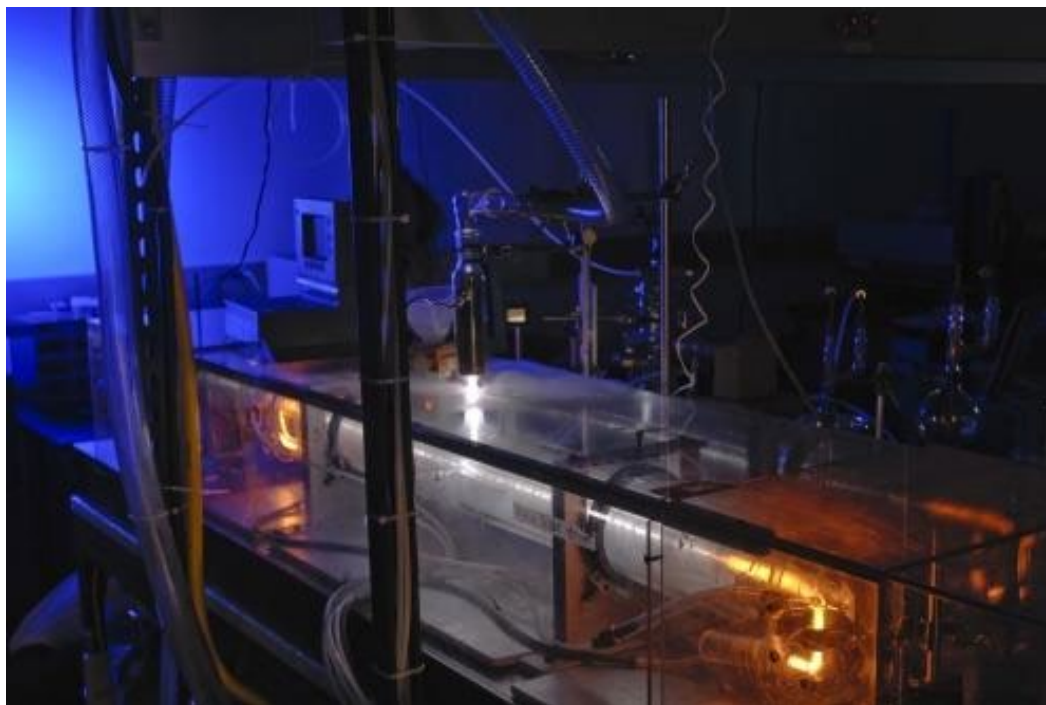


Selective Generation of Metastable Excited Species in Ns Pulse and Hybrid Plasmas for Plasma Chemistry and Plasma Catalysis Applications

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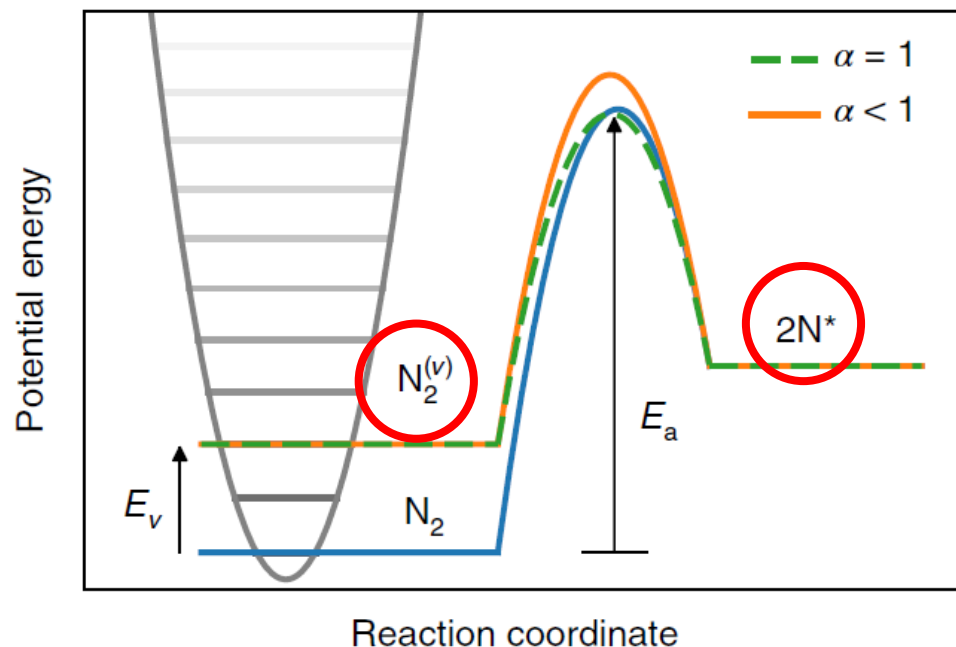
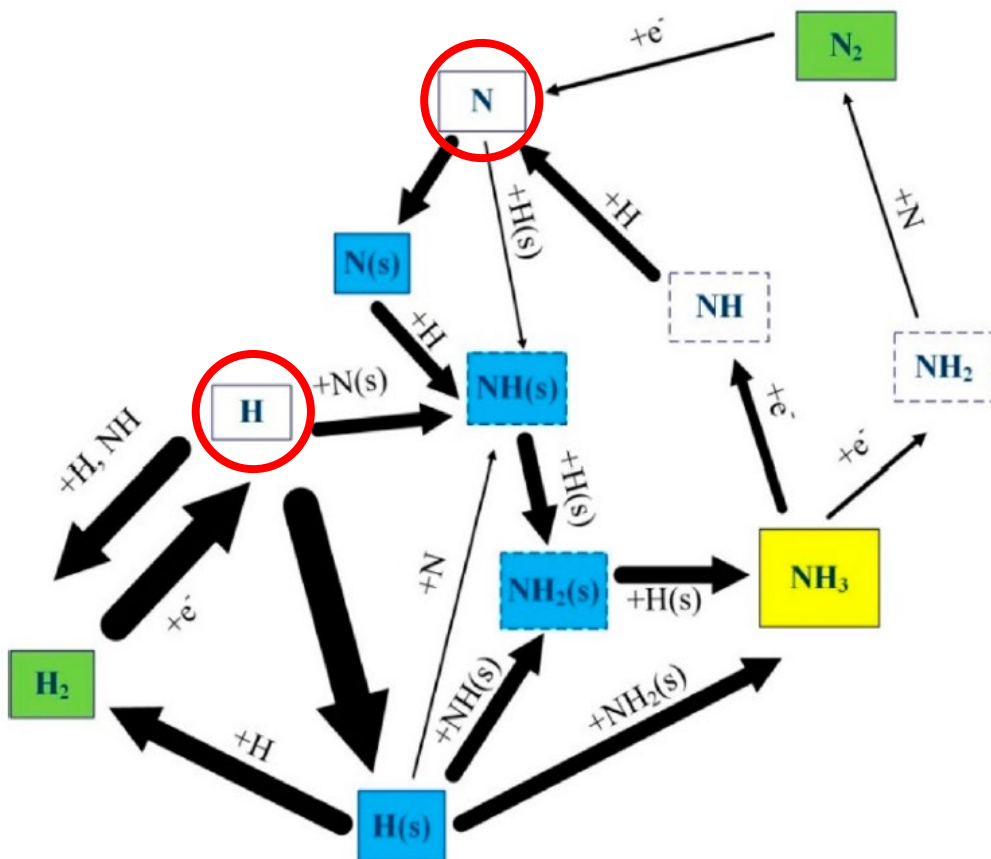
Nonequilibrium Thermodynamics Laboratory: Research Fields

- **Kinetics of low-temperature plasmas and high-speed nonequilibrium flows**
- **Molecular energy transfer, nonequilibrium chemical reactions**
- **Laser diagnostics of plasmas and reacting flows**
- **Development of new molecular gas lasers**
- **Applications for plasma chemical reactors, propulsion and combustion, high-speed aerodynamics, hypersonic flows, and biology**

Excited Species and Radicals in Reacting Plasmas: Outstanding Challenges

- **Energy partition** in nonequilibrium plasmas controlled by **reduced electric field (E/N)**:
 - Vibrational excitation at low E/N
 - Electronic excitation and molecular dissociation at high E/N
- Excited species and radicals enable **low-temperature reaction pathways** in reacting flows: plasma-assisted combustion, plasma-assisted catalysis
- **Isolating and quantifying the effect** of excited electronic species, reactive radicals, and vibrationally excited molecules **remains an open question**
 - H_2 - O_2 combustion: H and O atoms vs. $H_2(X^1\Sigma, v)$ and $O_2(a^1\Delta)$
 - NH_3 and NO_x synthesis: electronically excited N_2^* , O_2^* vs. $H_2(v)$, $N_2(v)$
 - CO_2 dissociation: via electronic or vibrational excitation?
 - CH_4 / CO_2 conversion into CO / H_2
- **Selective generation** of excited species and radicals, **isolating their effect** is challenging

Plasma Catalytic Synthesis of NH_3 : Reaction Pathways



- Process dominated by surface reactions of **N** and **H** (generated by electron impact)

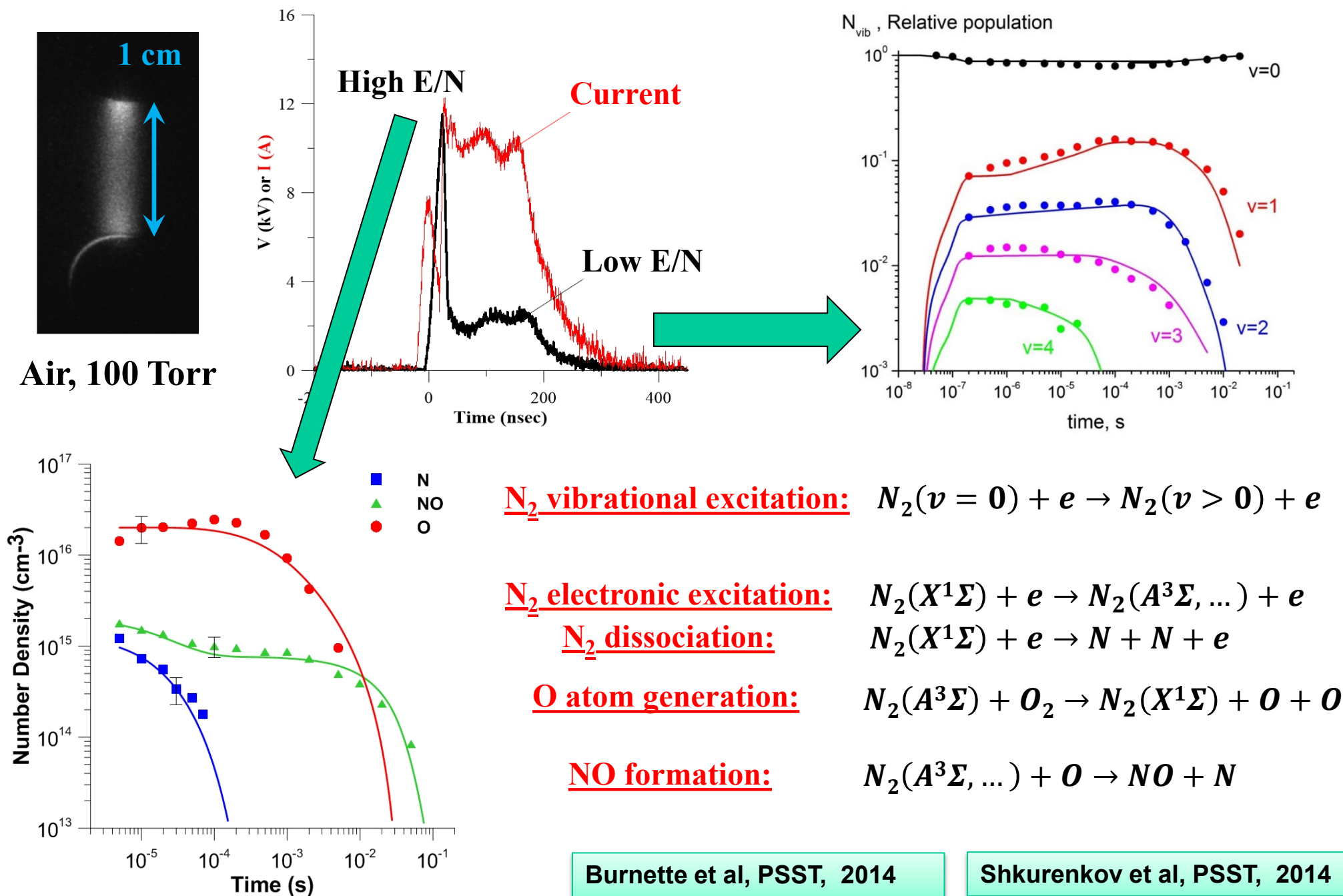
- Vibrational excitation of **N₂** reduces barrier for surface dissociation reaction (?)

