Selective generation of excited species in ns pulse / RF hybrid plasmas for plasma chemistry applications

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Selective Generation of Excited Species in Ns Pulse / RF Hybrid Plasmas for Plasma Chemistry Applications


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Abstract

Hybrid plasmas, sustained by a repetitive ns pulse discharge and a sub-breakdown RF waveform in N\textsubscript{2} and its mixtures with H\textsubscript{2}, CO, and CO\textsubscript{2}, are studied using laser diagnostics and kinetic modeling. Plasma emission images show that adding the RF waveform to the ns pulse train does not result in a discharge instability development, since the RF field does not produce additional ionization. Unlike a ns pulse / DC discharge, the ns pulse / RF plasma is sustained using a single pair of electrodes external to the discharge cell. Measurements of electronically excited molecules, N\textsubscript{2}(A\textsuperscript{3}\Sigma\textsubscript{u}\textsuperscript{+}), and vibrationally excited molecules in the ground electronic state, N\textsubscript{2}(X\textsuperscript{1}\Sigma\textsubscript{g}\textsuperscript{+},v), demonstrate that these species are generated selectively. N\textsubscript{2}(A\textsuperscript{3}\Sigma\textsubscript{u}\textsuperscript{+}) molecules are produced predominantly by the ns pulse discharge waveform, while vibrational excitation of the ground electronic state N\textsubscript{2} is mainly due to the RF waveform. Strong vibrational nonequilibrium is maintained at a low translational-rotational temperature. The ns pulse / RF discharge data demonstrate that the quenching of N\textsubscript{2}(A\textsuperscript{3}\Sigma\textsubscript{u}\textsuperscript{+}) is not affected by N\textsubscript{2} vibrational excitation. Kinetic modeling shows that the rate of N\textsubscript{2}(A\textsuperscript{3}\Sigma\textsubscript{u}\textsuperscript{+}) quenching in a ns pulse discharge in nitrogen is underpredicted, and the modeling predictions agree with the data only if the rate of N atom generation by electron impact dissociation of N\textsubscript{2} is increased by approximately an order of magnitude. This suggests a significant effect of excited electronic states on the net dissociation rate. Infrared emission spectra of ns pulse / RF hybrid plasmas in CO-N\textsubscript{2} and CO\textsubscript{2}-N\textsubscript{2} mixtures show that the present approach also generates strong vibrational excitation of CO and CO\textsubscript{2}, with the CO yield in the CO\textsubscript{2}-N\textsubscript{2} mixture approximately a factor of two higher compared to that in a ns pulse discharge alone. This indicates a significant contribution of the vibrationally enhanced CO\textsubscript{2} dissociation in the hybrid plasma. The present results demonstrate that sustaining the hybrid plasma in reacting molecular gas mixtures may isolate the plasma chemical reaction pathways dominated by vibrationally excited molecules from those of electronically excited molecules and atomic species.
1. Introduction

Energy-efficient applications of nonequilibrium plasmas to chemical syntheses, such as plasma-assisted combustion, fuel reforming, and catalysis require generation of excited species and radicals which enhance the desired reaction pathways in the most effective way. Although the electric discharge energy partition among different species and energy modes in molecular plasmas is well understood [1], self-sustained electric discharges allow only a limited degree of control over the reduced electric field (E/N) and the species generated in the plasma. The use of hybrid electric discharges, sustained by two independent voltage waveforms, helps circumvent this constraint. This approach has been used in the past, e.g. in high-power CO$_2$ [2] and CO [3] lasers, electrically excited oxygen-iodine laser [4], and a supersonic wind tunnel generating vibrationally nonequilibrium flows [5]. In most of these cases, the plasma was sustained by a combination of two fully overlapping discharges, (i) high peak voltage, high repetition rate, ns pulse discharge producing electron impact ionization, and (ii) sub-breakdown DC discharge, which does not generate ionization by itself but couples additional energy to the pre-ionized flow. This approach improves the discharge stability at high pressures and maximizes the energy input into generation of the desired metastable excited species, such as N$_2$(X$^1\Sigma^+_g,v$) and O$_2$(a$^1\Delta_g$). Basically, the transition to the high-temperature, near-equilibrium plasma is delayed by reducing the discharge pulse duration, and the energy coupling to the targeted modes is optimized by combining a high peak E/N ns pulse waveform with a low “tailored” E/N value in the DC discharge. However, this method has several limitations, such as employing two separate pairs of electrodes, the necessity of using bare metal electrodes for the DC discharge, and DC discharge self-sustaining in the cathode layer. This complicates the plasma chemical reactor design and results in the ionization instability development at high pressures and high discharge powers.

A straightforward modification of this approach is to replace the DC discharge with a capacitively coupled, non-self-sustained (sub-breakdown) RF discharge. The advantages of this method include the use of a single pair of electrodes, which can be external to the plasma chemical reactor, as well as better stability at high pressures and input powers, since the RF discharge may remain non-self-sustained in the entire gap. Previously, this approach has been used to generate an RF-enhanced optically pumped CO-N$_2$ plasma at pressures of up to 1 atm, sustained by resonance absorption of CO laser radiation resulting in associative ionization of highly vibrationally excited CO molecules [6,7]. RF energy coupling to the plasma increases CO vibrational level populations by up to an order of magnitude [6], while N$_2$ vibrational temperature, measured by spontaneous Raman scattering, increases by up to a factor of two [7]. This method (i.e. combining a short-duration ionizing pulse train with a sub-breakdown RF waveform) may be viewed as an extension of the RF voltage waveform “tailoring”, such as discussed in detail Ref. [8]. In this technique, a summation of several RF harmonics is used to localize the electron heating in the plasma both spatially and temporally, thereby enabling control of the electron energy distribution function (EEDF) in high-pressure plasmas. Uncoupling the ionization from the electron heating, in addition to the use of a superposition of multiple RF waveforms, may well provide additional control authority over the EEDF, the charged particle fluxes, and the selectivity of the species generated in the plasma.

