Measurements of $N_2(A^3\Sigma_u^+)$ Populations in a Nanosecond Pulse Discharge in Nitrogen

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Abstract

Absolute time-resolved populations of $N_2(A^3\Sigma_u^+)$ excited electronic state generated in a repetitive ns pulse discharge in nitrogen have been measured by Cavity Ring Down Spectroscopy (CRDS) and Tunable Diode Laser Spectroscopy (TDLAS). CRDS measurements of $N_2(A^3\Sigma_u^+, v=0-2)$ populations are made in the discharge afterglow at a pressure of 11 Torr. Peak $N_2(A^3\Sigma_u^+, v=0,1)$ populations after a 10-pulse ns discharge burst are $1.5 \times 10^{11}$ cm$^3$. In the afterglow, these populations exhibit a relatively slow decay with the characteristic time of approximately 500 μs. The $N_2(A^3\Sigma_u^+, v=2)$ population in the afterglow shows a transient rise. TDLAS data have been taken at a higher pressure of 130 Torr. Absolute time-resolved $N_2(A^3\Sigma_u^+, v=0)$ number density is measured during a 5-pulse ns discharge burst and in the afterglow, peaking at $5 \times 10^{12}$ cm$^3$. The results indicate that $N_2(A^3\Sigma_u^+)$ is generated after every discharge pulse, on a ~50 μs time scale, and decays between the pulses. The decay rate increases during the discharge burst. In the afterglow, $N_2(A^3\Sigma_u^+, v=0)$ population decays significantly more rapidly compared to the low-pressure CRDS conditions, with the characteristic time of approximately 100 μs.

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1. Introduction

A metastable electronic 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 nonequilibrium reacting flows. Collisional quenching of $N_2(A^3\Sigma_u^+)$ is one of the major sources of O atoms, H atoms, and hydrocarbon radicals in air and fuel-air mixtures [1], which is essential for kinetics of low-temperature plasma assisted combustion. Reactions of $N_2(A^3\Sigma_u^+)$ with O$_2$ and O atoms are also among the dominant channels of O and NO formation in low-temperature air plasmas [2] and atmospheric pressure Ar plasma jets [3]. Both O atoms and NO are of considerable importance for plasma applications in chemistry and biology, due to their high reactivity [4]. Finally, rapid energy transfer from $N_2(A^3\Sigma_u^+)$ to nitric oxide and excitation of the radiative NO$(A^2\Sigma)$ state generate NO $\gamma$ band emission in air and N$_2$:O$_2$ plasmas [5,6], and may also be responsible for NO $\gamma$ band emission from strong shock waves in air [7].

Quantitative measurements of absolute populations of $N_2(A^3\Sigma_u^+)$ are challenging. In the present work, we use Cavity Ring Down Spectroscopy (CRDS) and single-pass Tunable Diode Laser Absorption Spectroscopy (TDLAS) to measure absolute populations of vibrational levels 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 10-130 Torr. 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 $N_2(A^3\Sigma_u^+,v)$ populations during the discharge pulse burst and in the afterglow, for quantitative insight into the kinetic processes of their generation and decay.

2. Experimental and Data Reduction

The schematic of the CRDS experiment is shown in Fig. 1. To produce a spectrally narrow tunable output, a Nd:YAG laser (Continuum PowerLite Precision II), operated at 10 Hz, pumps a narrowband tunable dye laser (Continuum Vista). The dye laser output is frequency-shifted using a Raman cell filled with 15 bar of hydrogen. The wavelength and the linewidth of the first Stokes beam, 745 to 770 nm and 0.07 cm$^{-1}$, respectively, with the energy of 1-2 mJ/pulse, are monitored by a wavemeter (High Finesse WS6). The ring-down cavity is a 10 mm x 22 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=0.99995) are attached to the ends of the cavity using stainless steel adjustable mounts. The CRDS measurements have been made in nitrogen at a pressure of 11.3 Torr and a flowrate of 0.24 SLM. The ring down traces are measured by the amplified silicon photodiode (Thorlabs PDA36A) 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. 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 1·10$^{-5}$ cm$^{-1}$, 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 nitrogen, at a higher pressure and flowrate of 130 Torr and 1.30 SLM, respectively.