J. Shah et al, ACS Appl. Energy Mater. 2018

P. Mehta et al., Nature Catalysis 2018

N / H or $\text{N}_2(\text{v})$? It is difficult to generate them independently

Air Plasma Chemistry: Low and High E/N Reaction Pathways

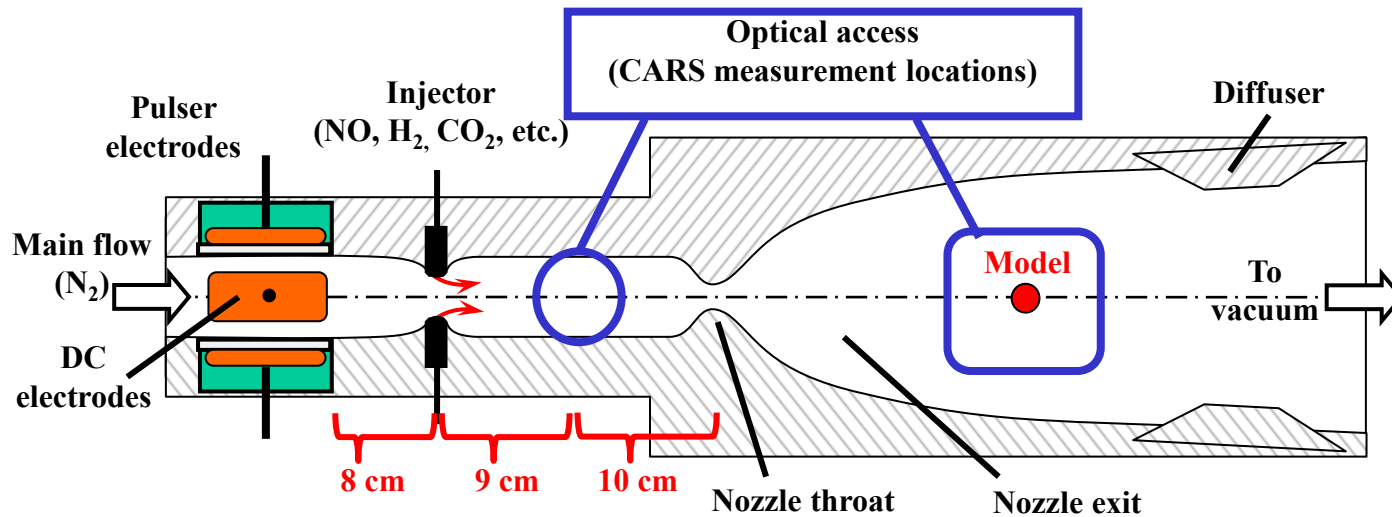


“Hybrid” Plasmas: How Do They Work?

- **Non-self-sustained (“hybrid”) discharges: separate waveforms for ionization and main energy loading**
 - **Ionization and energy addition are uncoupled**
 - **Stable at high pressures and discharge powers**
 - **Previously used for efficient molecular lasers (CO₂, CO, COIL)**
- **External ionization sources:**
 - **High-energy electron beam (challenging in operation)**
 - **High-voltage, ns duration pulses (most popular approach)**
- **Main energy loading waveforms:**
 - **DC: may need separate electrodes, cathode layer unstable at high pressures**
 - **RF: electrodes external to reactor, heating electrons by drift oscillations**
- **Can hybrid plasmas be used for selective generation of excited species and radicals, using two separate waveforms (e.g. ns pulses and RF voltage)?**

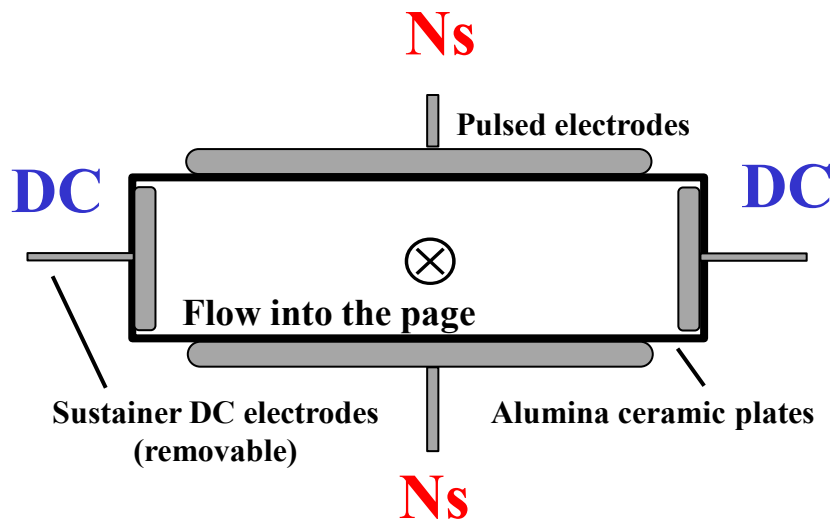
Background: Ns Pulse / DC Hybrid Plasma

Mach 5 Nonequilibrium Plasma Wind Tunnel



Wind tunnel parameters:

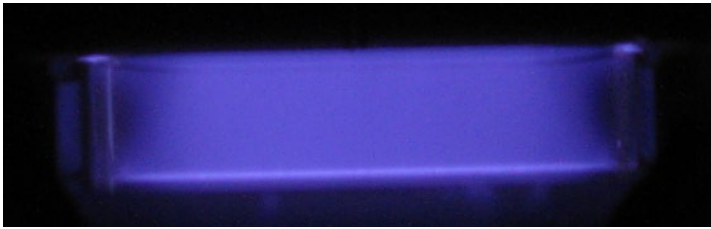
- Plenum pressure 0.5-1.0 atm
- Mach 5 flow in test section
- Steady-state run time 5-10 s



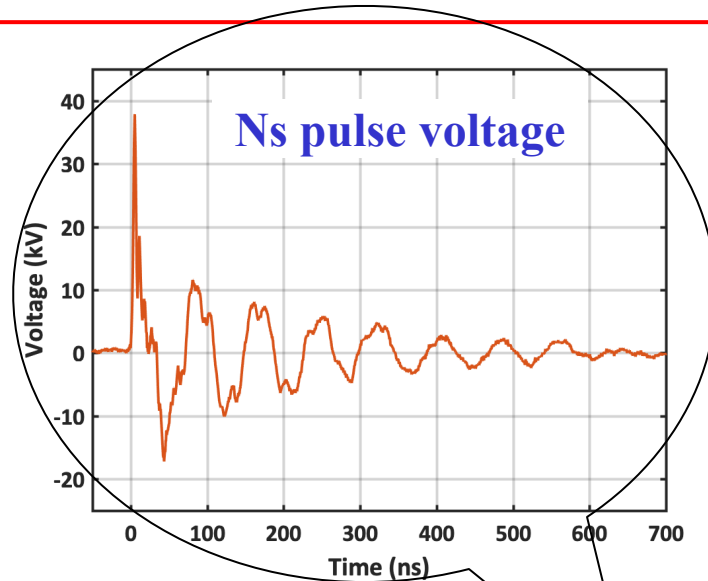
Sustaining nonequilibrium flow:

