Online Low Temperature Plasma (OLTP) Seminar

February 25, 2025

Nonequilibrium Plasma Kinetics in a Heated Flow Reactor Excited by a Ns Pulse Discharge

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Background / Technical Approach

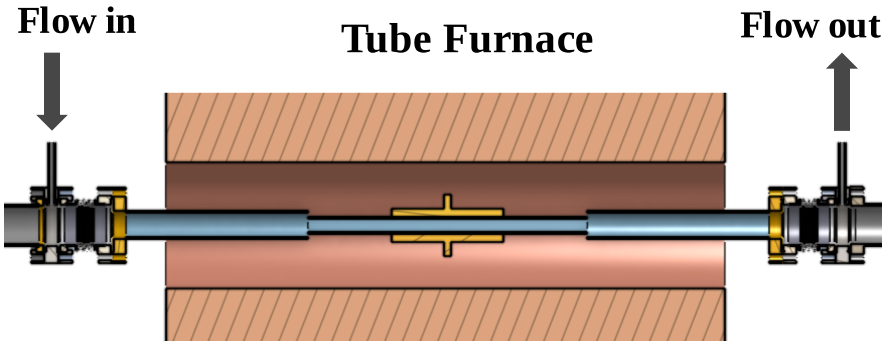
Ns pulse burst discharges in preheated reacting gas flows:

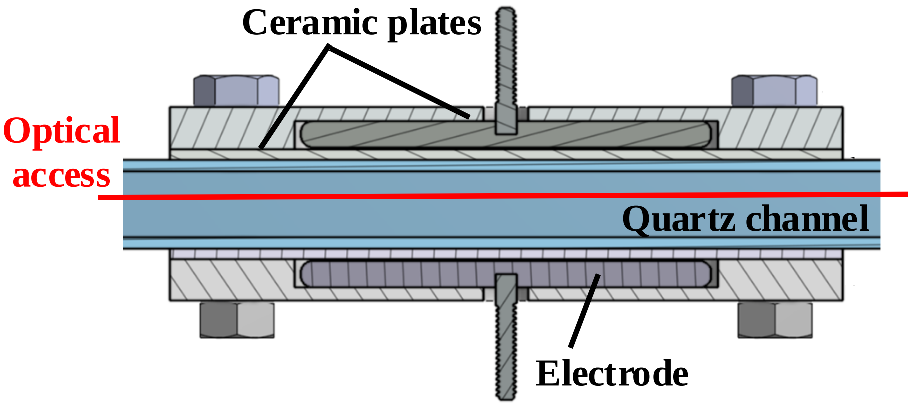
- **High reduced electric field (E/N): generation of excited species and radicals**
- **Low duty cycle (~ 1/1000): superior stability at high pressures**
- **Discharge electrodes external to reactor: no catalytic effect**
- **Excitation energy controlled by varying number of pulses**
- **Large-volume, quasi-0-D plasmas sustained at pressures up to 1 atm**
- **Time-resolved measurements of plasma parameters, species over a wide range of time scales (ns to ms)**

Previous work: kinetics of plasma-assisted combustion

- **Time-resolved, absolute measurements of temperature, N_2(v) populations, atoms (O, H, N), radicals (OH, HO_2), products of H_2 and C_xH_y oxidation**

Experiment Schematic: Heated Plasma Flow Reactor





Nitrogen, T_0=300 K, P=100 Torr

- Nitrogen, N_2-NO, N_2-O_2, O_2-Ar, N_2-H_2, P = 0.1 – 1 atm, slow flow (0.1-1 m/s)
- Independent temperature control: flow preheated in tube furnace, T_0 = 300-1000 K
- Parallel plate electrodes external to reactor: no catalytic effect

Optical access for diagnostics

- Laser absorption spectroscopy
- Cavity Ring Down Spectroscopy
- Vacuum UV absorption
- Single-Photon and Two-Photon LIF
- CARS

Outline

I. Kinetics of Ionization in Nitrogen and in N_2-O_2 Plasmas

II. Kinetics of O Atom Recombination in Partially Dissociated O_2-Ar

III. Kinetics of Plasma Catalytic Ammonia Synthesis in N_2-H_2

I. Kinetics of Ionization in N_2 and N_2-O_2 Plasmas

Motivation:

- Plasmas around atmospheric reentry vehicles cause communication blackouts
- Associative ionization: primary mechanism of plasma generation,

$$N + O \longrightarrow NO^+ + e, \qquad N + N \longrightarrow N_2^+ + e$$

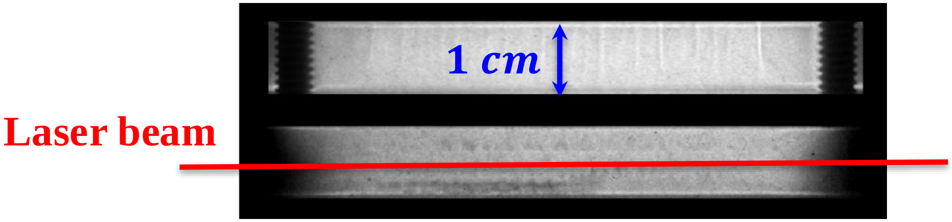
- Excitation (N^*, O^*) enhances ionization rate

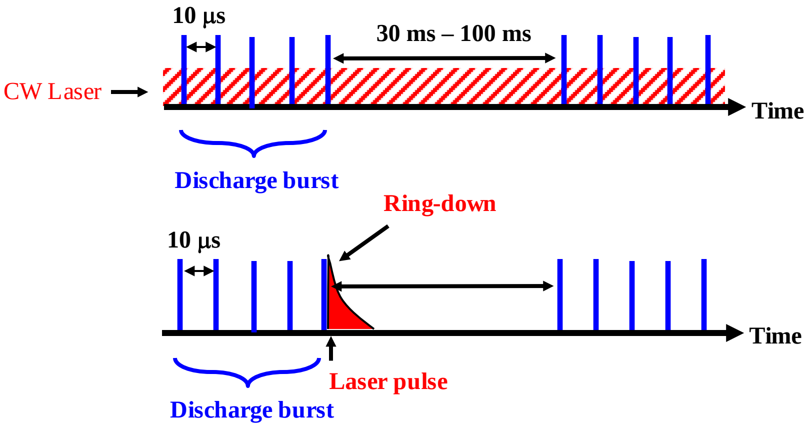
Objectives:

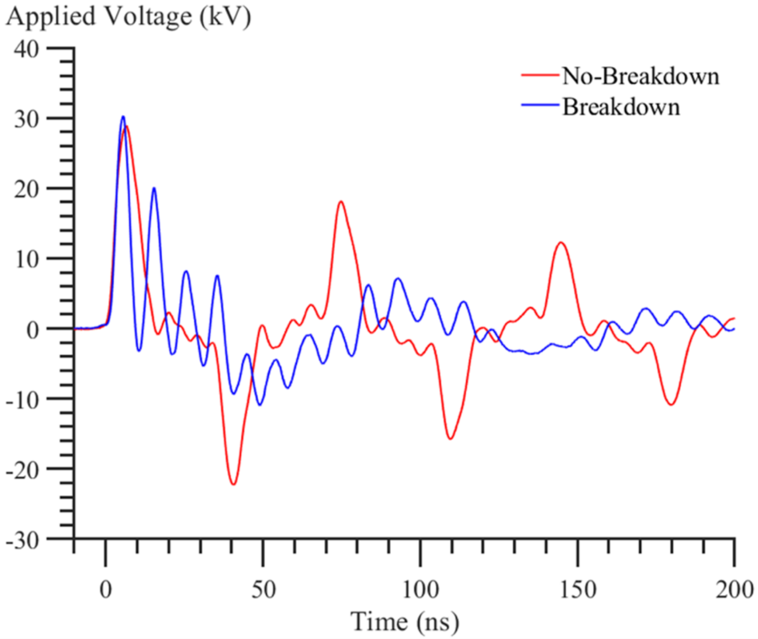
- Measure metastable $N_2(A^3\Sigma_u^+)$ molecules (precursor of metastable atoms)
- Measure metastable $N(^2D,^2P)$ atoms (ionization precursors)
- Measure ions (N_2^+) generated by associative ionization of $N(^2P) + N(^2P)$
- Measure ions (NO^+) generated by associative ionization of $N(^2D) + O(^3P)$
- Infer rates of associative ionization of excited atoms in the afterglow