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 discharge in the cell is sustained by a high-voltage pulse generator producing alternating polarity pulses with peak voltage up to 15 kV and pulse duration of approximately 100 ns FWHM. Typical discharge voltage and current traces at these conditions are shown in Fig. 3. 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 CRDS measurements are made in the afterglow after the burst, for different delays between the burst and the laser pulse. The cw TDLAS measurements are made continuously, both during the discharge burst and in the afterglow.

For the present experimental apparatus, the cavity mode spacing is \( m = c / 2L_{\text{cell}} = 6 \cdot 10^{-3} \) cm\(^{-1} \). For the average dye laser FWHM linewidth of 0.07 cm\(^{-1} \), the light is coupled to the cavity on about 30 modes. For the absorption transition FWHM linewidth of approximately 0.03 cm\(^{-1} \) (dominated by the Doppler broadening at P=11 Torr and T=300 K), the light is absorbed on approximately 10 cavity modes, as shown schematically in Fig. 4. The absorption rate for each mode frequency \( \nu_m \) is affected both by the laser line shape, \( g_L(\nu_m) \), and by the absorption line shape, \( g_A(\nu_m) \), in addition to the number density of the absorption species. The net absorption rate measured by the detector is

\[
I = c_1 \exp \left(-\frac{ct(1-R)}{L_{\text{cell}}}ight) \sum_m g_L(\nu_m) \exp \left(-\frac{c g_A(\nu_m) \alpha L_{\text{abs}} t}{L_{\text{cell}}}ight),
\]

where \( \alpha \) is the line-integrated absorption coefficient (in m\(^{-1} \)Hz), such that \( \alpha(\nu) = \alpha g_A(\nu) \), and the sum is evaluated for all cavity modes overlapping with the absorption line. In Eq. (1), both line shapes are normalized to one. In the present measurements, the laser line shape is assumed to be Gaussian with the average FWHM of 0.07 cm\(^{-1} \), measured by the wavemeter during the experiment. The spectral absorption coefficient inferred from the CRDS measurements or measured directly by TDLAS (in m\(^{-1} \)), is related to the absolute population (number density) of a particular vibrational-rotational state of the absorbing species, \( N(\nu'', J'') \) (in m\(^{-3} \)), as follows [8],

\[
N(\nu'') = \frac{\alpha(\nu)}{2\Phi \pi^2 \nu_0 \frac{2B_{\nu''}}{3kT} S_{J, J''} q_{\nu', \nu''}(R_e(\tilde{r}_{\nu', \nu''}))^2 \exp \left(-\frac{BN''(N'' + 1)hc}{kT_{\text{rot}}}ight) g(\nu).}
\]

In Eq. (2), \( \Phi \) is the nuclear spin statistical weight, \( B_{\nu''} \) is the rotational constant of the \( \nu'' \) state, \( N'' \) is the total orbital angular momentum excluding spin, \( g(\nu) \) is the normalized apparent absorption line profile (a convolution of the laser and the absorption line shapes) (in Hz\(^{-1} \)), \( S_{J, J''} \) is the HönLondon factor (rotational line strength) [9], \( q_{\nu', \nu''} \) is the Franck-Condon factor, and \( R_e(\tilde{r}_{\nu', \nu''}) \) is the electronic transition moment, both taken from Ref. [10].

3. Results and Discussion
Figures 5 and 6 show typical plasma emission images during a ns pulse discharge in nitrogen at pressures of 11 Torr and 130 Torr (pulse # 2 in a 10-pulse discharge burst). It can be seen that 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.

Figure 7 compares the typical ring down traces in the empty cavity and in nitrogen at a pressure of 11 Torr, 25 $\mu$s after the last pulse in a 10-pulse discharge burst. A single exponential decay in the empty cavity (ring down time of 60 $\mu$s) is a straight line. 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. 4, the multi-exponential decay in Fig. 7 is due to the laser linewidth being larger than the absorption linewidth (also see [11]). The spectral absorption coefficient is inferred from the data using Eq. (1). Figure 8 plots a typical CRDS spectrum acquired 75 $\mu$s after the last discharge pulse in the burst at the conditions of Fig. 7, with several absorption transitions labeled. The spectral scan covers approximately 1 nm, incorporating nearly 30 rovibrational lines, in the $(3\rightarrow 1)$ vibrational band of the first positive system of nitrogen, $N_2(B^3\Pi_g \leftarrow A^3\Sigma^+_u)$. Each data point in the spectra such as in Fig. 8 is an average of ten single-laser-shot ring-down times, and nearly every absorption transition has been identified. Absorption line assignments are obtained from the line positions reported in Ref. [12].