In the present work, we use the hybrid ns pulse / RF plasma to generate excited species in molecular gas mixtures. Operating the repetitively pulsed ns discharge at high peak E/N values (i) produces pre-ionization for the RF discharge, and (ii) generates electronically excited molecules and atomic species, such as N$_2$(A$^3\Sigma_u^+$) and N atoms in nitrogen. Adding the RF waveform between
the ionizing pulses heats up the electrons in the recombining plasma, to the range of electron temperatures most efficient for vibrational excitation of molecules in their ground electronic state, e.g. \( \text{N}_2(X^1\Sigma_g^+) \), but too low for electronic excitation, dissociation, and ionization. Therefore changing the RF peak voltage makes possible variation of the vibrational level populations, \( \text{N}_2(X^1\Sigma_g^+,v) \), without a significant effect on the number densities of atoms and electronically excited molecules. This helps isolate the possible effect of vibrationally excited molecules on plasma chemical processes, such as the ammonia synthesis in plasma-enhanced catalysis [9], suggested as an alternative to the mechanism involving surface reactions of atomic species [10]. The objective of this study is to demonstrate the use of this approach for selective generation of reactive species in high-pressure molecular plasmas, for potential applications such as plasma-assisted combustion, plasma chemical processing, and plasma-assisted catalysis.

2. Experimental Setup and Kinetic Model

A schematic of the discharge cell used in the present work is shown in Fig. 1. The cell is a 22 mm x 10 mm rectangular cross section quartz channel 20 cm long, with the fused silica optical access windows at the Brewster angle at both ends. The same geometry cell, but with CaF\(_2\) optical access windows, was used for taking plasma infrared emission spectra. Nitrogen (99.998\% purity) or its mixtures with H\(_2\) (99.999\% purity), CO (99.5\% purity), and CO\(_2\) (99.5\% purity) flow through the cell at the flow rate of 0.15-0.5 slm. The flow rates of the mixture components are regulated by the mass flow controllers. The pressure in the cell is maintained at 50-100 Torr. The total leak rate of the discharge cell and the gas delivery system is approximately \( 10^{-4} \) of the flow rate, such that the estimated oxygen and water vapor impurity level is \( \sim 10 \) ppm and \( \sim 1 \) ppm, respectively.

The flow in the cell is excited by a double dielectric barrier discharge sustained between two parallel rectangular plate copper electrodes 60 mm long and 12 mm wide, mounted to the top and bottom walls of the cell, as shown in Fig. 1. The electrodes are attached to the walls by a silicon rubber adhesive, to prevent the corona discharge formation in ambient air near the electrode surfaces. The discharge is sustained by a combination of two high-voltage power supplies. The first is a custom-made ns pulse generator [11] producing alternating polarity pulse bursts with peak voltage of 15 kV and pulse duration of approximately 100 ns, at the pulse repetition rate of 10 kHz, burst repetition rate of 10 Hz, and up to 300 pulses in a burst. The second is a broadband RF power amplifier (ENI 3200L) with a Heathkit SA-20-60A Antenna Tuner, powered by an IFR 2023 signal generator and operated at the frequency of 13.56 MHz and peak voltage up to 1 kV. Both power supplies are connected to the same pair of electrodes, as shown in Fig. 1, such that the high-voltage ns pulse and RF waveforms are applied to the opposite electrodes. The ns pulse voltage and current are measured by custom-made, high bandwidth capacitive voltage probes and shunt current probes [12], and the RF voltage and current waveforms are measured by a Tektronix P6015 high-voltage probe and Pearson 2877 current monitor. The ns pulses and RF bursts are separated in time, as shown schematically in Fig. 1, to prevent the pulse distortion by the RF current passing through the ns pulse generator. 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).

Vibrational level populations of nitrogen molecules in the ground electronic state are measured by broadband N\(_2\) vibrational CARS, shown schematically in Fig. 2 and described in detail in our previous work [13]. Briefly, 80\% of the second harmonic output of an externally triggered, injection-seeded, ns Nd:YAG laser (Surelite, SLIII-10, pulse energy of 80 mJ) 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 6.8 mJ and 5.2 mJ, respectively. The two beams are combined using a delay line and dichroic mirrors and focused in the test section by a 21 cm focal distance lens, in collinear phase matching geometry. The length of the probe volume (i.e. the region where over 95% of the CARS signal is generated), measured by translating a microscope slide along the focused beams, is approximately 10 mm. 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 0.44 cm\(^{-1}\) FWHM. After the plasma emission background subtraction, the experimental spectra are divided by the non-resonant signal spectrum obtained from 760 Torr of argon, and a square root of the normalized intensity is taken. \(N_2\) vibrational populations and vibrational temperature are inferred from the integrated area under the vibrational band peaks, \(I_v \approx n_v - n_{v+1}\). The rotational-translational temperature is inferred by fitting the experimental square root intensity of \(N_2(v=0)\) band spectra with synthetic CARSFT [14] spectra.

The number density of nitrogen molecules in the first excited electronic state, \(N_2(A^3\Sigma)\), is measured by Tunable Diode Laser Absorption Spectroscopy (TDLAS), shown schematically in Fig. 3. Briefly, a collimated output beam of a 20 mW continuous wave diode laser (New Focus Velocity 6312, scan range 764-781 nm, nominal linewidth \(<0.3\) MHz), is directed along the cell, as shown in Fig. 3. The beam diameter is approximately 1 mm. The laser wavelength is scanned by a piezoelectric driver and is monitored during the experiment by a wavemeter (High Finesse WS6). The transmitted beam is detected by a silicon photodiode (Thorlabs DET36A), monitored by an oscilloscope (Agilent DSO-X 4032A). Some of the TDLAS data have been taken using double-pass absorption. The experiment is controlled by a computer running a LabView script, which varies the piezoelectric driver voltage, records the laser wavelength measured by the wavemeter, and saves the time-resolved transmitted signal intensity traces taken by the oscilloscope. The \(N_2(A^3\Sigma)\) number density inference from the TDLAS data is discussed in Ref. [15].

