Characterization and Kinetic Modeling
of Ns Pulse and Hybrid Ns Pulse / RF Plasmas

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Abstract

Electric field evolution during ns pulse breakdown in nitrogen in plane-to-plane geometry is measured by ps Electric Field Induced Second Harmonic (E-FISH) generation and predicted by kinetic modeling. The results indicate the formation of two ionization waves in the discharge gap. The first wave is produced by “sweeping” the initial electrons in the gap to the anode by the applied voltage pulse. The second wave is formed due to the field enhancement in the charge separation region. The anode-directed front of this wave is detected by the EFISH measurements. The measurements and the modeling predictions exhibit a strong electric field overshoot in the middle of the gap, caused by the second wave. The electron density and coupled energy distributions predicted by the model at the end of the discharge pulse are nearly uniform, except near the cathode-adjacent wall. Time-resolved, absolute number densities of metastable N$_2$(A$^3\Sigma_u^+$) molecules and N atoms in the nitrogen plasma during a ns pulse burst are measured by Tunable Diode Laser Absorption Spectroscopy (TDLAS) and Two-Photon Absorption Laser-Induced Fluorescence (TALIF). The pulse energy coupled to the plasma and the number densities of N$_2$(C$^3\Pi_u$) and N$_2$(B$^3\Pi_g$) molecules remain approximately the same during the burst. Comparison of the measurement results and the modeling predictions indicates an additional major channel of N$_2$ dissociation in the plasma, by energy pooling in collisions of two N$_2$(A$^3\Sigma_u^+$) molecules. Strong vibrational nonequilibrium is measured in the nitrogen plasma by Coherent Anti-Stokes Raman Spectroscopy (CARS). The plasma is generated by a combination of a ns pulse train and a sub-breakdown RF voltage, using a custom-designed external circuit. This result has a potential for isolating and quantifying the effect of the reactions of vibrationally excited molecules on plasma chemical and plasma-catalytic processes.
1. Introduction

Diagnostics and predictive modeling of plasmas sustained by nanosecond pulse discharges, as well as discharges enhanced by DC or RF waveforms heating the electrons between the pulses, are essential for their applications in plasma chemistry and plasma-assisted catalysis. These discharges, sustained at high pulse repetition rates of 1-100 kHz, have been recently used in plasma flow reactors for studies of plasma-assisted combustion kinetics [1-4]. Time-resolved electric field distribution in these plasmas, as well as the number densities of vibrationally excited molecules, electronically excited metastable species, and atoms are the major parameters affecting the plasma reactivity and the specific reaction pathways. Although these parameters have been measured in ns pulse discharges previously [5-10], this has been done at different geometries and different operating conditions, such that comparison with the modeling predictions and isolating specific molecular energy transfer and plasma transport processes remain rather challenging.

In plasma chemistry experiments, sustaining stable diffuse plasmas at well characterized, reproducible conditions is critical for the analysis of the results. Double dielectric barrier, ns pulse discharges in quasi-one-dimensional, plane-to-plane geometry are attractive in that respect since they generate spatially uniform plasmas at high pressures [1,4], making comparison with kinetic modeling predictions straightforward. The objective of the present work is to study the fundamental plasma kinetics in this type of the discharge, using multiple laser diagnostics and kinetic modeling. The focus of the present measurements and modeling predictions is on the nitrogen plasma, including the electric field evolution during ns pulse breakdown, number densities of metastable electronically excited N$_2$(A$^3\Sigma_u^+$) molecules and N atoms, gas temperature, and vibrational level populations of nitrogen molecules in the ground electronic state, N$_2$(X$^1\Sigma_g^+,v$). Since additional data in ns pulse discharges other molecular gas mixtures have recently become available [11,12], the present approach will also be applied to these results in our future work.