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. 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. For each vibrational state, isolated rotational lines are used to infer temporal evolution of the absolute populations of vibrational levels of $N_2(A^3\Sigma^+_u,v=0-2)$. For these measurements, the probe beam is tuned to 770.2923 nm, 760.7832 nm, and 745.5000 nm, respectively, which corresponds to rovibrational transitions $^3Q_{31}(3)$ for $N_2(B,v'=2 \leftrightarrow A,v''=0)$, $^3Q_{12}(10)$ for $N_2(B,v'=3 \leftrightarrow A,v''=1)$, and $^3Q_{32}(7)$ for $N_2(B,v'=4 \leftrightarrow A,v''=2)$ 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. (2), assuming the temperature in the afterglow of T=300 K. This assumption 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.

Figure 9 plots the time-resolved number densities of $N_2(A^3\Sigma^+_u,v=0=2)$. At the end of the discharge burst, the populations of vibrational levels $v=0,1$ exceed that of $v=2$ by approximately two orders of magnitude. $N_2(A^3\Sigma^+_u,v=0,1)$ populations after the discharge burst appear to follow a single exponential decay with the characteristic time of 500 $\mu$s. 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 nitrogen molecules in the ground electronic state. The transient rise of $N_2(A^3\Sigma^+_u,v=2)$ population, on the time scale of $t=0-500$ $\mu$s, suggests that it may be populated by the near-resonance vibrational-vibrational (V-V) exchange process with the vibrationally excited molecules in the ground electronic state [1]. Although vibrational excitation of the ground electronic state $N_2$ in a repetitive ns pulse discharge at similar conditions was found to be not very significant [13], this process would affect the $N_2(A^3\Sigma^+_u,v=0)$ population if the number density of $N_2(X^1\Sigma_g^+, v=1)$ is of the order of $10^{11}$ cm$^{-3}$ or higher.
To understand the $\text{N}_2(\text{A}^3\Sigma_u^+)$ 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 130 Torr, during and after a 5-pulse discharge burst. Figure 10 shows a scan of the cw diode laser across two partially overlapping rotational lines in the $\text{N}_2(\text{B},v'=2\rightarrow\text{A},v''=0)$ vibrational band, $R_{11}(6)$ and $P_{33}(14)$. These data are taken 25 $\mu$s after the last discharge pulse, and every data point is averaged over 50 discharge bursts. It can be seen that the peak absorption of $\sim 10^{-3}$ is measured, with the detection limit below $\sim 10^{-4}$. Figure 10 also shows a synthetic spectrum, where each of the two lines has the Voigt profile with the Doppler broadening at $T=300$ K and pressure broadening (with the pressure broadening parameter of $\gamma=0.15$ cm$^{-1}$atm$^{-1}$) incorporated. The population of the rotational states follow the Boltzmann distribution with $T=300$ K.

For time-resolved TDLAS measurements, the diode laser wavelength is tuned to the peak absorption of the rotational line $Q_{11}(12)$, and the absorption signal, averaged over 200 bursts, was measured during the entire discharge pulse burst and in the afterglow. The results are plotted in Fig. 11, which shows both the absorption and the absolute number density of $\text{N}_2(\text{A}^3\Sigma_u^+,v=0)$. It can be seen that after each discharge pulse, the $\text{N}_2(\text{A})$ population increases, as expected. At these conditions, $\text{N}_2(\text{A}^3\Sigma_u^+,v=0)$ 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 $\text{N}_2(\text{A})$ population first levels off and then begins to decay. Peak $\text{N}_2(\text{A}^3\Sigma_u^+,v=0)$ number density of approximately $5\times 10^{12}$ cm$^{-3}$ is detected after the pulse #4. The rate of the decay appears to accelerate during the discharge burst, such that the number density measured after pulse #5 is somewhat lower. The population decay after the discharge burst is a single exponential, with the characteristic decay time of $\sim 100$ $\mu$s, significantly faster compared to that inferred from the CRDS measurements at the pressure of 11 Torr. At this time, the kinetics of such a rapid $\text{N}_2(\text{A}^3\Sigma_u^+,v=0)$ population decay is not completely understood, and comparison with the kinetic modeling predictions, which is expected to provide insight into this process, is underway.