Discharge Waveforms and Plasma Images

N_2, T_0=1000 K, P=100 Torr



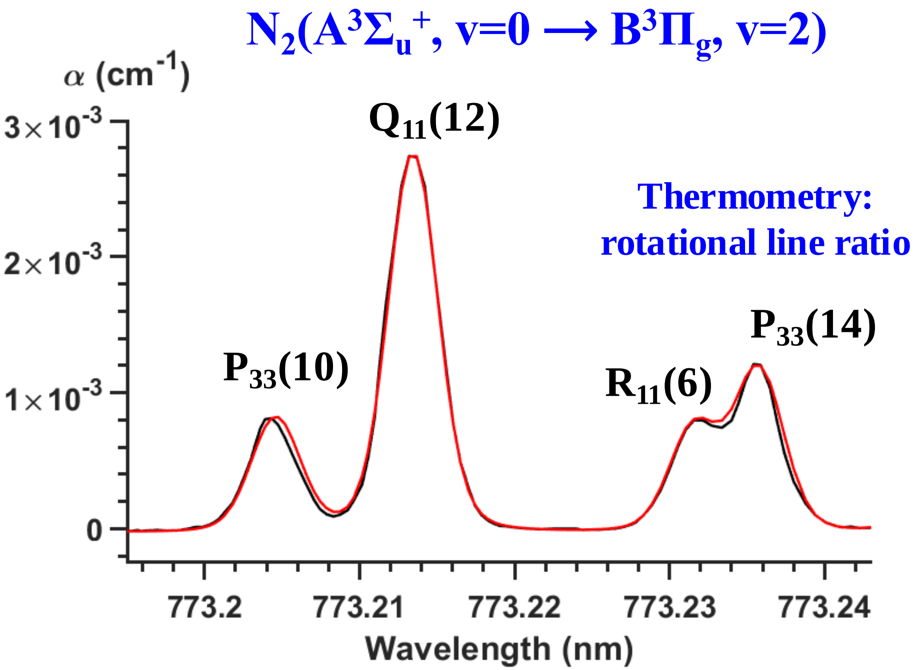




- Ns pulse discharge excitation (30 kV, 10 ns @ 100 kHz): stable, diffuse plasma
- Tunable Diode Laser Absorption Spectroscopy (TDLAS), $N_2(A^3\Sigma_u^+,v)$
- UV Cavity Ring Down Absorption Spectroscopy (CRDS), $N_2^+(v)$
- Vacuum UV absorption, $N(^2D,^2P)$ (in progress); Mid-IR CRDS, NO^+ (in progress)

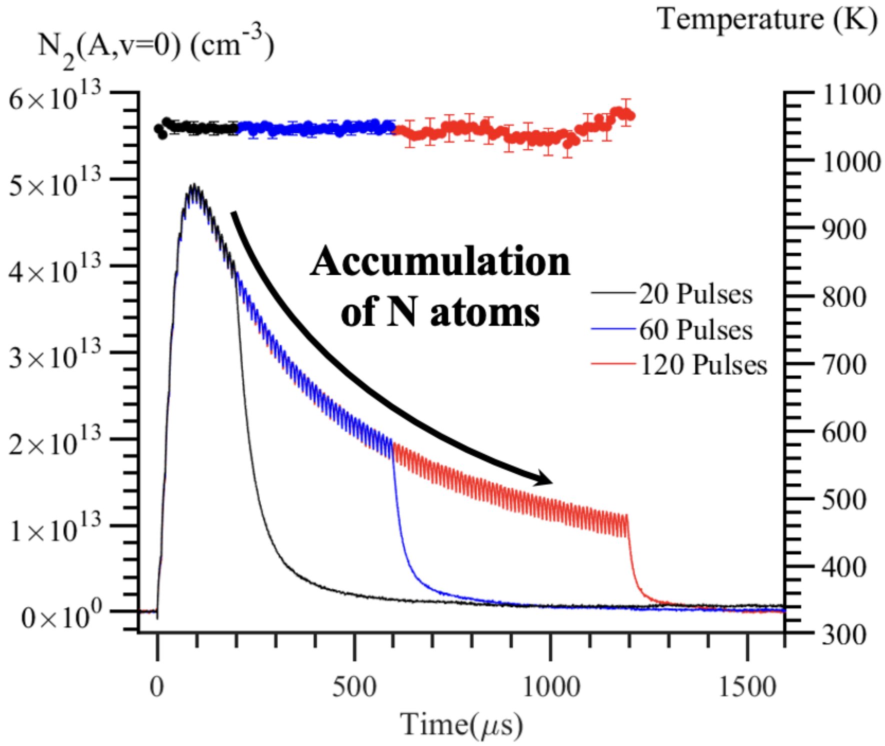
$N_2(A^3\Sigma_u^+, v=0,1)$ Measurements (TDLAS)