2. Diagnostics and Kinetic Model

The schematic of the discharge cell is shown in Fig 1. The plasma is generated in a rectangular cross section quartz channel (22 mm x 10 mm or 16 mm x 8 mm), with the fused silica or CaF$_2$ optical access windows at the Brewster’s angle at both ends. Nitrogen flows through the cell at the flow rate of 0.1-1.0 SLM and pressure of 100-150 Torr. The discharge in the cell is produced between two parallel rectangular plate copper electrodes 60 mm long and 12 mm wide, mounted to the top and bottom outside walls of the cell, as shown in Fig. 1. The electrodes are attached to the walls by a silicon rubber adhesive, to prevent corona discharge formation near the electrode surfaces. The discharge is sustained by one of three different ns pulse generators operated in burst mode, (i) a custom-made generator producing alternating polarity pulses with peak voltage of 16 kV and pulse duration of 90 ns FWHM, (ii) FID GmbH FPG 60-100MC4 generator (30 kV, 10 ns), and (iii) positive polarity MegalImpulse NPG-18/100k generator (25 kV, 15 ns), with burst duration of 5-150 pulses, and burst repetition rate of 10 Hz. The pulse voltage and current waveforms are measured by custom-made, high bandwidth capacitive voltage probes and shunt current probes [13]. Broadband plasma emission images are taken using a gated PI-MAX 3 ICCD camera with a UV lens.

To heat the electrons generated by the ns discharge pulses and generate additional vibrational excitation of N$_2$ molecules, in an additional series of experiments the electrodes are powered both by a MegalImpulse ns pulse generator and a Dressler Cesar 5 kW, 13.56 MHz RF
generator, using a circuit shown in Fig. 2. The circuit is designed to isolate the plasma generators from each other, using the high-voltage diodes to block the current produced by each waveform to the opposing power supply, as shown in Fig. 2. To enable the circuit operation, DC bias is added to the RF waveform using a 1:1 transformer, to maintain the positive polarity of the waveform. The DC bias is removed using an RC filter before the high-voltage electrode (see Fig. 2). To reduce the Joule heat dissipation on the resistor connected parallel to the load (discharge electrodes), the filter is engaged only during the ns pulse / RF burst, using a MOSFET trigger switch.

Ps Electric Field Induced Second Harmonic (E-FISH) generation diagnostic used for the electric field measurements, shown schematically in Fig. 3, is essentially the same as in our previous work [14]. Briefly, the fundamental 1064 nm output beam of a 150 picosecond pulse duration Nd:YAG laser (Ekspla SL333) is focused into the center of the discharge cell by a 50 cm focal distance lens. The second harmonic signal generated by the electric field in the plasma is separated from the fundamental beam and collected by a PMT detector. For the electric field distribution measurements, the discharge cell is mounted on a translation stage to allow scanning the laser beam across the discharge gap.

A schematic of the single-pass Tunable Diode Laser Absorption Spectroscopy (TDLAS) diagnostic [12], used for the measurements of N₂(A³Σ_u⁺,v=0,1) vibrational level populations in the plasma, is shown in Fig. 4. Briefly, a tunable diode laser (New Focus Velocity 6312, tuning range from 764 to 781 nm, nominal linewidth < 0.3 MHz) is scanned by varying the voltage on the piezoelectric driver of the laser, with the wavelength monitored continuously during the experiment by a wavemeter (High Finesse WS6-200-IR). The focused laser beam is directed along the discharge cell, and the transmitted beam focused into an optical fiber to reject the plasma emission, sent to a photodiode detector through a band pass filter, and monitored by an oscilloscope. The laser scan and data acquisition are controlled by a computer executing a LabView script.

A schematic diagram of the Two-photon Absorption Laser-Induced Fluorescence (TALIF) diagnostic, used for N atom number density measurements in the plasma, is shown in Fig. 5. For this, a Nd:YAG laser (Continuum, Powerlite 8010) pumps a tunable dye laser (Continuum ND6000) to generate the output at 621 nm, frequency doubled using a type I BBO crystal, and mixed with the dye laser output to generate a 205 nm beam, separated by a Pellin-Broca prism. A halfwave plate and polarizer combination is used to adjust the laser pulse energy, which is monitored by a calibrated photodiode. During the measurements, the laser is maintained within the quadratic TALIF signal range. The laser beam is focused by a 50 cm focal distance lens and directed along the discharge cell. The fluorescence signal is collected perpendicularly to the beam path, using a 10 cm focal length lens, and detected by a gated PMT (see Fig. 5). A slit mask 2 mm wide placed in front of the lens and a bandpass filter (10 nm bandpass, centered at 750 nm) are used to reduce the emission from the plasma. A neutral density filter is employed to operate the laser at the same power and PMT at the same gain during the absolute calibration of TALIF measurements using krypton, without saturating the PMT. The standard calibration technique is described in detail in Ref. [15].