4. Summary

In the present work, absolute time-resolved populations of the metastable excited electronic state of nitrogen, $\text{N}_2(\text{A}^3\Sigma_u^+)$, generated in a repetitive ns pulse discharge in nitrogen have been measured by Cavity Ring Down Spectroscopy (CRDS) and Tunable Diode Laser Spectroscopy (TDLAS). CRDS measurements of $\text{N}_2(\text{A}^3\Sigma_u^+,v=0-2)$ populations have been made in the discharge afterglow at a relatively low pressure of 11 Torr. Peak $\text{N}_2(\text{A}^3\Sigma_u^+,v=0,1)$ populations measured after a 10-pulse ns discharge burst are $1.5\times 10^{11}$ cm$^{-3}$. In the afterglow, these populations exhibit a relatively slow, single exponential decay with the characteristic time of approximately 500 $\mu$s, most likely due to quenching by the $\text{N}_2$ molecules in the ground electronic state. The $\text{N}_2(\text{A}^3\Sigma_u^+,v=2)$ population in the afterglow shows a transient rise, likely caused by the near resonance vibration-vibration energy transfer from the vibrationally excited molecules of the ground electronic state, $\text{N}_2(\text{X}^1\Sigma_g^+,v=1)$. TDLAS data have been taken at a significantly higher pressure of 130 Torr, when the $\text{N}_2(\text{A}^3\Sigma_u^+)$ number density is approximately one order of magnitude higher compared to the conditions used for the low-pressure CRDS measurements. Absolute time-resolved $\text{N}_2(\text{A}^3\Sigma_u^+,v=0)$ number density is measured during a 5-pulse ns discharge burst and in the afterglow, peaking at $5\times 10^{12}$ cm$^{-3}$. The results indicate that $\text{N}_2(\text{A}^3\Sigma_u^+)$ is generated after every discharge pulse, on a $\sim 50$ $\mu$s time scale, and decays between the pulses. The decay rate increases during the discharge burst. In the afterglow, $\text{N}_2(\text{A}^3\Sigma_u^+,v=0)$ population decays significantly more
rapidly compared to the low-pressure CRDS conditions, exhibiting a single-exponential decay with the characteristic time of about 100 μs. The results obtained using these two diagnostics are complementary, since TDLAS measurements can be used at the conditions when the N₂(A³Σu⁺) populations may be too high, or vary too rapidly for accurate CRDS measurements.

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References


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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=11 Torr, and (b) P=130 Torr.

Figure 4. Schematic of the calculated N₂ absorption line profile at T=300 K and P=11 Torr, with FWHM of 0.03 cm⁻¹ dominated by the Doppler broadening, laser line profile, assumed to be Gaussian with the measured FWHM linewidth of 0.07 cm⁻¹, and coupled cavity modes.
Figure 5. Single-shot, broadband nitrogen plasma emission image taken during a 10-pulse ns discharge burst, side view, pulse #2. P=20 Torr, camera gate 300 ns.

Figure 6. Single-shot, broadband nitrogen plasma emission image taken during a 10-pulse ns discharge burst, side view, pulse #2. P=134 Torr, camera gate 200 ns.
Figure 7. Typical cavity ring down traces for an empty cell and a 10-pulse ns discharge afterglow at P=11 Torr, 25 μs after the last discharge pulse. The ring down trace obtained from the data reduction, for the inferred value of the absorption coefficient, is also shown.

Figure 8. N₂(A³Σ_u⁺) CRDS spectrum taken 25 μs after a 10-pulse ns discharge, at P=11 Torr: N₂(B³Π_g, v = 3→A³Σ_u, v = 1).
Figure 9. Time-resolved N₂(A₃Σ⁺, v=0=2) vibrational level populations after a 10-pulse ns discharge in nitrogen at P=11 Torr.

Figure 10. TDLAS scan of two rotational lines in the N₂(B¹Πᵥ, ν = 2→A³Σ⁺, ν = 0) band. P=130 Torr, 5-pulse ns discharge burst, 25 µs after the last pulse.
Figure 11. Time-resolved number density of $N_2(A^3Σ_u,v=0)$ vibrational level during a 5-pulse ns discharge burst and the afterglow, at P=130 Torr.