- Ns pulse train / DC discharge in plenum
- Total power loading up to 3 kW

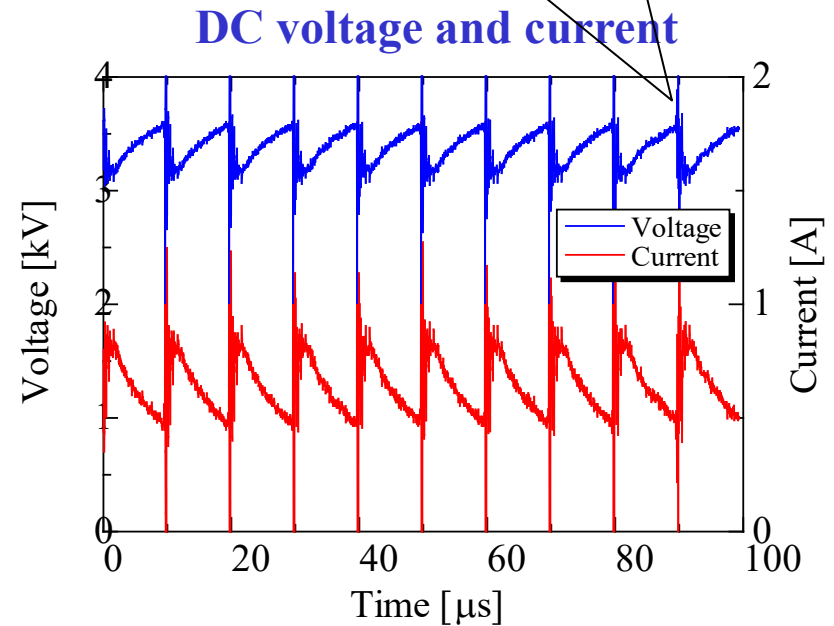
Ns pulse / DC discharge in plenum



Ns pulse discharge alone
 N_2 , $P=350$ torr, $\nu=100$ kHz

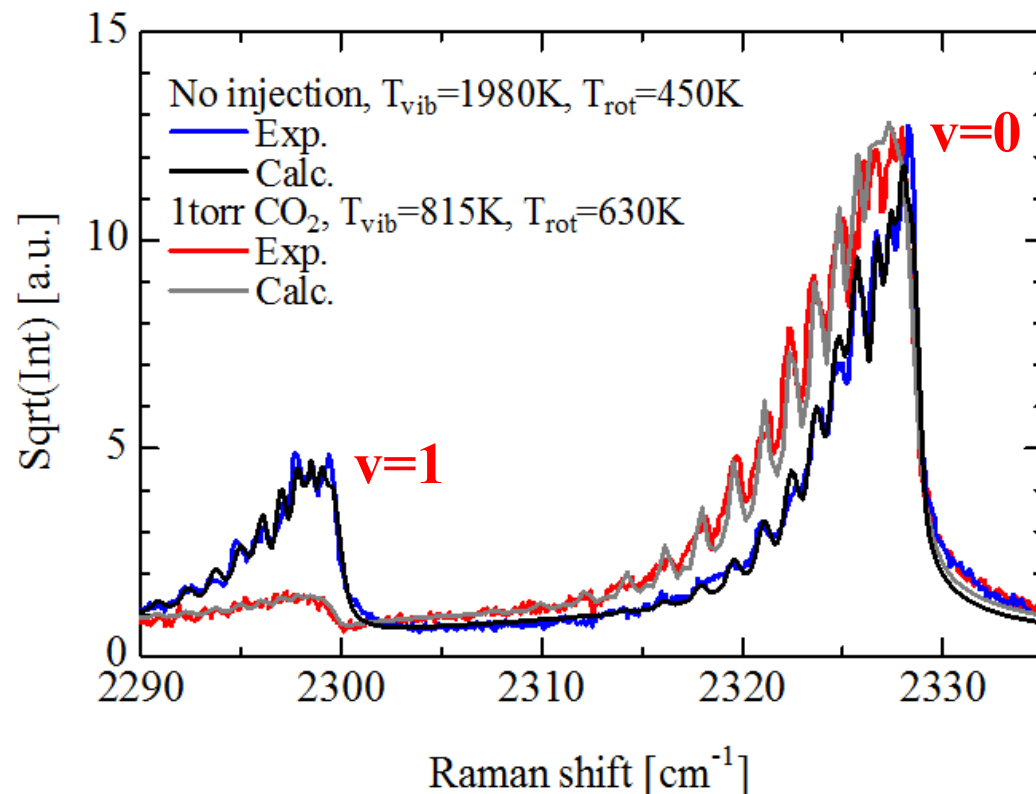


Ns pulse / DC discharge
 N_2 , $P=350$ torr, $\nu=100$ kHz, $U_{DC} = 2$ kV



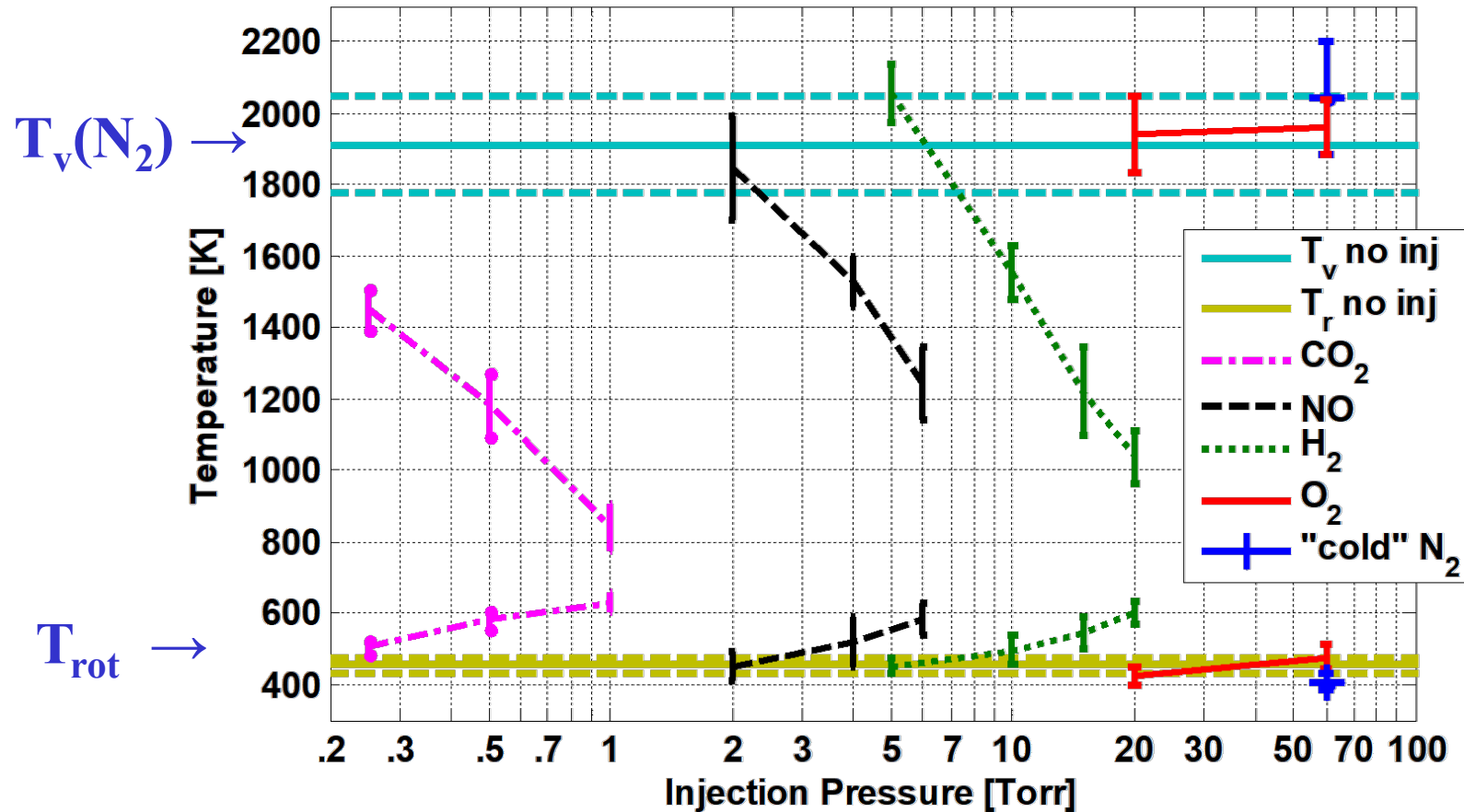
- Plasma does not fully decay between ns pulses
- Stable plasma at 0.5 atm, up to 3 kW DC power

CARS Measurements of T , $T_v(N_2)$ in the Plasma



- Nitrogen, $P = 300 \text{ Torr}$
- Strong vibrational nonequilibrium: $T_v(N_2) \approx 2000 \text{ K}$, $T_{\text{rot/trans}} = 450 \text{ K}$
- Less nonequilibrium when CO_2 is added: V-V energy transfer from N_2 to CO_2
- Similar results in $\text{N}_2\text{-H}_2$, $\text{N}_2\text{-O}_2$, $\text{N}_2\text{-NO}$, and $\text{N}_2\text{-CO}_2$ mixtures

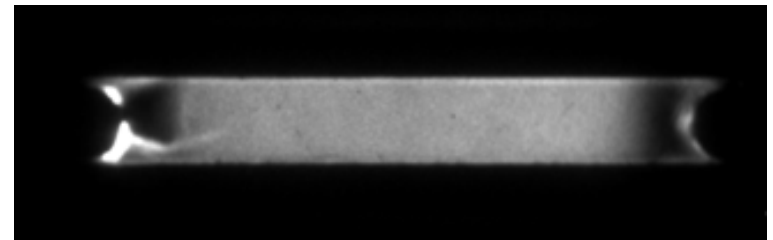
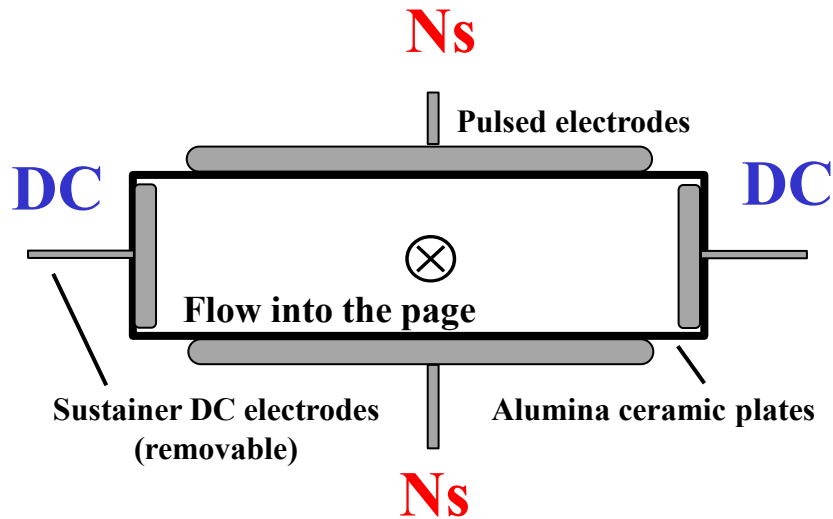
T and $T_v(N_2)$ in Different Gas Mixtures



- Baseline: $P = 300$ Torr, $T_v(N_2) \approx 2000$ K, $T_{rot/trans} = 450$ K
- Significant vibrational relaxation produced by adding relaxer species
- Application: effect of accelerated vibrational relaxation on supersonic flow

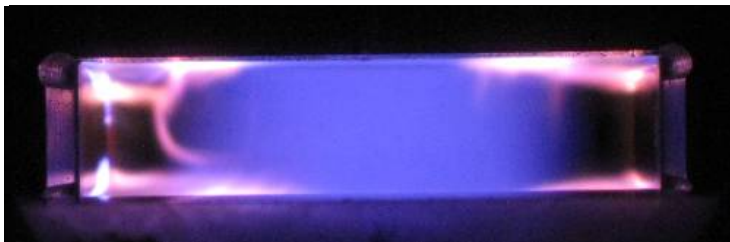
Ns pulse / DC Discharge Limitation:

Diffuse plasma always becomes unstable at high DC voltages



Ns pulse / DC discharge

N_2 , $P=300$ torr, $\nu=100$ kHz, $U_{DC} = 3$ kV

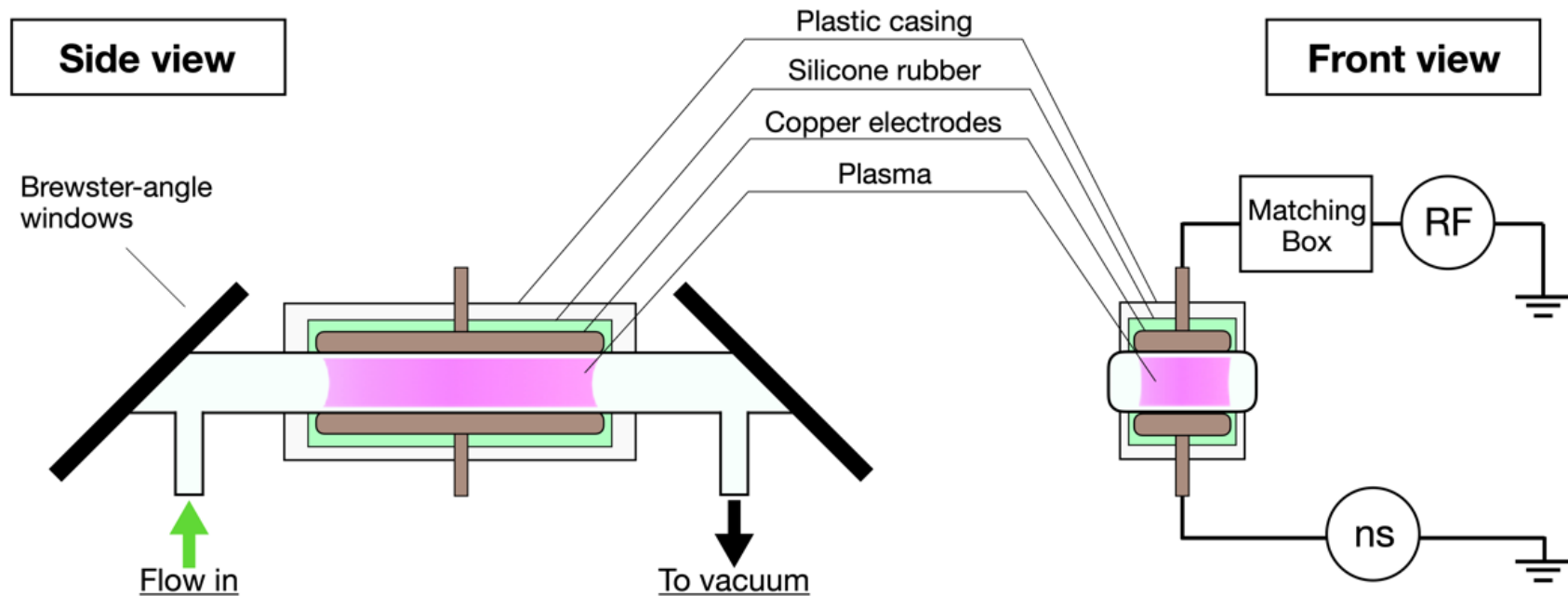


Ns pulse / DC discharge

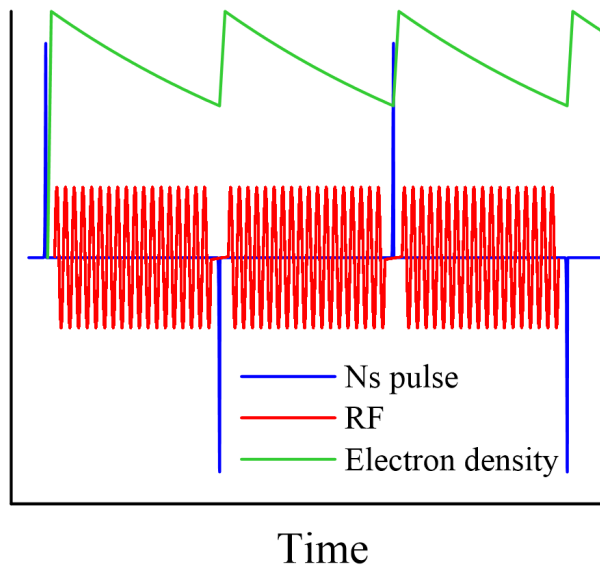
N_2 , $P=350$ torr, $\nu=100$ kHz, $U_{DC} = 3.5$ kV

- Cathode layer is always self-sustained
- Increasing DC voltage leads to cathode layer ionization instability

Present Approach: Ns Pulse / RF Hybrid Plasma

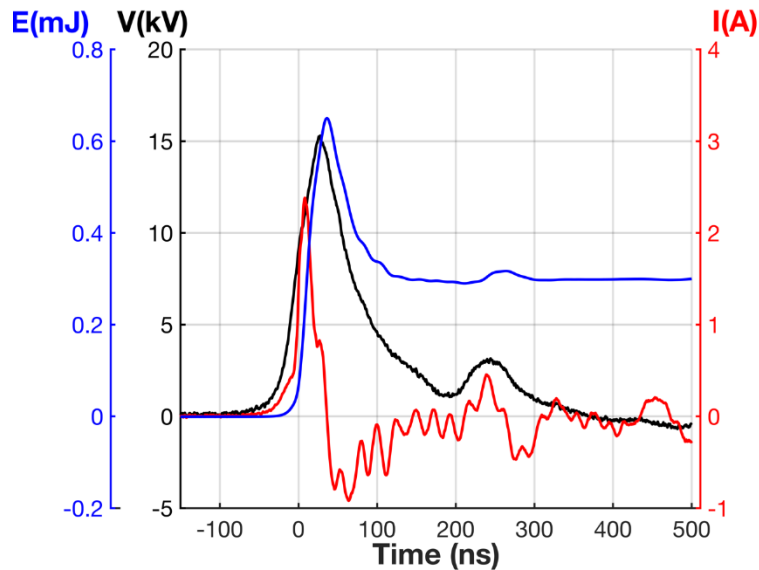


Voltage, Electron Density

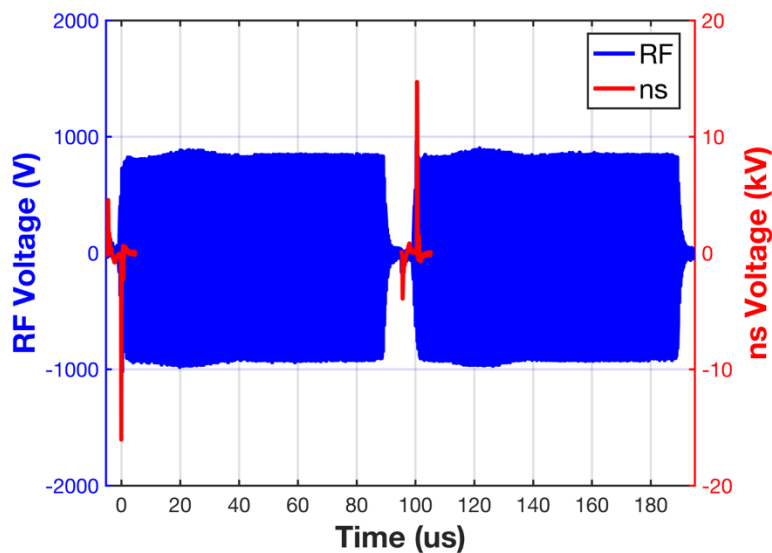


- Single pair of electrodes, external to the reactor
- Alternating pulse polarity (not critical)
- Ns pulses and RF bursts are separated in time
- RF voltage induces drift oscillations of electrons generated by the pulses
- RF plasma remains stable

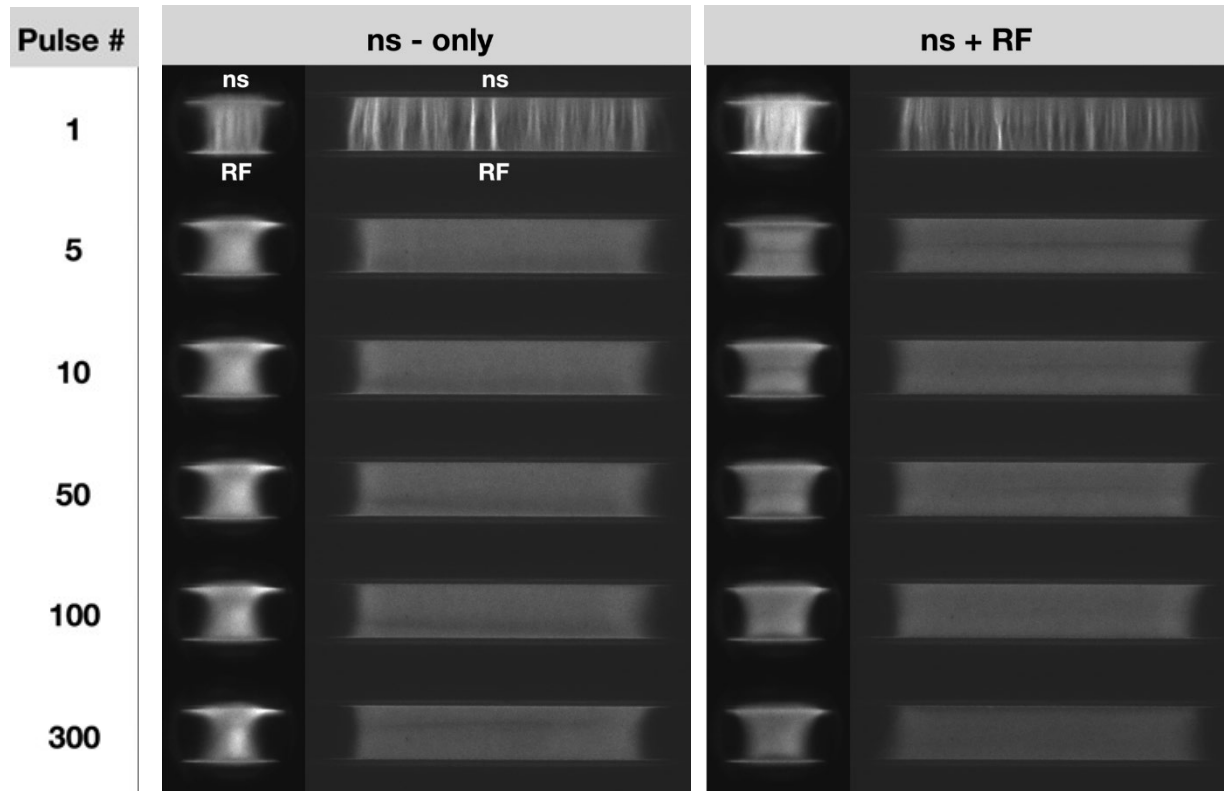
Discharge Waveforms and Plasma Emission Images