Vibrational level populations of nitrogen molecules in the ground electronic state are measured by broadband N₂ vibrational CARS [11], shown schematically in Fig. 6. Briefly, 80% of the second harmonic output of an externally triggered, injection-seeded, ns Nd:YAG laser (Surelite, SL.III-10) is used to pump a custom-built broadband dye laser to generate the Stokes beam with the FWHM of 7 nm, centered at 606 nm. The rest of the Nd:YAG laser output is used
as the CARS pump/probe beam. The pulse energies of the pump/probe and the Stokes beams are 10.0 mJ and 8.73 mJ, respectively. The two beams are combined using a delay line and dichroic mirrors and focused in the test section by a 22 cm focal distance lens, in collinear phase matching geometry. The CARS signal generated in the test section is separated from the pump and Stokes beams using dichroic mirrors and detected by an Andor 750 spectrometer with Andor EMCCD camera. The resolution of the broadband CARS spectra is dominated by the spectrometer instrument function, approximately 0.3 cm⁻¹ FWHM. N₂ vibrational and rotational-translational temperature are inferred from the CARS spectra using a CARSFT program [16], modified to infer these parameters independently.

In the present work, two different kinetic models are employed to interpret the experimental data. The first model, used to predict the electric field and electron density evolution during a single ns discharge pulse, is essentially the same as in Ref. [17]. The model solves the one-dimensional fluid equations for electron and positive ion number densities, coupled with the Poisson equation for the electric potential. The ionization coefficient and the charged species drift velocities are the functions of the reduced electric field, and the applied voltage waveform is a fit to the experimental voltage pulse shape. Since exercising this model for a long discharge burst is time-consuming, N₂(X¹Σg⁺,v) vibrational populations, N₂(A³Σu⁺,v) populations, and N atom number density during the burst of ns discharge pulses are predicted using a quasi-zero-dimensional kinetic model described in detail in Ref. [12]. This model solves the electron energy equation (a moment of the Boltzmann equation), the heavy species energy equation, and equations for the species concentrations. It incorporates the electron impact excitation and dissociation processes, vibrational relaxation, and reactions of excited electronic states of N₂. The time-resolved ns pulse discharge power waveform, used as an input in the model, is obtained from the experimental discharge voltage and current waveforms. The electron impact rate coefficients are predicted by the Boltzmann equation solver Bolsig+ [18]. In the present work, we assume that N₂ dissociation in the plasma occurs during the energy pooling of two N₂(A³Σu⁺) molecules,

\[
N_2(A^3Σ_u^+,v) + N_2(A^3Σ_u^+,w) \rightarrow \begin{cases} 
N_2(B^3Π_g) + N_2(X^1Σ_g^+) \\
N_2(C^3Π_g) + N_2(X^1Σ_g^+) \\
N(\text{i}S) + N(\text{i}S) + N_2(X^1Σ_g^+) 
\end{cases}, \tag{1}
\]

in addition to electron impact dissociation. Since the rate coefficient of this dissociation channel is not known, it is treated as an adjustable parameter. As shown in Section 3, this assumption results in good agreement with the measurements of N atom number density and N₂(A³Σu⁺,v) populations.

3. Results and Discussion

3.1. Electric Field Evolution (E-FISH)

Figures 7 and 8 show a collage of 50-pulse average, broadband plasma emission images, taken through the optical access window at the end of the cell (see Fig. 1), in the direction of the laser beam (see Fig. 3), along with the experimental electric field distributions in the gap, and kinetic model predictions for the electric field, ion density, and electron density. Figure 7 shows the data taken at t = -4 ns, -2 ns, and t = 0 ns, and Figure 8 the data taken at t = 1 ns, 2 ns, and t =
4 ns. Time moment $t = 0$ corresponds to the peak electric field measured on the centerline ($x=5$ mm). All data are taken during pulse #3 (negative polarity) in a 5-pulse discharge burst, produced by the custom-made pulse generator, at the pulse repetition rate of 10 kHz. In all images, the cathode (i.e. the negative high-voltage electrode) is on the left, and the anode (the grounded electrode) is on the right. The locations of the channel walls are indicated by vertical lines at $x=0$ and $x=10$ mm, and arrows indicate the approximate locations of the ionization wave peak.