Infrared emission spectra, used for the inference of vibrational level populations of CO and the detection of vibrationally excited \(CO_2\) in the discharge cell, are taken by an FTIR spectrometer (Bruker IFS-66) with an InSb detector. A long pass filter (cutoff near 2060 cm\(^{-1}\)) is used to prevent aliasing in the overtone emission spectra. The same spectrometer is used for the \textit{ex situ} measurements of CO and \(CO_2\) number densities, by sampling the flow from the exhaust line downstream of the discharge cell into an absorption cell placed in the absorption compartment of the FTIR spectrometer.

The quasi-zero-dimensional kinetic model is discussed in detail in our previous work [16]. In the present work, the model is exercised only for nitrogen. Briefly, the model incorporates the electron impact processes with cross sections taken from [17,18], reactions of excited electronic states of \(N_2\) [19-21]; state-specific vibration-translation (V-T) relaxation of the ground electronic state \(N_2\) and vibration-vibration (V-V) energy transfer for \(N_2-N_2\) [22], and N atom recombination. Vibrational levels of \(N_2(A^3\Sigma)\) electronic state, \(v=0-7\), are treated as separate species. The vibrational quantum number dependence of the \(N_2(A^3\Sigma,v)\) quenching rates, where available, is
taken from Ref. [20]. The state-specific rates of V-V exchange between \( N_2(A^3\Sigma) \) and the ground electronic state nitrogen,

\[
N_2(A^3\Sigma^+, v) + N_2(X^1\Sigma^+, w=0) \rightarrow N_2(A^3\Sigma^+, v-2) + N_2(X^1\Sigma^+, w=1)
\]  

which controls \( N_2(A^3\Sigma,v) \) populations between the discharge pulses, are taken from Ref. [21]. For the processes where the state-specific data are not available, such as the energy pooling,

\[
\begin{align*}
N_2(A^3\Sigma^+, v) + N_2(A^3\Sigma^+, w) & \rightarrow \left\{ N_2(B^3\Pi_u) + N_2(X^1\Sigma^+) \right\} \\
N_2(C^3\Pi_u) + N_2(X^1\Sigma^+) & 
\end{align*}
\]  

the rate coefficients are assumed to be independent of the quantum number, except for the electron impact excitation of \( N_2(A^3\Sigma) \) from the ground electronic state,

\[
N_2(X^1\Sigma^+) + e \rightarrow N_2(A^3\Sigma^+, v) + e
\]  

and \( N_2(A^3\Sigma) \) population by collisional quenching of \( N_2(B^3\Pi_u) \) state,

\[
N_2(B^3\Pi_u) + M \rightarrow N_2(A^3\Sigma^+, v) + M.
\]  

The process of Eq. (3) favors the excitation of high vibrational levels, \( N_2(A^3\Sigma,v=5-13) \), such that the direct electron impact population of vibrational levels \( v=0 \) and \( v=1 \), detected in the present experiments, is unlikely [21]. The nascent vibrational distribution of \( N_2(A^3\Sigma) \) in the process of Eq. (4), which is the dominant pathway of \( N_2(A^3\Sigma) \) generation at the present conditions, is not known. The branching ratio of \( k_4(v=3) / k_4(v=2) = 0.5 / 0.5 \) provides the best agreement with the present data (specifically, the \( v=0 \) population rise after the discharge pulse). Populating the higher or lower \( N_2(A^3\Sigma) \) vibrational levels would result in a slower or faster \( N_2(A^3\Sigma,v=0) \) rise, respectively, due to the varying time delay controlled by the V-V exchange of Eq. (1). However, this branching ratio may well vary, depending on the discharge pulse waveform, pressure, and gas mixture.

The plasma volume used in the model, 7.2 cm\(^3\), is estimated from the plasma emission images. Effects of diffusion, conduction heat transfer, and convection are incorporated as quasi-zero-dimensional corrections. Specifically, the decay of N atoms during and after the discharge burst is affected by the diffusion to the wall, followed by the surface recombination. The latter process is incorporated into the model as a zero-order reaction, with the characteristic frequency

\[
v_{diff} = \frac{L_{diff}^2}{D},
\]

where \( D \) is the N atom diffusion coefficient, \( L_{diff} \approx \frac{R}{2.4} \) is the spatial scale for the transverse diffusion in an axisymmetric geometry, and \( R \) is the effective channel radius (twice the ratio of the cross sectional area over the perimeter). The model is exercised using a Boltzmann equation solver for plasma electrons Bolsig+ [23], which predicts the electron impact rate coefficients vs. electron temperature, combined with ChemKin-Pro, which solves the electron energy equation predicting the electron temperature (a moment of Boltzmann equation), the heavy species energy equation, and a set of species concentration equations. The time-resolved ns pulse discharge power waveform, used as an input in the model, is obtained from the measured discharge voltage and current waveforms. Direct measurement of the RF power coupled to the plasma is more challenging, since at the present conditions the RF conduction current is much smaller.
compared to the significant capacitive current in the external circuit. Therefore the time-resolved
coupled RF power in the model is assumed to be proportional to the decaying electron density
between the pulses, and scaled to match the measured N$_2$ vibrational temperature (see Section 3).
The electron density during the discharge pulses is controlled primarily by the electron impact
ionization and plasma self-shielding due to charge separation. Between the pulses, the electron
density decays by electron-ion recombination, the rate of which is controlled by the electron
temperature and the ion conversion reactions. The electron temperature is determined by the
balance between the electron heating (by ns pulse and RF waveforms) and inelastic electron-
nuclear collision processes.