- **Nitrogen, P=100 Torr, T_0 = 1000 K**
- **$N_2(A)$ generation: $N_2(X) + e \longrightarrow N_2(A,B,C)$, $N_2(C) \longrightarrow N_2(B) \longrightarrow N_2(A)$**



$N_2(A^3\Sigma_u^+, v=0 \longrightarrow B^3\Pi_g, v=2)$

Thermometry: rotational line ratio

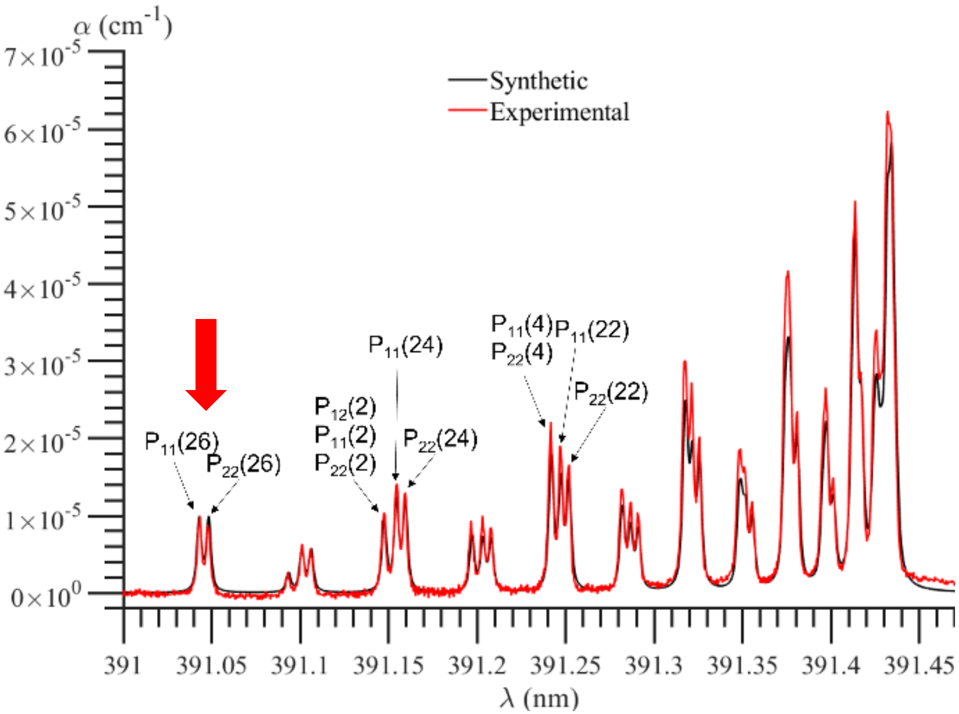


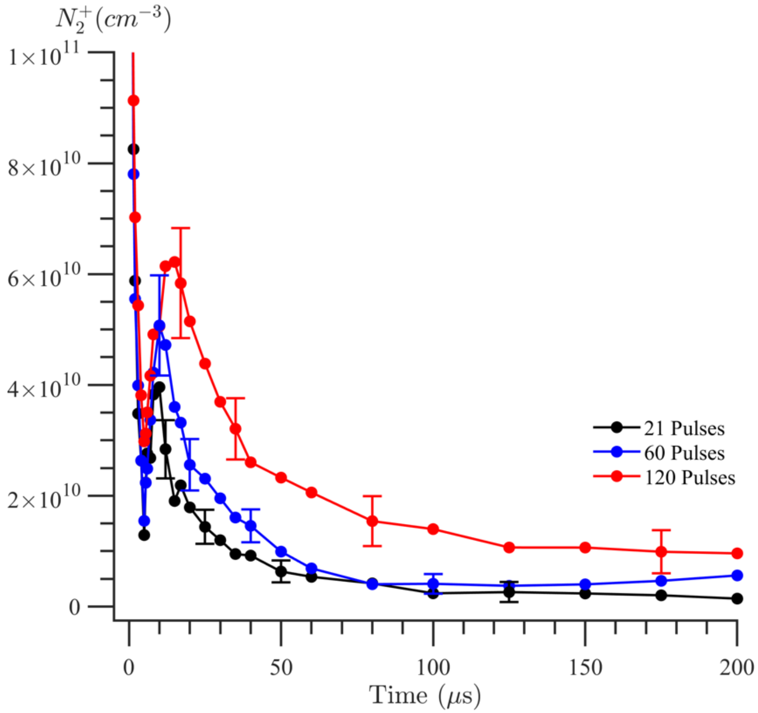
Accumulation of N atoms

- **Decay between pulses: energy pooling, $N_2(A) + N_2(A) \rightarrow N_2(B,C) + N_2$**
- **Decay during burst: quenching by N atoms, $N_2(A) + N \rightarrow N_2 + N^{(*)}$**