Comparison of the emission images with the electric field distribution and kinetic modeling predictions indicates the following trends. At the early time moments ($t = -4$ ns and earlier), the emission in the right half of the discharge gap, at $x > 5$ mm (see Fig. 7), is due to the residual electrons from the previous discharge pulse, displaced to the right by the applied electric field. Electric field enhancement due to the charge separation at $x < 5$ mm results in ionization, caused by the electrons emitted from the cathode wall and accelerated by the strong field. This generates emission in this region ($x = 1-3$ mm), previously dark, which becomes evident at $t = 2$ ns (see Fig. 7). The anode-directed ionization wave formed on the right of the ionization region (marked with an arrow in Fig. 7) is readily apparent from the E-FISH data and the modeling predictions. The peak amplitude of the wave, 12-15 kV/cm, is observed both in the modeling predictions and in the EFISH data from $t = 2$ ns to $t = 1$ ns. Strong electric field on the left of the ionization region, at $x < 1$ mm, predicted by the model, is not detected in the measurements, since the laser beam cannot be moved very close to the wall without clipping. The ionization region expands toward the anode, following the electric field peak, which becomes more pronounced.

From Fig. 8, it can be seen that, as the ionization wave enters a preionized region in the right half of the gap, it dissipates rapidly, leaving a residual electric field “dip” in the middle of the gap, also evident as a dark band in the emission images. The boundary between the two plasma domains, (i) the preionized region on the right and (ii) the region where the ionization wave is formed on the left, at $x = 5$ mm, is also detectable in the emission images taken with a long camera gate. However, at the end of the discharge pulse, the predicted electron density and the coupled discharge energy distributions in the gap becomes very nearly uniform, with the exception of a narrow region near the cathode-adjacent wall, at $x < 0.1$ mm (see Fig. 8). This suggests that the distributions of the number densities of the excited species generated in the discharge gap are also close to being uniform, justifying the use of a zero-dimensional kinetic model used in the rest of the present work.

Figure 9 compares the time-resolved electric field measured midway through the gap, at $x=5$ mm, with the kinetic modeling predictions. The electric field initially follows the applied Laplacian field, $\frac{u_{app}(t)}{d}$, then “dips” slightly below it, before exhibiting a strong overshoot (by nearly a factor of 2), followed by a rapid decay (see Fig. 9, left). The peak of the overshoot predicted by the model is close to the value measured in the experiment, $\approx 14$ kV/cm. After peaking, the measured electric field decays to near detection limit, $\approx 0.5$-1.0 kV/cm. Comparison of the experimental data and the modeling predictions exhibits similar trends.

3.2. $N_2(A^2\Sigma_u^+)$ and $N$ atom number densities (TDLAS and TALIF)

Figure 10(a) plots the waveforms of voltage, current, and energy coupled to the nitrogen plasma at $P = 150$ Torr, sustained by a ns pulse train produced by the FID generator, with peak voltage of 26 kV, FWHM pulse duration of 10 ns, and pulse repetition rate of 100 kHz. The energy
is coupled to the plasma both during the incident voltage pulse and several successive reflected pulses, with the total coupled energy of 3.3 mJ. Figure 10(b) plots both the energy coupled by the incident pulse and the total coupled energy, for different pulse number during a 150-pulse burst 1.5 ms long. It can be seen that the coupled pulse energy remains nearly the same, decreasing by about 10% during the burst. This modest reduction is likely due to the gradual temperature rise in the plasma during the burst.

Figure 11 shows a collage of single-shot, broadband plasma emission images taken during the 150-pulse discharge burst at these conditions. The images are taken both through the side wall of the discharge cell (side view) and through the optical access window at the end of the channel (end view, see Fig. 1), with the camera gate 250 ns long incorporating both the incident pulse and the reflected pulses. It can be seen that the plasma remains diffuse and uniform during the first 100 pulses, with the exception of pulse #1, which exhibits a strongly filamentary structure, due to the low residual ionization remaining from the previous pulse burst generated 100 ms earlier. After pulse #100, diffuse filaments gradually begin to form in the plasma near the electrode edges, most likely due to the onset of the ionization / heating instability. During the entire burst, the plasma remains confined to the region between the electrodes 6 cm long, such that the absorption path for the TDLAS measurements can be determined with the uncertainty of approximately 10%.