3. Results and Discussion

The positive polarity ns pulse discharge voltage, current, and coupled energy waveforms
in nitrogen at 100 Torr, measured by the high bandwidth probes, are plotted in Fig. 4(a). The
negative polarity waveforms look similar. The coupled pulse energy, 0.28 ± 0.04 mJ/pulse, is
nearly constant during the pulse burst, except for the first few pulses, when it reaches
approximately 0.5 mJ/pulse. The uncertainty (one standard deviation) of the coupled pulse energy
is determined by measuring it for 50 individual discharge pulses, for the same pulse number in the
burst. The energy coupled during the negative polarity pulses is consistently lower, 0.26 ± 0.06
mJ/pulse, although the difference is comparable with the measurement uncertainty, and remains
nearly constant during the entire burst. Figure 4(b) plots the overlapped ns pulse and RF discharge
voltage waveforms, to illustrate the timing of the ns pulse train and RF bursts. As discussed in
Section 2, the RF voltage is turned off 10 µs before each ns pulse, to prevent the distortion of the
pulse shape by the RF current passing through the pulse compression circuit, such that the RF burst
duration, 90 µs, is somewhat shorter compared to the time interval between the ns pulses, 100 µs.

Figure 5 shows a collage of single-shot, broadband plasma emission images taken at these
conditions during a ns pulse burst 300 pulses long, with the RF voltage turned on and off. As
expected, the first pulse in the burst, produced at a very low initial electron density, is strongly
filamentary. All subsequent discharge pulses, generated in a pre-ionized flow, produce a diffuse
and stable plasma. From the end view images taken without the RF voltage, it can be seen that the
width of the plasma steadily decreases during the burst, likely due to the gradual heating of the
flow resulting in a faster ionization and higher electron density on the centerline. It is evident that
turning the RF voltage on suppresses this trend, increasing the plasma volume and visibly reducing
the emission intensity variation. This effect is most likely caused by the RF-induced drift
oscillations of the electrons between the discharge pulses, with the estimated amplitude of $a \sim \frac{v_{dr}}{2\nu_{RF}}$
~ 0.1 cm, where $v_{dr} \approx 3 \times 10^6$ cm/s is the electron drift velocity at $E/N \approx 2 \times 10^{16}$ V·cm$^2$ and $\nu_{RF}$
=13.56 MHz. The drift oscillations enhance the electron transport and reduce the electron density
gradients in the decaying plasma between the pulses. At all operating conditions, the plasma was
generated only when the ns pulse train was on, such that the RF discharge remained non-self-
sustained. The length of the plasma, critical for the accuracy of the absorption path averaged
TDLAS measurements is close to the length of the electrodes, $L = 6.0 \pm 0.5$ cm.

Figure 6 shows a typical TDLAS scan for several rotational lines in the N$_2$(B$_3^3\Pi_g$, $v' = 2 \leftarrow
A^3\Sigma_u^+$, $v'' = 0$) absorption band in nitrogen at P=100 Torr, compared with the synthetic spectrum
predicted using the line positions and strength predicted by P_gopher software [24] and taking into
account the Doppler and pressure line broadening. The laser scan is taken during 300-pulse, 10 kHz pulse repetition rate discharge bursts repeated at 10 Hz, and the absorption signal is recorded 28 μs after the 3rd pulse in the burst. It can be seen that the experimental and synthetic spectra are in excellent agreement. The rotational-translational temperature in the plasma, \( T = 315 \pm 10 \text{ K} \), is inferred from the synthetic fit of the rotational manifold. The time-resolved absolute population of \( N_2(A^3\Sigma, v=0) \) inferred from the TDLAS spectra during a 300-pulse ns discharge burst at the conditions of Figs. 4, 5, with and without RF voltage applied, is plotted in Fig. 7. It can be seen that the \( N_2(A^3\Sigma) \) decay time between the pulses, \( \approx 50 \mu\text{s} \), is much shorter compared to the flow residence time between the electrodes, \( \approx 50 \text{ ms} \), justifying the use of the plasma length as the absorption path in the TDLAS data analysis.

The results shown in Fig. 7 indicate several dominant trends. First, the \( N_2(A^3\Sigma, v=0) \) population increases only during the first ~5 pulses in the burst, after which it begins to decay gradually, reaching a quasi-steady-state after 50-100 pulses. Second, it is apparent that the population decay between the individual discharge pulses becomes increasingly more pronounced and rapid during the burst, indicating the accumulation of an efficient \( N_2(A^3\Sigma) \) quenching species.

The sawtooth shape of the time-resolved population, with the peak number density after the odd (positive polarity) pulses slightly exceeding that after the even (negative polarity) pulses is consistent with the higher coupled pulse energy measured for the positive polarity pulses. Finally, it is clear that adding the RF voltage waveform on top of the ns pulse train results only in a modest increase of the quasi-steady-state \( N_2(A^3\Sigma, v=0) \) population, within about 20-30%, showing that the additional energy coupling to the plasma by the non-self-sustained RF discharge does not affect electronic excitation of nitrogen molecules by electron impact in a significant way, as expected.

Adding 1% of hydrogen to the nitrogen flow at these conditions results in a significant reduction of the peak \( N_2(A^3\Sigma, v=0) \) population, by about a factor of 2 (see Fig. 8). It can also be seen that the \( v=1 \) population exceeds that of \( v=0 \), similar to our previous measurements in nitrogen [15]. It is readily apparent that the \( N_2(A^3\Sigma, v=0,1) \) populations decay between the pulses increasingly more rapidly, indicating the accumulation of an additional rapid quenching species (compare the decay at \( t=0-2 \text{ ms}, \text{Fig. 8(a)} \) and at \( t=20-22 \text{ ms}, \text{Fig. 8(b)} \)). This is almost certainly due to the rapid (nearly gas kinetic [20]) \( N_2(A^3\Sigma^+, v) \) quenching by H atoms,

\[
N_2(A^3\Sigma^+, v) + H \rightarrow N_2(X^1\Sigma^+) + H .
\] (5)

H atoms in the plasma are generated both by electron impact dissociation of hydrogen molecules and by the reactive quenching of the excited electronic states of \( N_2 \). Generation of significant amounts of N and H atoms suggests that a repetitive ns pulse discharge may be used for plasma-catalytic ammonia generation in high-pressure \( N_2-H_2 \) gas mixtures. Since adding 1% of \( H_2 \) to the mixture does not result in a significant change of \( N_2 \) vibrational excitation in the ns pulse / RF discharge (see the discussion of the CARS measurements below), we have no reason to believe that the effect of RF excitation on the \( N_2(A) \) population would be more pronounced compared to that in pure nitrogen, shown in Fig. 7. Therefore the \( N_2(A) \) population with the RF waveform turned on have been measured only in pure nitrogen.