Pulse voltage and current



Ns pulse / RF voltage waveforms

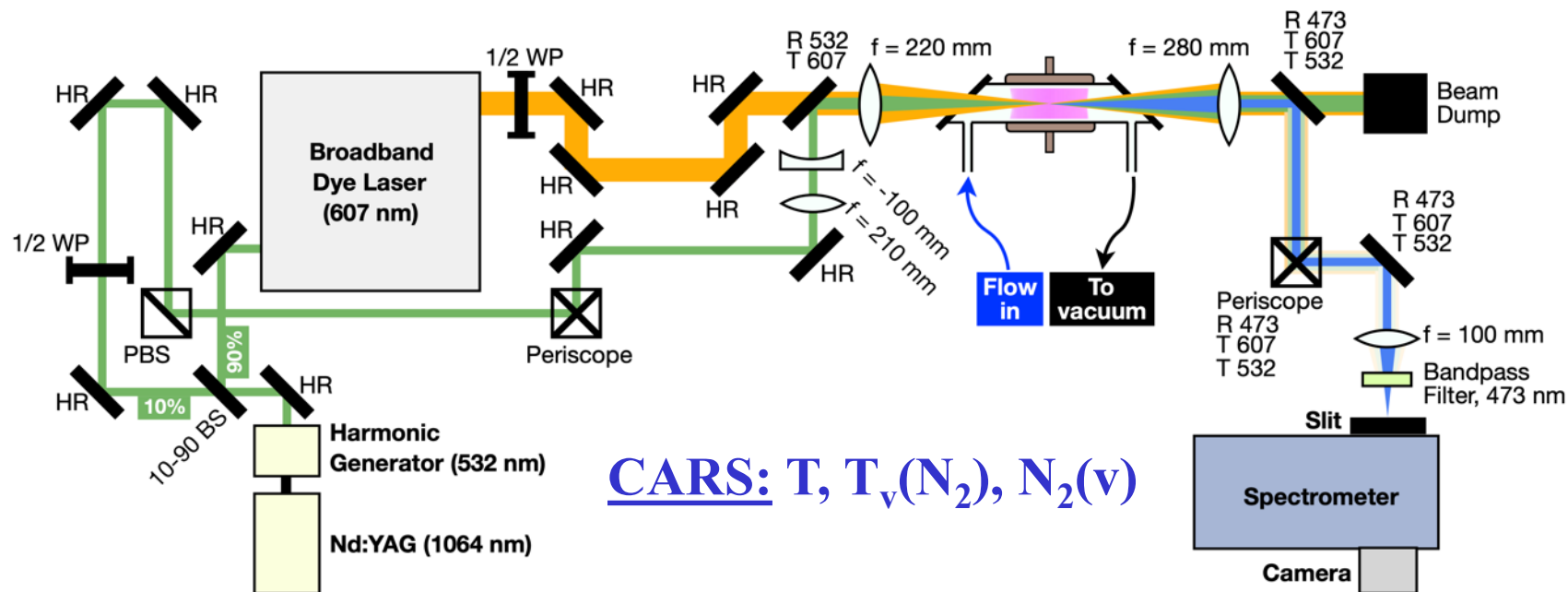


- Diffuse plasma during entire burst, after pulse #1
- RF-induced electron drift oscillations improve plasma uniformity
- Similar observations in N_2 and H_2-N_2 , up to $P=1$ atm and $\nu=100$ kHz

Can Both Waveforms in a Hybrid Plasma Generate Desired Species Selectively?

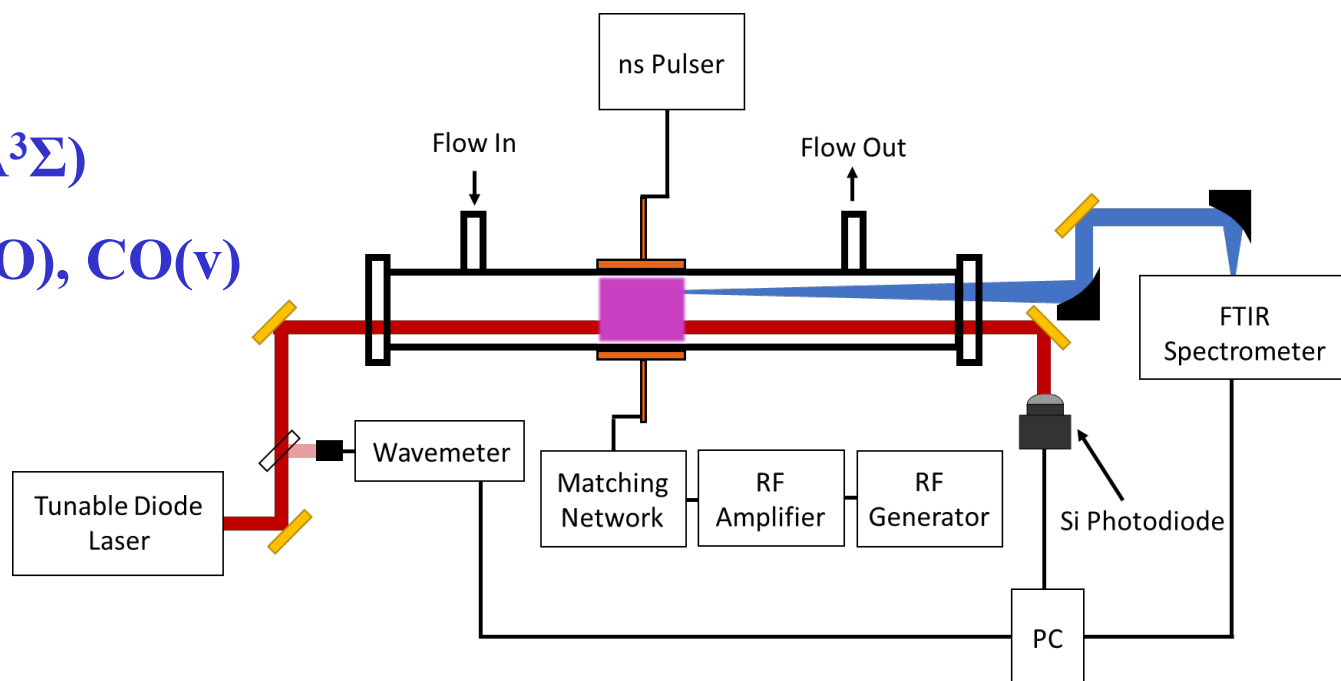
- High peak E/N ns pulses:
 - Sustain ionization and
 - Generate electronically excited species, e.g. $\text{N}_2(\text{A}^3\Sigma_u^+)$, and atoms (N, H, O)
- Quasi-steady-state, low E/N waveform:
 - Generate vibrationally excited molecules, e.g. $\text{N}_2(\text{v})$, $\text{H}_2(\text{v})$, $\text{CO}(\text{v})$, $\text{CO}_2(\text{v}_1, \text{v}_2, \text{v}_3)$
- Goal: isolate and quantify the effect of atoms / radicals and vibrationally excited species on plasma assisted chemistry and catalysis
- Goal: develop energy-efficient plasma chemical syntheses at atmospheric pressure

Diagnostics



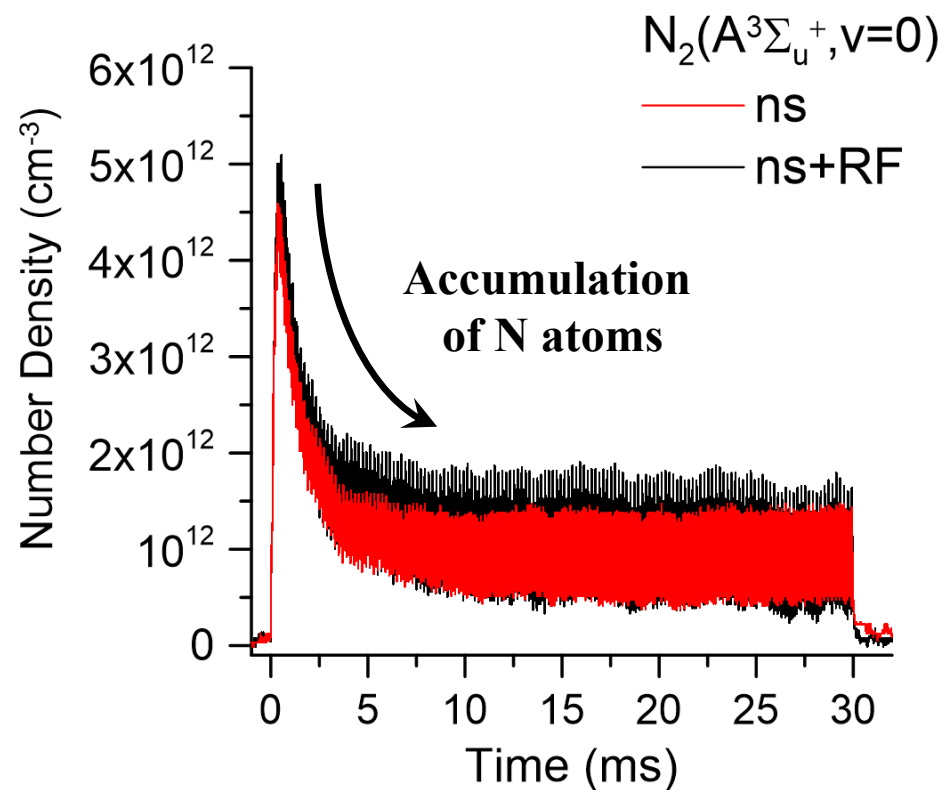
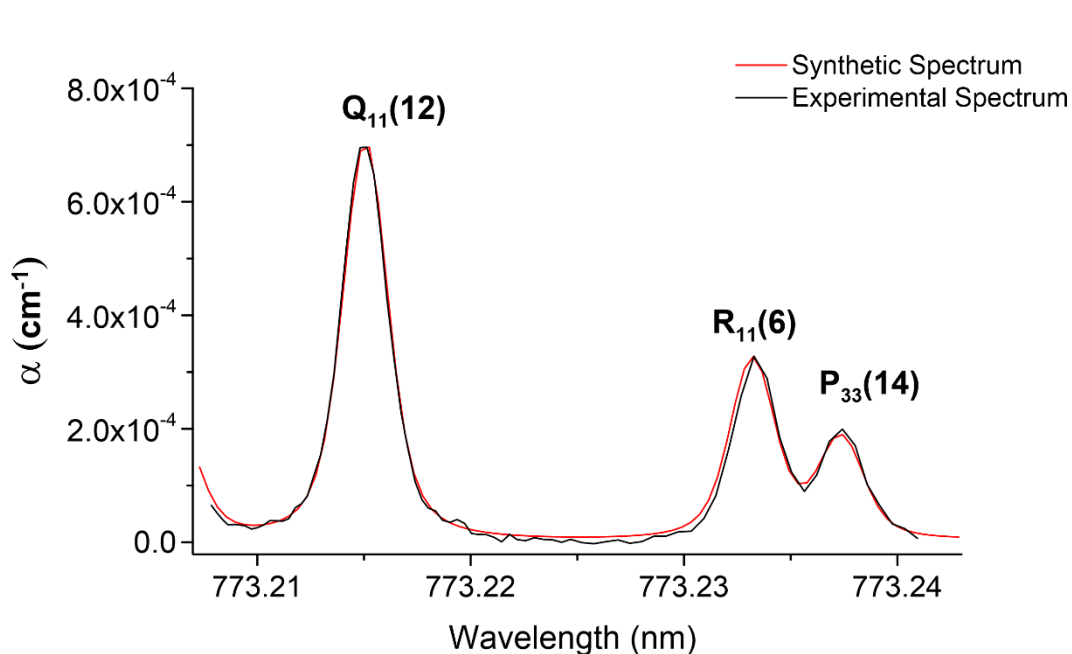
TDLAS, CRDS: T , $N_2(A^3\Sigma)$