It is evident that the dark band formed during the ionization wave propagation (see discussion in Section 3.1), clearly visible during pulses #5 and #10, is located close to the cathode-adjacent wall (the bottom wall in Fig. 11), within ≈ 1 mm, rather than in the middle of the gap (see Fig. 8). Kinetic modeling calculations indicate that this is due to the much shorter voltage pulse duration, 10 ns in Fig. 11 vs. 90 ns in Figs. 7,8. At these conditions, the displacement of the residual electrons by the applied voltage is much smaller, such that the ionization wave formed in the charge separation region near the cathode does not travel far across the gap, before it dissipates in the preionized region. This justifies the use of the quasi-zero-dimensional kinetic model for the prediction of the number densities of the excited species and atoms.

Time-resolved optical emission spectra from the center of the plasma, taken at these conditions, indicate that the emission intensity of the N₂ second positive band system, N₂(C^3Π_u→B^3Π_g), does not vary significantly during the burst, decreasing by 15% over the first 100 pulses and by 30% over the entire 150-pulse burst. The emission intensity of the first positive bands, N₂(B^3Π_g→A^3Σ_u^+) decreases by about 5%. Based on these results, along with the measurements of the coupled pulse energy, we conclude that the number densities of the excited electronic states of nitrogen produced by electron impact during the discharge burst, N₂(C^3Π_u) and N₂(B^3Π_g), scale approximately with the discharge pulse energy and do not change significantly.

Figure 12(a) plots the time-resolved, absolute N₂(A^3Σ_u^+, v=0) vibrational level population during a 150-pulse discharge burst, at the conditions of Figs. 10,11, measured by TDLAS. The uncertainty of these measurements, approximately 10%, is controlled mainly by the uncertainty of the absorption path through the plasma. The experimental data (red curve) are compared with the kinetic modeling predictions (blue curve), exhibiting good agreement. As discussed in detail in our previous work [12], both the gradual decay of the N₂(A^3Σ_u^+) number density during the burst and the increasingly rapid decay after each discharge pulse, evident in Fig. 12(a), are due to its rapid quenching by N atoms accumulating during the burst,

\[ N₂(A^3Σ_u^+, v) + M \rightarrow N₂(X^3Σ_g^+) + M. \]  (2)
This process, along with the energy pooling process of Eq. (1), is the dominant mechanism of \( \text{N}_2(A^3\Sigma_u^+) \) decay in the nitrogen plasma. Figure 12(b) plots the rotational-translational temperature during the discharge burst at these conditions, inferred from the \( \text{N}_2(A^3\Sigma_u^+) \) absorption line intensity ratio \( [12] \), illustrating the gradual temperature rise due to the relaxation and quenching of the excited states generated in the plasma.

Figure 12(c) plots the N atom number density during the burst, measured by TALIF (blue symbols), as well as the number density of N atoms generated per discharge pulse, inferred from these data (red symbols). Finally, Fig. 12(d) plots the N atom number density vs. the time delay after a 50-pulse discharge burst, illustrating that on the time scale of the discharge burst (0.5-1.5 ms) the N atoms decay by only about 10%. This illustrates that during the discharge burst, the removal of N atoms due to recombination, diffusion to the walls, and convection with the flow, is clearly insignificant. Therefore the N atom number density measured during the burst is controlled only by the rate of \( \text{N}_2 \) dissociation in the plasma, i.e. the number density of N atoms generated per pulse plotted in Fig. 12(c).