Figure 9 plots the broadband \( N_2 \) vibrational CARS spectra taken at the end of a 300-pulse ns discharge burst at the conditions of Figs. 4, 5 (100 Torr nitrogen, pulse repetition rate 10 kHz), with and without RF voltage applied. It is readily apparent that turning on the RF waveform results in a significant 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, \( N_2(v=0-3) \)
vibrational bands are detected. The first level N₂ vibrational temperature, \( T_v(N_2) = \frac{\theta_{vib}}{n_0} \), where \( \theta_{vib} \) = \( \omega_v(1 - 2x_d) \) is the characteristic vibrational energy, and \( n_0 \), \( n_1 \) are the populations of vibrational levels \( v=0 \) and 1, is \( T_v(N_2) = 1230 \pm 110 \) K in the ns pulse discharge only and \( T_v(N_2) = 1880 \pm 115 \) K in the ns pulse / RF discharge. The data of Figs. 7 and 9 demonstrate that at the present conditions, the RF waveform predominantly results in the N₂ vibrational excitation, with a relatively modest increase in the population of the lowest excited electronic state, \( N_2(A^3\Sigma) \), and without producing sufficient ionization for RF discharge self-sustaining. 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 illustrated in Fig. 10. The accuracy of the temperature inference is determined by processing 100 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 \( \pm 12 \) K. The rotational temperature at the end of the ns pulse / RF discharge burst, inferred from the spectrum in Fig. 10, is \( T = 396 \pm 10 \) K (with the uncertainty based on the 20% rise of the least squares error).

Time-resolved translational-rotational and N₂ vibrational temperatures measured in a 300-pulse (30 ms long) ns discharge burst in nitrogen and 1% H₂-N₂ mixture at \( P=100 \) Torr, with the RF voltage applied, are plotted in Fig. 11(a,b). As expected, both temperatures gradually increase during the burst, peaking at \( T = 375 \) K and \( T_v(N_2) = 1880 \) K in nitrogen, and decay during the 70 ms interval between the bursts. Adding 1% H₂ to the mixture somewhat reduces the N₂ vibrational temperature and increases the kinetic mode temperature, due to the V-T relaxation of N₂ by H₂ [5]. The translational-rotational and N₂ vibrational temperatures measured at the end of the pulse burst without RF voltage applied, shown for comparison in Fig. 11, illustrate the significant vibrational excitation and noticeable additional heating generated by the RF discharge.

Comparison of the experimental results with the kinetic modeling predictions in a ns pulse discharge in nitrogen, plotted in Fig. 12, shows that the kinetics of \( N_2(A^3\Sigma,v=0) \) quenching during the ns pulse discharge burst is not completely understood. Although the modeling predictions are in qualitative agreement with the data, they indicate that the rate of the gradual \( N_2(A^3\Sigma) \) population decay during the burst is strongly underpredicted (see Fig. 12(a), baseline model). Since the pulse energy coupled to the plasma (after the first few pulses) remains nearly constant, the \( N_2(A^3\Sigma) \) decay between the pulses clearly accelerates during the burst (see Fig. 12(a), experiment). This points to the gradual accumulation of a “rapid quencher” species in the plasma, in addition to the \( N_2(A^3\Sigma) \) quenching by the energy pooling process of Eq. (2). To accumulate, the quenching species needs to have a relatively long lifetime, on the order of \( \sim 10 \) ms. The two species that fit this requirement are the vibrationally excited N₂ molecules in the ground electronic state, \( N_2(X^1\Sigma,v) \), and N atoms.

Previous studies of \( N_2(A^3\Sigma) \) quenching in a discharge afterglow, in the presence of vibrationally excited N₂ molecules [25] suggested the existence of a rapid energy transfer process,

\[
N_2(A^3\Sigma_u^+) + N_2(X^1\Sigma_g^+,v \geq 5) \rightarrow N_2(B^3\Pi_g) + N_2(X^1\Sigma_g^+,w < v), \quad k=3.5 \times 10^{-12} \text{ cm}^3/\text{s}. \tag{6}
\]

To estimate the possible effect of this process on the \( N_2(A^3\Sigma) \) decay at the present conditions, it was added to the kinetic model, assuming that the vibrational states of \( N_2(A^3\Sigma,v=0-7) \), are also quenched by the lower vibrational levels of \( N_2(X^1\Sigma,v=0-4) \) at the same rate, as long as the
quenching process has no energy barrier. The modeling predictions demonstrated that the process of Eq. (6) has almost no effect on the rate of \( N_2(A^3\Sigma_v=0) \) decay during the discharge burst (within ~ 10%), even at the conditions when a strong additional \( N_2 \) vibrational excitation is produced by the RF waveform. This is consistent with the experimental observations, which exhibit nearly the same \( N_2(A^3\Sigma_v=0) \) decay rates with and without the RF voltage (see Fig. 7). Note that the effective rate of \( N_2(A^3\Sigma) \) quenching by the process of Eq. (6) is in fact slower than suggested by an estimate based on its rate coefficient, since the collisional quenching of \( N_2(B^3\Pi_g) \), Eq. (4), results mainly in the repopulating of the \( N_2(A^3\Sigma) \) state [26]. This leaves the \( N_2(A^3\Sigma) \) quenching by N atoms,

\[
N_2(A^3\Sigma_{u^+}, v) + N \rightarrow N_2(X^1\Sigma_g^+) + N,
\]

as the only remaining possibility (short of an unknown quenching process that has not been detected in any of the previous \( N_2(A^3\Sigma) \) kinetics studies). However, the rate of N atom generation predicted by the present model, approximately \( 10^{12} \text{ cm}^{-3} \) pulse (based on the \( N_2 \) dissociation cross section taken from Ref. [18]), is far too low to account for the measured \( N_2(A^3\Sigma) \) decay rate (see Fig. 12(a)). The modeling predictions match the experimental data only if the electron impact \( N_2 \) dissociation rate is increased by a factor of 8, to generate the sufficient number of N atoms (see Fig. 12(a), increased dissociation). Specifically, increasing the dissociation rate matches the rate of \( N_2(A^3\Sigma_v=0) \) decay between the discharge pulses (see Fig. 12(b), baseline model and increased dissociation). Without increasing the dissociation rate, the baseline kinetic model underpredicts the \( N_2(A^3\Sigma,v=0) \) quenching frequency between the pulses by well over a factor of 2.