FTIR emission: T , $T_v(CO)$, $CO(v)$



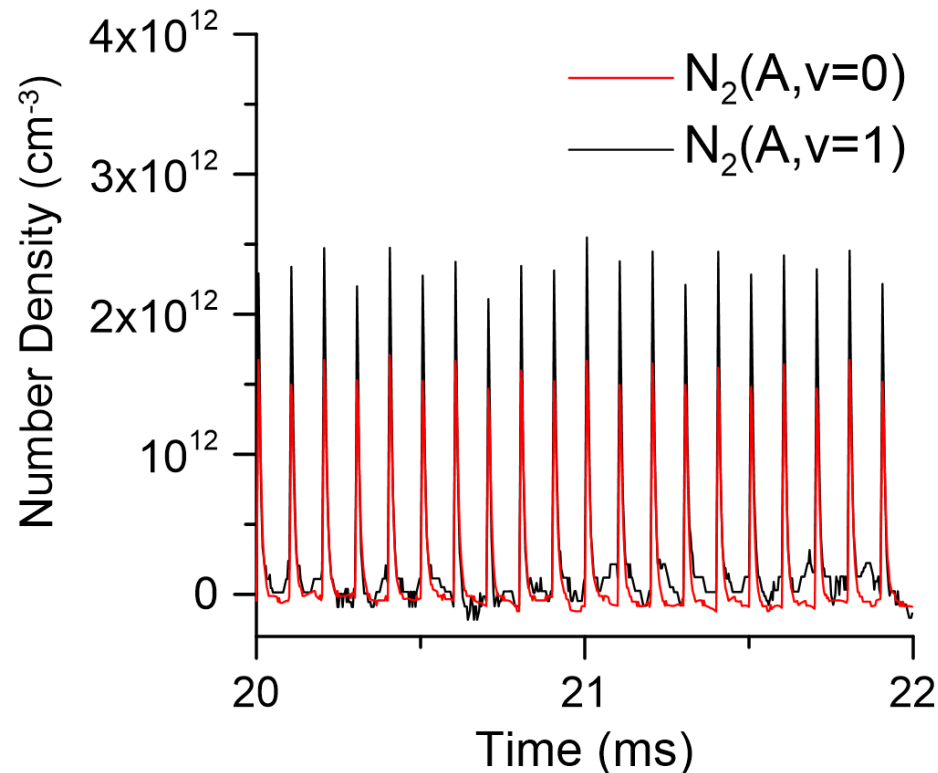
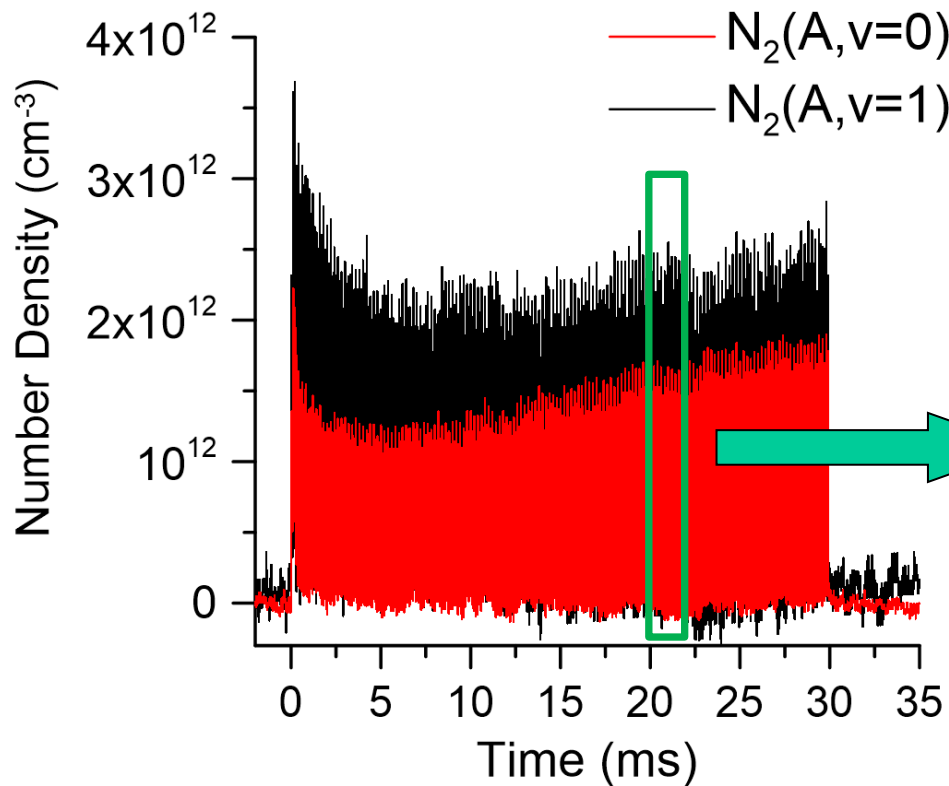
Ns Pulse Discharge Alone in Nitrogen:

Generation of $N_2(A^3\Sigma_u^+)$ and N atoms by Electron Impact



- TDLAS scan with several $N_2(A, v=0)$ absorption lines
- Absorption sensitivity 10^{-4} cm⁻¹, $T=320 \pm 10$ K
- Nitrogen, $P=100$ Torr, pulse repetition rate 10 kHz
- Almost no effect of RF voltage on $N_2(A)$ number density, as expected (E/N is low)
- $N_2(A)$ decay due to quenching by N atoms, $N_2(A) + N \rightarrow N_2(X) + N$
- Time-resolved $N_2(A, v=0)$ populations with and without RF (for 50 pulses)

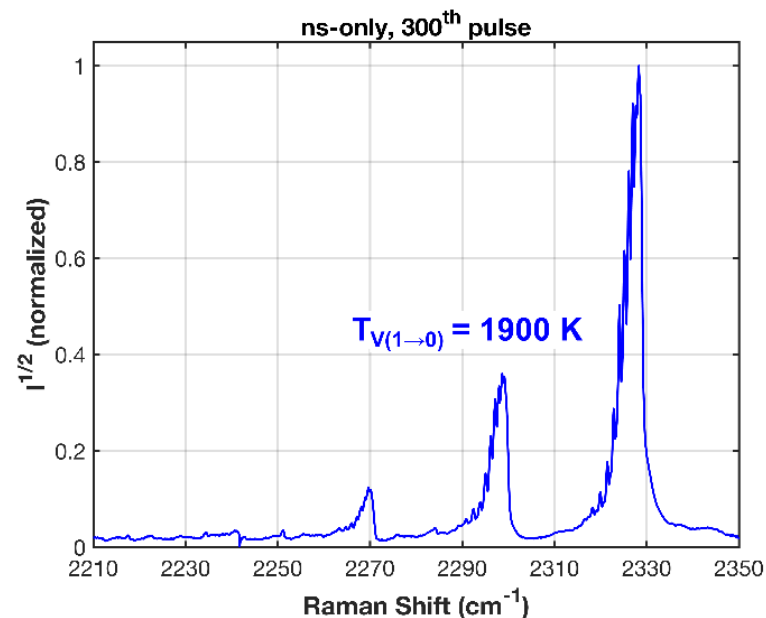
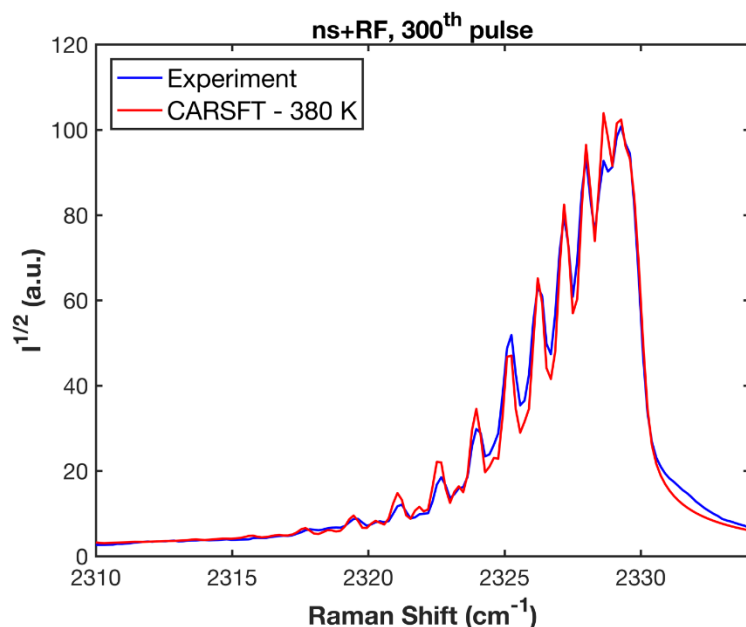
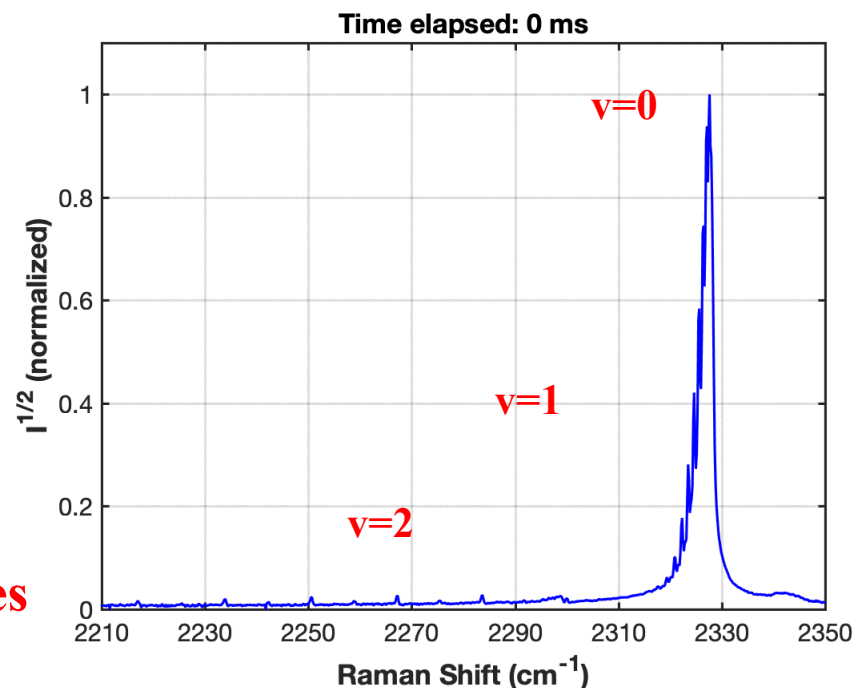
Ns Pulse Discharge Alone in $\text{H}_2\text{-N}_2$: Generation of $\text{N}_2(\text{A}^3\Sigma_u^+)$, N, and H Atoms