Comparing the \( \text{N}_2(A^3\Sigma_u^+,v=0) \) population (see Fig. 12(a)) and the rate of N atom generation per pulse (see Fig. 12(c)), it is readily apparent that they both decrease significantly during the burst, by a factor of 3-5. Note that this occurs at the conditions when both the discharge pulse energy and the emission intensity from the \( \text{N}_2(C^3\Pi_u) \) and \( \text{N}_2(B^3\Pi_g) \) states do not exhibit significant variation. This strongly suggests that the rate of \( \text{N}_2 \) dissociation in the plasma is coupled to the \( \text{N}_2(A^3\Sigma_u^+) \) number density. The effect of highly vibrationally excited molecules in the ground electronic state is unlikely, since the rate of dissociation is highest at the beginning of the burst (see Fig. 12(c)), when the \( \text{N}_2(X^1\Sigma_g^+,v) \) populations, which accumulate during the burst [11], are still low. Therefore we have to conclude that \( \text{N}_2 \) dissociation in the plasma occurs in collisions of two metastable electronic states, both of which are generated in sufficient quantities, otherwise the contribution of this process would be insignificant. Assuming that dissociation occurs in one of the channels of the energy pooling process of Eq. (1), \( \text{N}_2(A^3\Sigma_u^+) + \text{N}_2(A^3\Sigma_u^+) \rightarrow \text{N}(^4\Sigma) + \text{N}(^4\Sigma) + \text{N}_2(X^1\Sigma_g^+) \), with the relative weight of 60%, provides good agreement of the modeling predictions both with the \( \text{N}_2(A^3\Sigma_u^+,v=0) \) population and with the N atom number density (see Fig. 12(a,c)). Not including this dissociation process into the kinetic model results in a strong underprediction of the N atom number density, and therefore significant overprediction of the \( \text{N}_2(A^3\Sigma_u^+,v=0) \) during the burst.

### 3.3. Enhanced vibrational excitation in a ns pulse / RF plasma

In the present work, we use a ns pulse train combined with the RF voltage to enhance vibrational excitation in the plasma. The feasibility of this approach was demonstrated in our previous work [11]. Briefly, operating the repetitively pulsed ns discharge at high peak reduced electric field (E/N) values produces pre-ionization for the non-self-sustained RF discharge. Since the RF voltage is operated at much lower E/N, significantly below breakdown, it generates efficient vibrational excitation of \( \text{N}_2 \) molecules in the ground electronic state, without producing additional electronically excited molecules and atoms. By varying the RF voltage amplitude, vibrational excitation in the plasma can be controlled independently, potentially isolating the reaction pathways of vibrationally excited molecules, such as the ammonia synthesis in plasma-enhanced catalysis [19], suggested as an alternative to the mechanism involving surface reactions of atomic species [20], or NO generation in air plasmas [8]. This is critical for applications of high-
pressure molecular plasmas to plasma-assisted combustion, plasma chemical processing, and plasma-assisted catalysis. In the present study, we extend this approach to significantly higher peak voltage ns pulses, by isolating the MegaImpulse ns pulse generator and the Dressler RF generator from each other (see Fig. 2).

Figure 13 shows the combined ns pulse / RF voltage waveform used to generate the nitrogen plasma at P = 100 Torr, measured on the high-voltage electrode. In Fig. 13, the pulse repetition rate is 10 kHz, burst duration is 100 pulses (10 ms long), and the burst repetition rate is 10 Hz, to match the pulse repetition rate of the CARS laser system, shown schematically in Fig. 6. The insets show the ns pulse voltage and the RF waveform separately.

Figure 14 plots typical broadband N_2 CARS spectra measured at the end of a 100-pulse ns discharge burst, with and without the RF voltage applied between the pulses, compared to the CARSFT synthetic spectra. Clearly, adding the RF waveform results in an additional vibrational excitation of N_2. In the baseline ns pulse discharge, the N_2(v=1) vibrational band intensity is significantly lower, while in the ns pulse / RF discharge, N_2(v=0-5) vibrational bands are detected. The N_2 vibrational temperature is T_v(N_2) = 1650 K in the baseline ns pulse discharge, and T_v(N_2) = 2760 K in the ns pulse / RF discharge. This is significantly higher compared to the results of our previous work [11]. The translational-rotational temperature in the plasma is inferred from the rotational structure of the N_2(v=0) vibrational band, using the best fit CARSFT spectra, as shown in Fig. 15. The accuracy of the temperature inference is determined by processing 20 room temperature CARS spectra, taken in a 100 Torr nitrogen without the plasma, yielding the mean temperature of T=292 K and the standard deviation of ± 8 K. The rotational temperatures at the end of the ns pulse and ns pulse / RF bursts, both 10 ms long, inferred from the spectra in Fig. 10, are T = 307 K and T = 414 K, respectively.