It is conceivable that the N atom number density in the plasma is enhanced by the electron impact dissociation of the excited electronic states of \( N_2 \), due to their lower dissociation energy. Since in the present study the N atom number density is not measured directly, we are unable to conclude that the observed \( N_2(A^3\Sigma) \) decay rate is entirely due to the quenching by N atoms. However, we are confident that quenching by the vibrationally excited molecules in the ground electronic state, \( N_2(X^1\Sigma,v) \), is not the determining factor, and we are not aware of other kinetic processes that may account for the present observations. As discussed in Section 2, the present data cannot be explained by the \( N_2(A^3\Sigma) \) quenching by impurities such as oxygen or water vapor, since their estimated upper bound concentrations in the flow are far too low (~ 10 ppm and ~ 1 ppm, respectively).

Figure 13 plots the gas temperature and \( N_2 \) vibrational temperature in the ns pulse / RF discharge in nitrogen, calculated by the kinetic model, showing that the modeling predictions are in satisfactory agreement with the experimental data. The ratio of the RF discharge energy coupled to the decaying plasma between the ns discharge pulses to the ns pulse energy, averaged over the entire burst of 300 pulses, is approximately 4.8, i.e. the RF discharge couples nearly 5 times more energy to the plasma compared to the ns pulse discharge. It can be seen that the model somewhat underpredicts the temperature rise in the plasma, suggesting that the net rate of heat transfer by convection and transverse conduction, taken into account as a quasi-zero-dimensional correction, may be overpredicted.

To assess the potential of the present approach to plasma chemical processing of other molecular gas mixtures, additional data were taken in hybrid ns pulse / RF plasmas sustained in a 1% CO - \( N_2 \) mixture and in a 0.1% \( CO_2 \) - \( N_2 \) mixture. The low CO and \( CO_2 \) fractions were chosen to keep the mixtures optically thin and reduce the vibrational relaxation rate of \( CO_2 \) at a relatively low ns pulse discharge repetition rate used in the present work. In this case, the ns pulse discharge
train was operated continuously at 5 kHz, rather than in burst mode. Figure 14(a) compares the fundamental infrared emission spectra from the vibrationally excited CO in the discharge cell at P=50 Torr, with the RF waveform turned on and off. In a ns pulse discharge without the RF waveform, only emission from the CO $v=1 \rightarrow v=0$ band is detected, while in the ns pulse / RF discharge, higher vibrational bands, up to at least $v=10 \rightarrow v=9$, are populated, while the emission intensity increases by over an order of magnitude. Since the fundamental emission spectra ($\Delta v=1$) cannot be used for the quantitative analysis, due to the significant self-absorption by the partially relaxed CO along the long optical path in the cell ($\approx 10$ cm, see Fig. 3), CO first overtone emission spectra ($\Delta v=2$) were also taken, at a lower spectral resolution of 8 cm$^{-1}$. Figure 14(b) compares the experimental and the synthetic [27] CO overtone spectra, indicating that CO vibrational levels up to $v=10$ are populated and radiating. The CO normalized vibrational level populations, inferred from this spectrum, are plotted in Fig. 15. The CO vibrational temperature, based on the slope of the vibrational distribution function for $v=2-5$, is $T_v(CO) = 3330 \pm 30$ K, significantly higher compared to the $N_2$ vibrational temperature measured in the ns pulse / RF plasma in nitrogen at similar conditions (P=100 Torr, 300-pulse burst at 10 kHz). A modest overpopulation of vibrational levels $v=7-10$, due to the anharmonic V-V pumping, is also evident (see Fig. 15). The rotational-translational temperature, inferred from the R-branch of rotationally resolved $v=2 \rightarrow v=1$ band not affected by self-absorption, is $T = 460 \pm 15$ K.

Figure 16(a) plots the fundamental infrared emission spectra from the 0.1% CO$_2$ - N$_2$ mixture excited by a continuous 2.5 kHz ns pulse discharge train and by a hybrid ns pulse / RF discharge at P=60 Torr. Again, it can be seen that turning on the RF waveform dramatically increases the emission from the excited vibrational levels of CO$_2$ (asymmetric stretch vibrational mode, some of it strongly self-absorbed by the atmospheric CO$_2$) and CO, which in this case is the product of CO$_2$ dissociation in the plasma. CO$_2$ vibrational mode temperatures are inferred from the best fit synthetic spectrum generated using the HITEMP database [28], plotted in Fig. 16(b). The custom synthetic spectrum code was compared with the recently published line-by-line infrared emission / absorption code RADIS [29], exhibiting no discrepancies. The synthetic spectrum incorporates emission and self-absorption by vibrationally excited CO$_2$ (three most abundant isotopes), as well as absorption by the atmospheric CO$_2$. The vibrational distributions of all CO$_2$ normal vibrational modes were assumed to be Boltzmann. A Gaussian instrument function with a FWHM of 0.36 cm$^{-1}$ was used, obtained from the isolated CO emission lines. Self-absorption was determined by fixing the atmospheric CO$_2$ concentration at 400 ppm, while varying the effective absorption path length and ambient temperature (2.8 m and 320 K respectively). This also accounts for the self-absorption by CO$_2$ at a higher temperature in the discharge cell. Strong vibrational excitation of CO$_2$ in the plasma is readily apparent, indicated by the emission in the 2250-2320 cm$^{-1}$ region, which is not absorbed by atmospheric CO$_2$. The CO$_2$ mode temperatures inferred from the synthetic spectrum are $T = 570$ K, $T_{12} = 760$ K, and $T_3 = 1725$ K, for the rotational-vibrational mode, symmetric stretch / bending vibrational modes, and asymmetric stretch vibrational mode temperatures. At these conditions, 99.7% of all CO$_2$ molecules are populating the asymmetric stretch vibrational levels $v_3 = 0-3$, demonstrating that the use of the HITEMP database, which includes vibrational levels up to $v_3 = 6$, is adequate. This result demonstrates that strong vibrational nonequilibrium in the hybrid ns pulse / RF plasma can be maintained in the presence of a rapid vibrational relaxer species (CO$_2$), at a relatively low pulse repetition rate.
Finally, comparison of the ex situ FTIR CO absorption spectra, taken by sampling the flow downstream of the discharge cell into the FTIR spectrometer shows that the number density of CO generated in the ns pulse / RF discharge, $2 \times 10^{15}$ cm$^{-3}$ (0.1% mole fraction in the mixture) exceeds that in the ns pulse discharge alone by approximately a factor of 2. This indicates a nearly complete CO$_2$ dissociation in the hybrid plasma and demonstrates a significant contribution of CO$_2$ dissociation via vibrational excitation, enhanced by the RF waveform, into the total CO yield.

