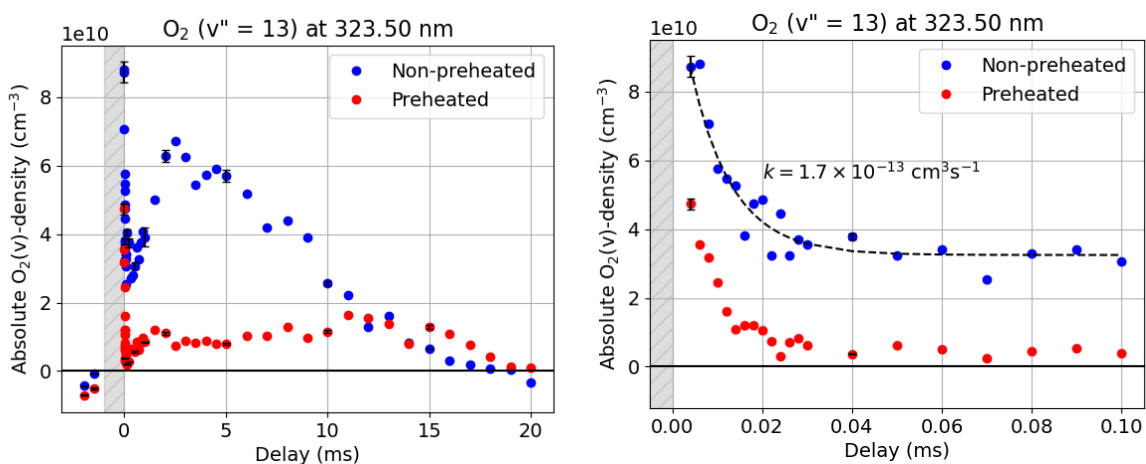


Figure 12. Time-resolved $\text{O}_2(\text{X}^3\Sigma_g^-, v=13)$ vibrational level populations in the non-preheated and preheated 20% O_2 -Ar mixtures vs. delay time after the excitation by the discharge burst, plotted on two different time scales. The shaded bar indicates the discharge burst excitation 1 ms long. The dashed black line shows an exponential fit to the data in the non-preheated flow up to 100 μs , along with the inferred decay rate coefficient.

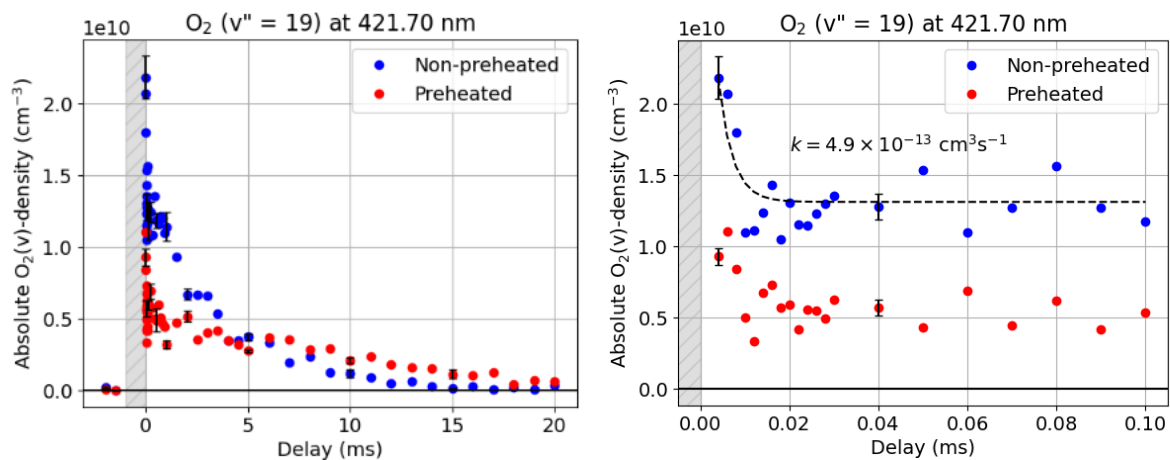


Figure 13. Time-resolved $O_2(X^3\Sigma_g^-, v''=19)$ vibrational level populations in the non-preheated and preheated 20% O_2 -Ar mixtures vs. delay time after the excitation by the discharge burst, plotted on two different time scales. The shaded bar indicates the discharge burst excitation 1 ms long. The dashed black line shows an exponential fit to the data in the non-preheated flow up to 100 μs , along with the inferred decay rate coefficient.

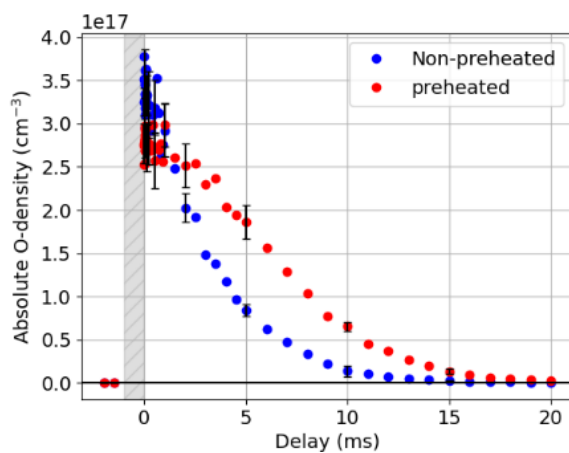


Figure 14. Time-resolved, absolute O atom number density in non-preheated and preheated 20% O_2 -Ar mixtures, plotted vs. delay time after the excitation by the discharge burst.