4. Summary

In the present work, electric field distributions during ns pulse breakdown in nitrogen between two parallel plate, dielectric-covered electrodes are measured by ps EFISH and predicted by a one-dimensional fluid kinetic model. Both the measurement results and the modeling predictions, as well as the plasma emission images, indicate formation of two well-defined ionization waves in the discharge gap. The first wave is produced by “sweeping” the initial electrons toward the anode by the applied voltage pulse. The second wave originates in the charge separation region between the cathode and the first wave front, due to the electric field enhancement. The anode-directed front of this wave is detected by the EFISH measurements. The measurements and the modeling predictions exhibit a strong electric field overshoot on the discharge centerline, caused by the second wave. However, the electron density and coupled energy distributions predicted by the model at the end of the discharge pulse are nearly uniform, except near the cathode-adjacent wall. This shows that the distributions of the number densities of the excited species generated in the discharge gap are also nearly uniform, justifying the use of the reduced order, quasi-zero-dimensional kinetic models.

Time-resolved, absolute number densities of metastable N_2(A^3Σ_u^+) molecules and N atoms in the nitrogen plasma during and after the ns pulse discharge burst are measured by TDLAS and TALIF. At these conditions, the discharge pulse energy coupled to the plasma, as well as the number densities of electronically excited N_2(C^3Π_g) and N_2(B^3Π_g) molecules remain approximately the same during the burst. Comparison of the measurement results and the modeling
predictions, specifically the significant reduction of the N\(_2\)(\(^3\Sigma_u^+\),v=0) population and the rate of N atom generation during the discharge burst, identifies an additional major channel of N\(_2\) dissociation in the plasma, by energy pooling in collisions of two N\(_2\)(\(^3\Sigma_u^+\)) molecules.

Strong vibrational nonequilibrium is sustained in the nitrogen plasma generated by a combination of a ns pulse train and a sub-breakdown RF voltage, using a custom-designed circuit isolating the plasma generators from each other. Further enhancement of vibrational nonequilibrium in the ns pulse / RF plasma can be achieved by increasing the ns pulse repetition rate and the RF voltage amplitude. The ns pulse and RF generators used in the present work can be operated at the pulse repetition rates of up to 100 kHz and RF amplitude up to 2 kV, and these measurements are underway. The main objective of these experiments is isolating and quantifying the effect of the reactions of vibrationally excited molecules on plasma chemical and plasma-catalytic processes.

5. Acknowledgments

The support of NSF grant “Nanosecond Pulse Discharges at a Liquid-Vapor Interface and in Liquids: Discharge Dynamics and Plasma Chemistry”, US DOE Center on Plasma Interaction with Complex Surfaces, and US DOE Collaborative Research Center for Studies of Plasma-Assisted Combustion and Plasma Catalysis is gratefully acknowledged. We would also like to thank Dr. Nikolay Popov from Moscow State University, Russia, for helpful and productive discussions.

References


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Figure 1. Schematic of the discharge cell, with the electrodes powered by a ns pulse generator.

Figure 2. Schematic of the discharge cell and the external circuit used to generate a ns pulse train overlapped with the sub-breakdown RF waveform.
Figure 3. Schematic of EFISH diagnostic: L1, focusing lens; M1 and M2, 1064 nm high reflector mirrors; F1, long pass filter; W1 and W2, Brewster’s angle windows of the discharge cell, A1, aperture; L2, collimating lens; M3, dichroic mirror (high reflector at 1064 nm, transmission at 532 nm); PM1, dispersion prism; BD1 and BD2, beam dumps; PD1, photodiode; M4, 532 nm high reflector mirror; F2, band pass filter; P1, polarizer.

Figure 4. Schematic of Tunable Diode Laser Absorption Spectroscopy diagnostic, used for measurements of $N_2(A^3Σ_u^+,v=0,1)$ vibrational level populations.
Figure 5. Schematic diagram of the Two-photon Absorption Laser-Induced Fluorescence (TALIF) diagnostic, used for N atom number density measurements.