4. Summary

In the present work, stable and diffuse hybrid plasmas are sustained by a combination of a ns pulse discharge train and a sub-breakdown, capacitively coupled RF waveform in nitrogen and its mixtures with H$_2$, CO, and CO$_2$. Plasma emission images show that adding the RF waveform does not produce a discharge instability, since the RF electric field is too low to generate additional ionization. In fact, the RF field increases the plasma volume and somewhat improves the plasma uniformity, most likely due to the electron drift oscillations induced in the plasma, which reduce the electron density gradients. Although the present measurements have been made at the same RF frequency, 13.56 MHz, reducing the frequency would increase the amplitude of the drift oscillations and enhance the electron transport further. Also, the superposition of the RF waveforms with different frequencies may provide additional control over the amplitude and phase of the electron oscillations, as well as the electron temperature variation between the ionizing pulses. The hybrid plasma is generated using a single pair of electrodes external to the discharge cell, which is an advantage compared to a ns pulse / DC discharge. The present approach may also resolve the problem caused by self-sustaining the cathode layer of a non-self-sustained DC discharge, which results in the instability development and discharge filamentation at high currents [5].

Measurements of the metastable nitrogen molecules in the lowest excited electronic state, N$_2$(A$^3\Sigma^+$) (by TDLAS) and vibrationally excited molecules in the ground electronic state, N$_2$(X$^1\Sigma^+_g$) (by CARS), demonstrated that these species are generated in the hybrid plasma selectively. Specifically, electronically excited N$_2$(A$^3\Sigma^+$) molecules are produced by the ns pulse discharge waveform, and their number density is weakly affected by adding the RF waveform. On the other hand, vibrational excitation of the ground electronic state molecules is predominantly due to applying the RF voltage. A strong vibrational nonequilibrium is maintained at low translational-rotational temperatures. The same trend is observed in the 1% H$_2$-N$_2$ mixture, although in this case both the N$_2$(A$^3\Sigma^+$) number density and the ground electronic state N$_2$ vibrational temperature are somewhat lower. This demonstrates that sustaining the hybrid ns pulse / RF discharge in a reacting molecular gas mixture can isolate the plasma chemical reaction mechanisms dominated by vibrationally excited molecules from those of electronically excited molecules and atomic species.

Kinetic modeling, based on the experimental coupled power waveform and using up-to-date data on the electron impact cross sections and plasma chemical reaction rates, shows that the quenching rate of N$_2$(A$^3\Sigma^+$) molecules in a ns pulse discharge in nitrogen is significantly underpredicted. The experimental results indicate the accumulation of a rapid quenching species in the plasma, such as N$_2$(X$^1\Sigma^+_g$,v) molecules or N atoms. However, N$_2$(A$^3\Sigma^+$) measurements in the hybrid ns pulse / RF discharge, when the N$_2$ vibrational populations are much higher, show that the rapid quenching is not affected by the additional vibrational excitation. This is consistent with
the analysis of the modeling predictions, which also indicate that the effect of N₂ vibrational excitation on N₂(A³Σ) quenching is relatively insignificant. The kinetic modeling prediction agree with the experimental data only if the rate of the ground state N₂ dissociation by electron impact is increased by almost an order of magnitude, to generate the sufficient N atom number density and match the measured rate of N₂(A³Σ) decay. This suggests a significant contribution of excited electronic states into the net rate of N₂ dissociation at the present conditions, although in the absence of direct measurements of the N atom number density, no definite conclusion can be made.

FTIR emission spectra, taken in hybrid plasmas sustained in 1% CO-N₂ and 0.1% CO₂-N₂ mixtures, demonstrate that the present approach also generates strong vibrational excitation of CO and CO₂. FTIR absorption spectra of the flow downstream of the discharge cell show that the CO yield in the CO₂-N₂ mixture excited by the ns pulse / RF discharge is approximately a factor of 2 higher compared to that in a ns pulse discharge without the RF waveform. This indicates a significant effect of the vibrationally enhanced CO₂ dissociation pathway in the hybrid plasma, which can be isolated from other CO₂ dissociation mechanisms using the present approach. Future work will focus on the measurements of CO₂ vibrational level populations by tunable laser absorption spectroscopy, such as has been done in a recent study [30] and quantifying the rate of dissociation by this mechanism in the hybrid plasma.

The present approach may also be extended to other reacting molecular gas mixtures, such as H₂-air, CH₄-air, and CH₄-CO₂, to generate electronically excited molecules as well as N, O, and H atoms (by the ns pulse train), and vibrationally excited N₂, H₂, CO₂, and CH₄ molecules (by the sub-breakdown RF waveform). The capability of selective generation of atomic species and vibrationally excited molecules is critical for determining their roles in plasma chemical processes, such as ignition of hydrogen-oxygen and methane-oxygen (O and H atoms vs. vibrationally excited H₂(X¹Σ,v) molecules and O₂(a¹Δ) molecules [31,32]). However, this capability critically depends on isolating the ns pulse and RF generators from the each other and operating the ns pulse train at a significantly higher pulse repetition rate, up to ~100 kHz. Although this has not been the main focus of the present study, it will need to be addressed in the future work.