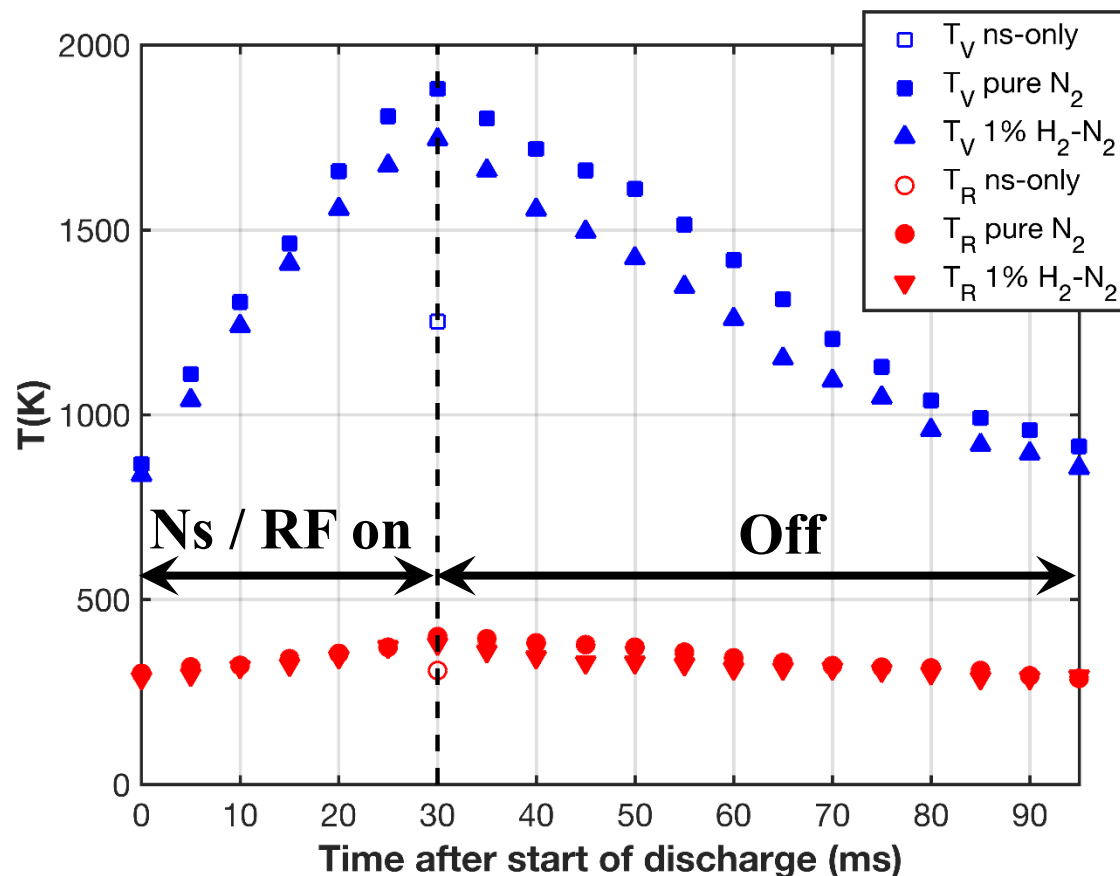
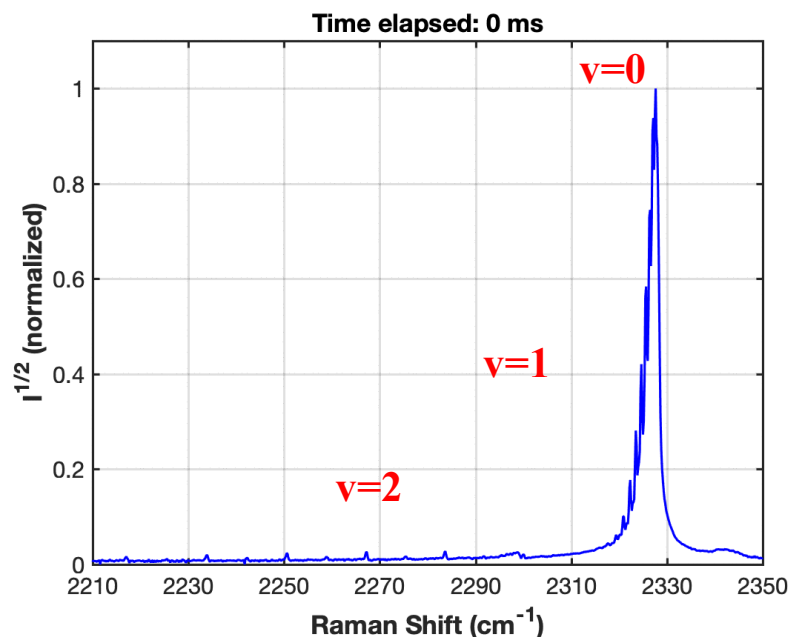
- 1% $\text{H}_2 - \text{N}_2$, $P=100$ Torr, pulse repetition rate 10 kHz
- Peak $\text{N}_2(\text{A})$ is lower, decay between the pulses: rapid quenching by N and H atoms,
 $\text{N}_2(\text{A}) + \text{N} \rightarrow \text{N}_2(\text{X}) + \text{N}$, $\text{N}_2(\text{A}) + \text{H} \rightarrow \text{N}_2(\text{X}) + \text{H}$
- Indication of H atom generation by electron impact

Ns Pulse / RF Discharge in **Nitrogen**: Strong N₂ Vibrational Nonequilibrium

- Animation CARS spectra
- Nitrogen, P=100 Torr
- Pulse repetition rate 10 kHz
- 300-pulse ns / RF bursts (30 ms on, 70 ms off)
- End of the burst: $T_v=1900$ K, $T=380$ K
- Ns and RF: selective generation of excited species

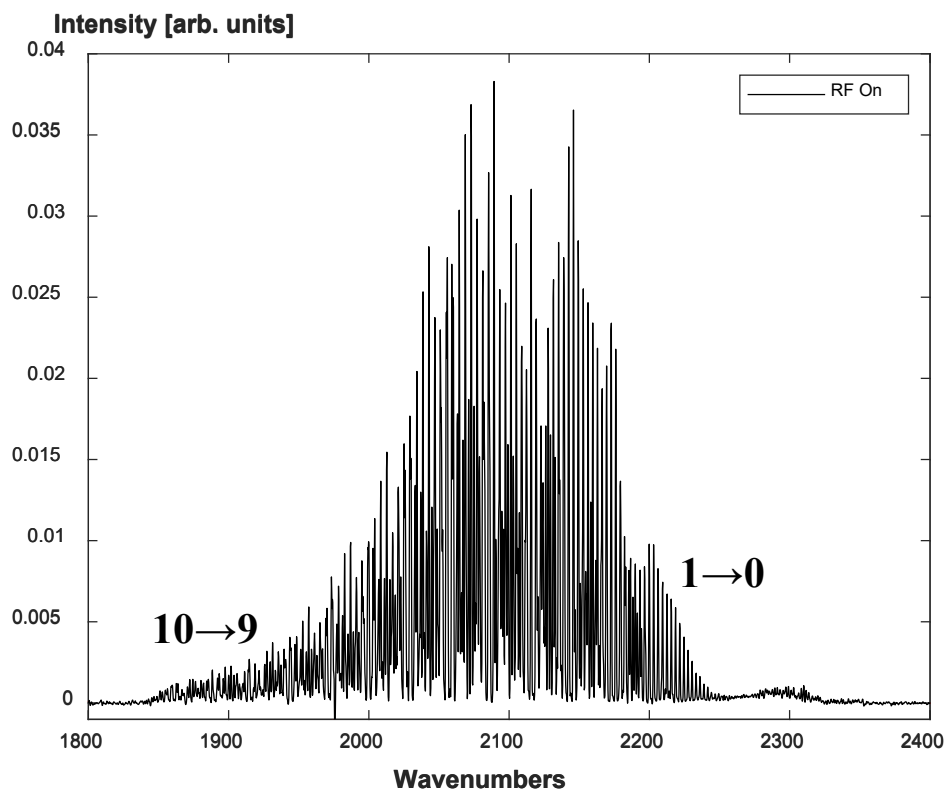


Ns Pulse / RF Discharge in N_2 , H_2 - N_2 : Vibrational Excitation and Relaxation

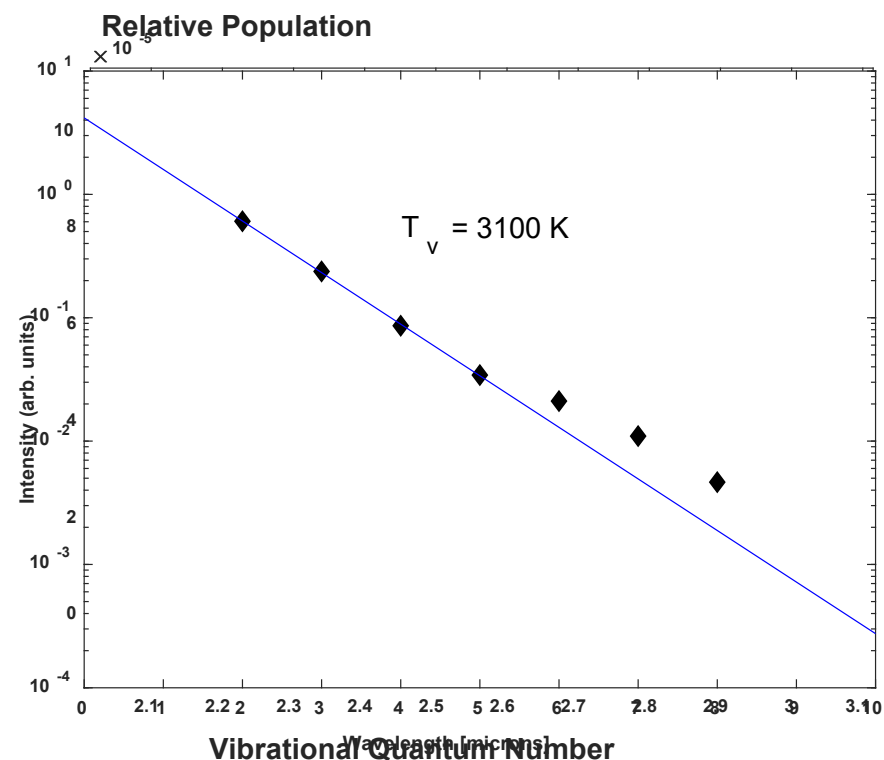


- N_2 and 1% H_2 – N_2 , $P=100$ Torr
- T , $T_V(N_2)$ during ns pulse / RF burst and the afterglow
- Strong vibrational nonequilibrium, relaxation over tens of ms
- Sufficient time for transport to porous catalyst downstream of the plasma