Figure 6. Schematic of broadband CARS diagnostic, used for $N_2(X^1\Sigma_g^+,v)$ populations and rotational-translational temperature measurements.
Figure 7. Collage of 50-pulse average, 0.44 ns camera gate ICCD plasma emission images (left), experimental electric field distributions (middle), and kinetic modeling predictions for electric field, ion density, and electron density (right), at different time moments during the discharge pulse. Top row: t = -4 ns, middle row: t = -2 ns, bottom row: t = 0 ns. Time moment t = 0 corresponds to the peak electric field measured on the centerline (x=5 mm). Arrows indicate approximate locations of the ionization wave peak.
Figure 8. Collage of 50-pulse average, 0.44 ns camera gate ICCD plasma emission images (left), measured electric field distributions (middle), and kinetic modeling predictions for electric field, ion density, and electron density (right) at different time moments during the discharge pulse. Time moment $t = 0$ corresponds to the peak electric field measured on the centerline ($x=5$ mm). Top row: $t = 1$ ns, middle row: $t = 2$ ns, bottom row: $t = 4$ ns. Time moment $t = 0$ corresponds to the peak electric field measured on the centerline ($x=5$ mm). Arrows indicate approximate locations of the ionization wave peak.
Figure 9. Time-resolved electric field measured during the discharge pulse on the centerline of the cell, at $x = 5$ mm (left). The operating conditions are the same as in Figs. 7, 8, $t=0$ corresponds to the peak electric field. Kinetic modeling predictions for the electric field and current on the discharge centerline, at $\frac{x}{d} = 0.5$ (right). The applied electric field, $\frac{U_{\text{app}}}{d}$, and the predicted Laplacian electric field across the gap, $\frac{U}{d}$, are also plotted. $d^* = d + \frac{2d}{\varepsilon}$.

Figure 10. (a) Voltage, current and coupled energy waveforms in a double dielectric barrier discharge ns pulse discharge in nitrogen at $P=150$ Torr, pulse repetition rate of 100 kHz, and burst repetition rate of 10 Hz; (b) Total coupled energy and coupled pulse energy of the incident pulse vs. pulse number in the train (error bars indicated standard deviations of multiple measurements).
Figure 11. Single-shot, broadband plasma emission images taken during a 150-pulse discharge burst, pulse repetition rate of 100 kHz, and burst repetition rate of 10 Hz, side view and end view. Nitrogen, P=150 Torr, camera gate 250 ns.

Figure 12. (a) N$_2$(A$^2$Σ$^+$,v=0) population; (b) gas temperature; (c) N atom number density (blue) and N atom generation per pulse (red) vs. the pulse number, during a 150-pulse discharge burst; (d) N atom number density vs. time delay after a 50-pulse discharge burst. Nitrogen, P=150 Torr, pulse repetition rate 100 kHz (100 pulses / ms). In panels (b-d), symbols are the experimental data, lines are the modeling predictions.
Figure 13. The combined ns pulse / RF voltage waveform, with the insets showing the ns pulse voltage and the RF waveform separately, on the shorter time scale. Nitrogen, P = 100 Torr, pulse repetition rate 10 kHz, burst duration 100 pulses, burst repetition rate 10 Hz.

Figure 14. Broadband N\textsubscript{2} CARS spectra measured at the end of a 100-pulse ns discharge burst, without (a) and with (b) RF voltage applied between the pulses, compared to the best fit CARSFT spectra. Nitrogen, P = 100 torr, flow rate 0.1 SLM. Inferred N\textsubscript{2} vibrational temperatures are $T_v(N\textsubscript{2}) = 1650$ K and $T_v(N\textsubscript{2}) = 2760$ K, respectively.
Figure 15. $\text{N}_2(\nu=0)$ CARS spectra measured at the end of a 100-pulse ns discharge burst, without (a) and with (b) RF voltage applied between the pulses, compared to the best fit CARSFT spectra. Nitrogen, $P = 100$ torr, flow rate 0.1 SLM. Inferred translational-rotational temperatures are $T = 307$ K and $T = 414$ K, respectively.