5. Acknowledgments

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References


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Figure 1. Schematic of the discharge cell (a) and the hybrid discharge waveforms (b).
Figure 2. Schematic of CARS diagnostics used for $N_2(X^1\Sigma_g^+,v)$ populations and rotational-translational temperature measurements.

Figure 3. Schematic of TDLAS diagnostics used for $N_2(A^3\Sigma_u^+,v)$ population and rotational-translational temperature measurements. Optical access for acquiring FTIR emission spectra and sampling of the products for acquiring FTIR absorption spectra are also shown.
Figure 4. (a) Ns pulse discharge waveforms (voltage, current, and coupled energy); (b) Ns pulse / RF discharge voltage waveforms, illustrating the timing of ns pulse train and RF bursts. Nitrogen, P=100 Torr, ns pulse repetition rate / RF burst repetition rate 10 kHz, each RF burst duration 90 μs.
Figure 5. Single-shot, broadband plasma emission images: (a) ns pulse train alone, (b) ns / RF waveform. Both side view and end view images are shown (see Fig. 1(a)). Nitrogen, P=100 Torr, ns pulse repetition rate / RF burst repetition rate 10 kHz, each RF burst duration 90 μs. ICCD camera gate 1 μs long is wrapped around the ns pulse discharge, pulse numbers in the train are indicated in the figure.
Figure 6. TDLAS scans and synthetic spectra of 3 rotational lines in the $N_2(B_3\Pi_{g}, \nu' = 2 \leftrightarrow A^3\Sigma_u^+, \nu'' = 0)$ absorption band. Nitrogen, $P=100$ Torr, 300-pulse ns discharge burst, 28 μs after the 3rd pulse in the burst. Inferred rotational-translational temperature is $T = 315 \pm 10$ K.

Figure 7. Time-resolved absolute population of $N_2(A^3\Sigma_u^+, \nu=0)$ during a 300-pulse ns discharge burst, with and without RF voltage applied: (a) first 50 pulses, (b) entire burst. Nitrogen, $P=100$ Torr, ns pulse repetition rate / RF burst repetition rate 10 kHz, each RF burst duration 90 μs.
Figure 8. Time-resolved absolute population of N$_2$(A'\Sigma_u^+, v=0) during a 20-pulse interval of a 300-pulse ns discharge burst without RF voltage applied. 1% H$_2$-N$_2$ mixture, operating conditions are the same as in Fig. 7.

Figure 9. Broadband N$_2$ vibrational CARS spectra taken at the end of a 300-pulse ns discharge burst without and with RF voltage applied. Nitrogen, P=100 Torr, ns pulse repetition rate / RF burst repetition rate 10 kHz, each RF burst duration 90 \mu s. “First level” N$_2$ vibrational temperatures inferred are T$_v$(N$_2$) = 1230 \pm 110$ K and 1880 \pm 115$ K, respectively.
Figure 10. Experimental and synthetic (CARSFT) N\textsubscript{2} vibrational CARS spectra (v=0 band) taken at the end of a 300-pulse ns discharge burst with RF voltage applied. 1\% H\textsubscript{2}-N\textsubscript{2} mixture, P=100 Torr, ns pulse repetition rate / RF burst repetition rate 10 kHz, each RF burst duration 90 μs. Rotational temperature inferred is T = 396 ± 10 K.

Figure 11. Translational-rotational temperature and N\textsubscript{2} vibrational temperature during and after a 300-pulse ns discharge burst 30 ms long with RF voltage applied. (a) Nitrogen and (b) 1\% H\textsubscript{2}-N\textsubscript{2} mixture, P=100 Torr, ns pulse repetition rate / RF burst repetition rate 10 kHz, each RF burst duration 90 μs. Temperature and N\textsubscript{2} vibrational temperature measured at the end of the pulse burst, without RF voltage applied, are shown for comparison.
Figure 12. Comparison of experimental $N_2(A^3\Sigma_u^+, v=0)$ population during a 300-pulse ns discharge burst in nitrogen at the conditions of Fig. 7 (without RF voltage applied) with kinetic modeling predictions: (a) entire burst; (b) 10-pulse interval. The modeling predictions, including the N atom number density, are shown for the baseline model and for a model with the N$_2$ dissociation rate increased by a factor of 8.

Figure 13. Comparison of experimental and predicted gas temperature and N$_2$ vibrational temperature at the conditions of Fig. 11(a) (nitrogen, P=100 Torr, ns pulse repetition rate / RF burst repetition rate 10 kHz). N$_2$ dissociation rate in the model is increased by a factor of 8.
Figure 14. (a) CO fundamental emission spectra in a 5 kHz ns pulse discharge operated continuously, with and without 800 V peak RF voltage applied. (b) Experimental and best fit synthetic CO first overtone emission spectra in the ns pulse / RF discharge. 1% CO-N₂ mixture, P=50 Torr, flow rate 0.2 slm, resolution 0.5 cm⁻¹ (a) and 8 cm⁻¹ (b).

Figure 15. CO vibrational level populations during a 5 kHz ns discharge operated continuously, with RF voltage applied, inferred from the overtone spectrum shown in Fig. 14(b). CO vibrational temperature $T_v$(CO) = 3300 ± 30 K.
Figure 16. (a) CO$_2$ and CO fundamental emission spectrum during a 2.5 kHz ns discharge operated continuously, with and without 1 kV peak RF voltage applied. 0.1% CO$_2$-N$_2$ mixture, P=60 Torr, flow rate 0.15 slm. (b) Comparison of experimental and synthetic CO$_2$ emission spectra, for T$_3$=1725 K, T$_{12}$=760 K, and T=570 K.