Ns Pulse / RF Discharge in CO – N₂: Vibrational Excitation of Other Species



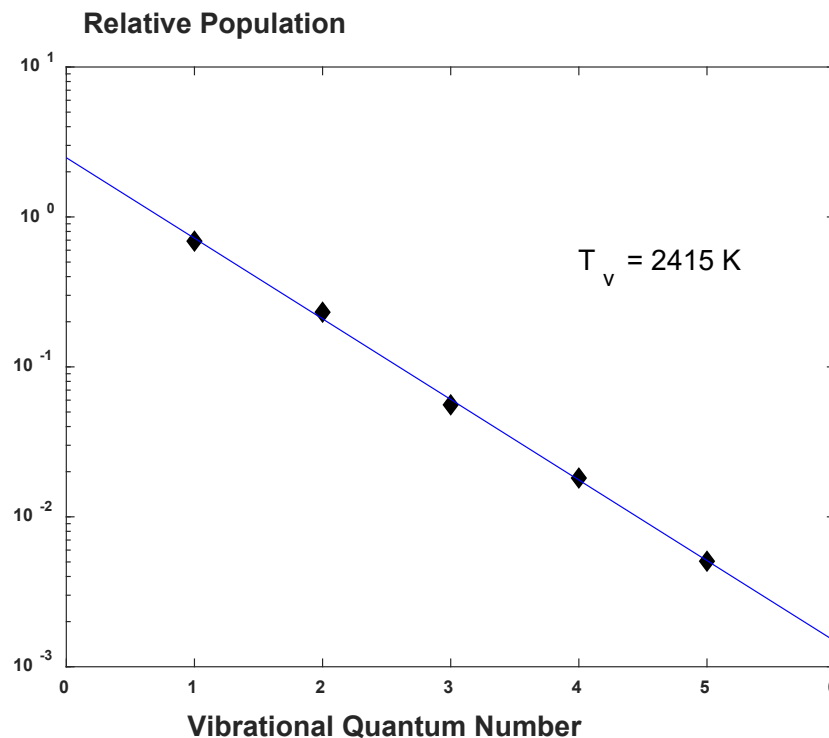
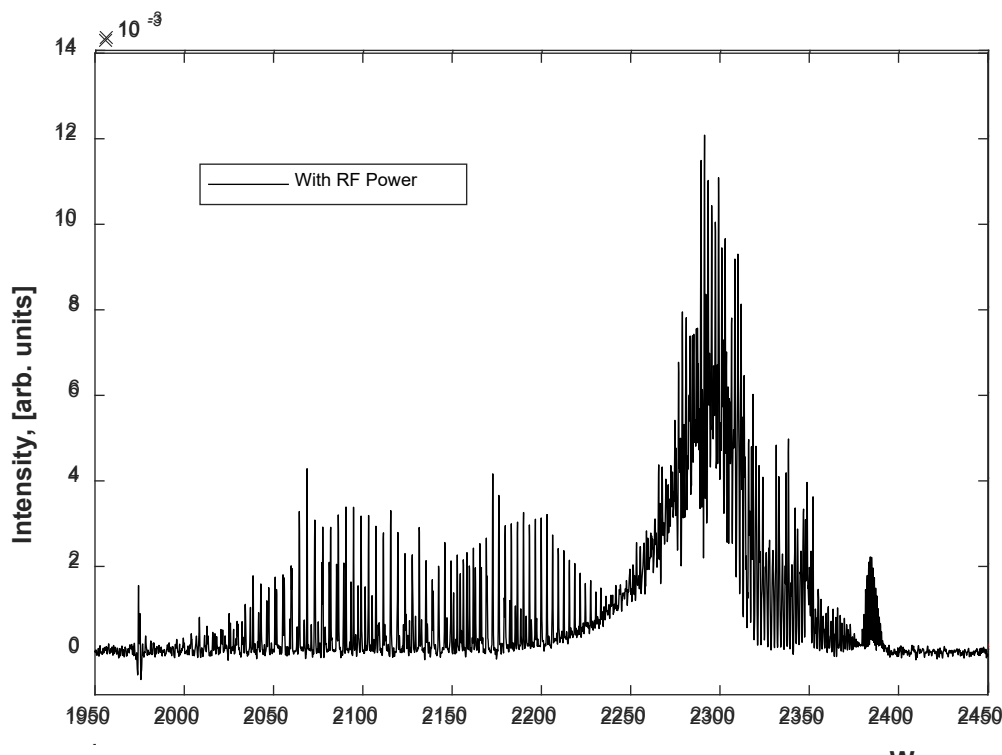
FTIR emission spectra, CO fundamental:
ns discharge with RF voltage **OFF** and **ON**



FTIR emission spectra, CO overtone:
ns discharge with RF voltage **ON**

- 1% CO – N₂ mixture, P=50 Torr, 5 kHz ns pulse / RF discharge
- Strong CO vibrational nonequilibrium, inferred from best fit synthetic spectra

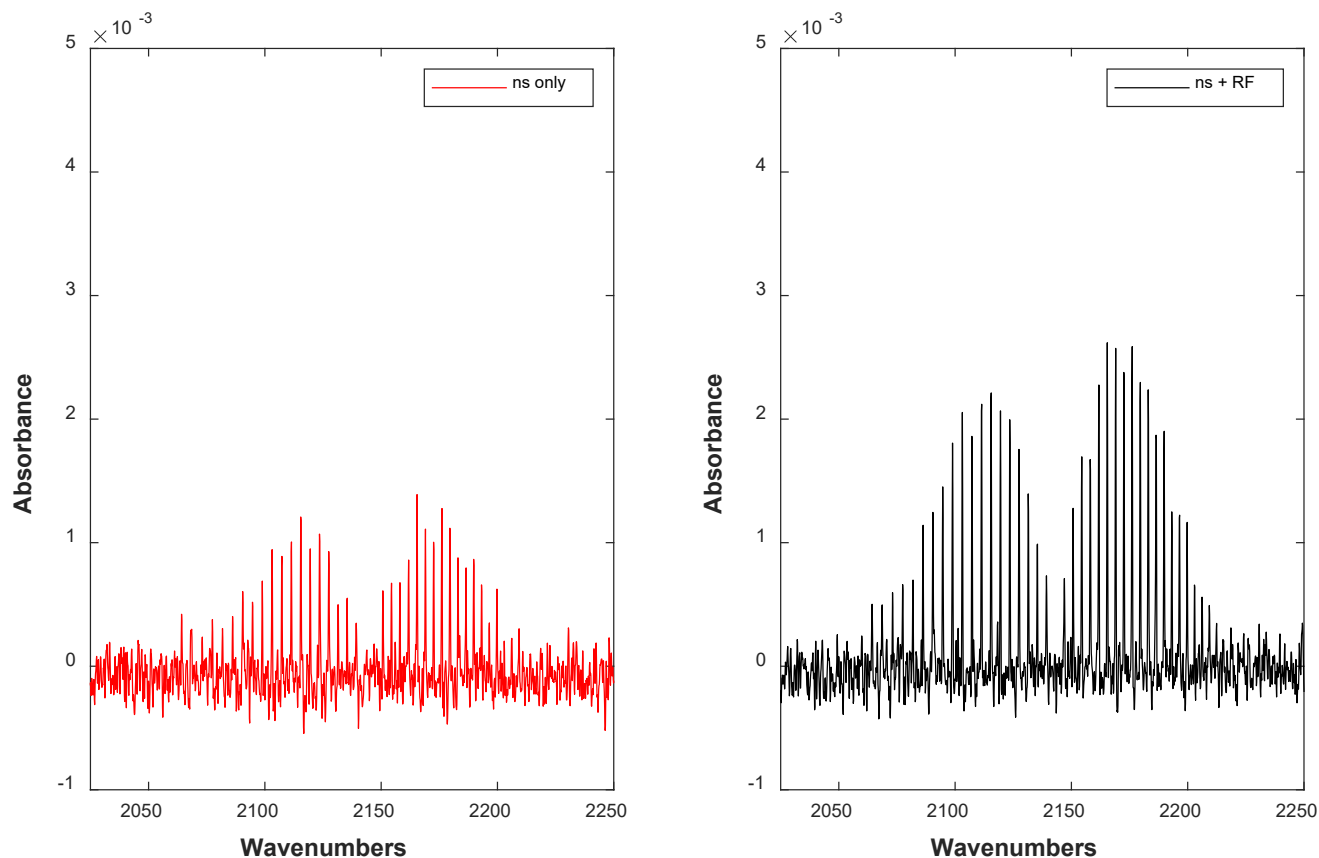
Ns Pulse / RF Discharge in $\text{CO}_2 - \text{N}_2$: Vibrationally Enhanced Plasma Chemistry



In situ FTIR emission spectra, CO and CO_2 : ns discharge with RF voltage OFF and ON

- 0.1% $\text{CO}_2 - \text{N}_2$ mixture, P=60 Torr, 2.5 kHz ns pulse / RF discharge
- Strong CO and CO_2 vibrational nonequilibrium: $T_v(\text{CO}) = 2400 \text{ K}$, $T = 580 \text{ K}$

Ns Pulse / RF Discharge in $\text{CO}_2 - \text{N}_2$: Vibrationally Enhanced Plasma Chemistry (cont.)



Ex situ FTIR absorption spectra, CO product: ns discharge with RF voltage **OFF** and **ON**

- 0.1% $\text{CO}_2 - \text{N}_2$ mixture, P=60 Torr, 2.5 kHz ns pulse / RF discharge
- Significant increase of CO number density due to vibrationally stimulated chemistry

Summary

- **Hybrid plasmas (ns pulse / DC and ns / pulse RF): stable, diffuse, pressure and volume scalable**
- **Ns pulse / RF plasmas: no catalytic effect of the electrodes, non-self-sustained in the entire volume**
- **Selective generation of**
 - **Electronically excited molecules and atomic species (ns pulse discharge)**
 - **Vibrationally excited molecules in ground electronic state (RF discharge)**
- **Demonstrated in nitrogen, $\text{H}_2\text{-N}_2$, CO-N_2 , and $\text{CO}_2\text{-N}_2$ mixtures**
- **Potential of isolating the effect of atomic species, radicals, and vibrationally excited molecules on plasma-induced chemistry and plasma-assisted catalysis**

Ongoing and Future Work

- Operate ns pulse discharge at higher peak voltage and pulse repetition rate
 - Enhance vibrational nonequilibrium
 - Extend to reacting mixtures containing rapid V-T relaxers (e.g. CO₂, CH₄)
- Measure H₂(v) (CARS); N, H, and O (TALIF); CO₂(v₁,v₂,v₃) (mid-IR DLAS)
- Isolate and quantify the effect of atomic species and radicals (ns pulse discharge), and vibrationally excited molecules (RF discharge):
 - Hydrogen combustion
 - Plasma chemical and plasma-catalytic dry methane conversion
 - Plasma chemical and plasma-catalytic ammonia synthesis

Acknowledgments

- **DOE Collaborative Research Center for Studies of Plasma-Assisted Combustion and Plasma Catalysis (2019 – 2024)**
- **AFOSR “Energy Transfer Processes in Nonequilibrium Hypersonic Flows” (2017 – 2020)**
- **NSF “Fundamental Studies of Accelerated Low Temperature Combustion Kinetics by Nonequilibrium Plasmas” (2016-2020)**
- **DOE PSAAP-2 Center “Exascale Simulation of Plasma-Coupled Combustion” (2014-2020)**
- **AFOSR “Nonequilibrium Molecular Energy Coupling and Conversion Mechanisms for Efficient Control of High-Speed Flow Fields” (2012 – 2015)**
- **DOE Plasma Science Center “Predictive Control of Plasma Kinetics: Multi-Phase and Bounded Systems” (2009-2019)**