$N_2^+(v=0)$ measurements (pulsed CRDS)

Nitrogen, P=100 Torr, T_0=1000 K



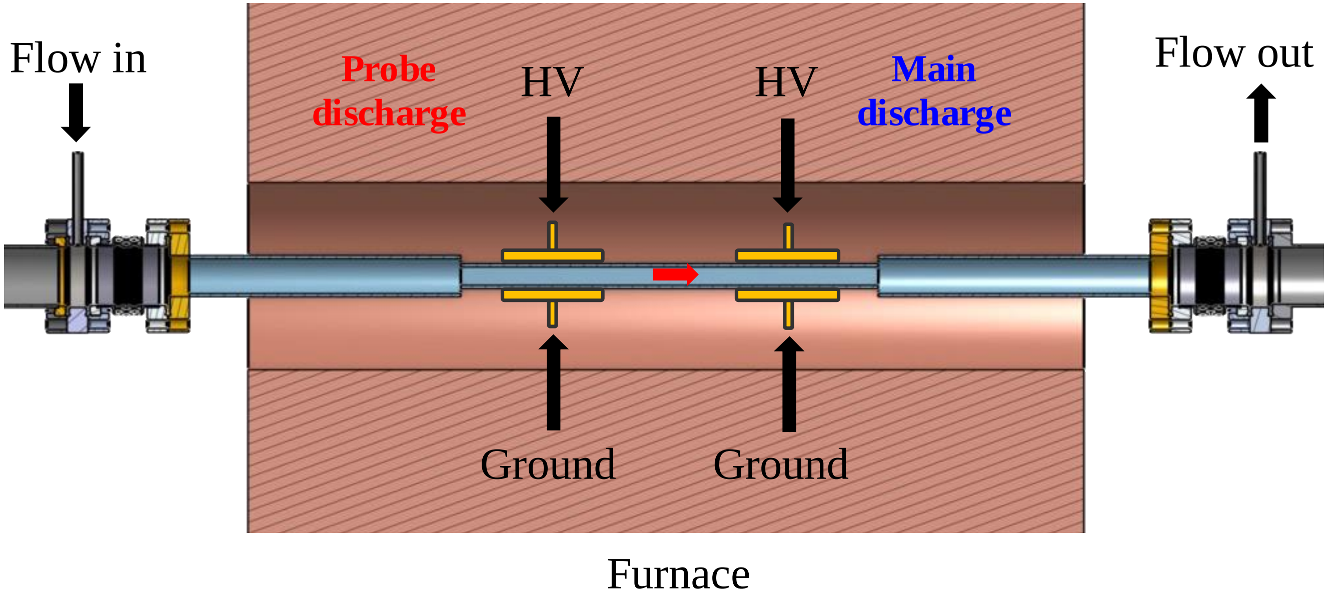


- **Ring down spectrum, 15 μs after the burst**
- **$[N_2^+(v=0)] = 5\cdot10^{10}$ cm^{-3}**
- **Uncertainty / detection limit ~ 10^8 cm^{-3}**

- **Non-monotonous variation of $[N_2^+]$ in the afterglow**
- **Associative ionization of N^* is unlikely (too slow)**

Measurements of N(^{2}P,^{2}D): Atomic Resonance Absorption Spectroscopy (ARAS)

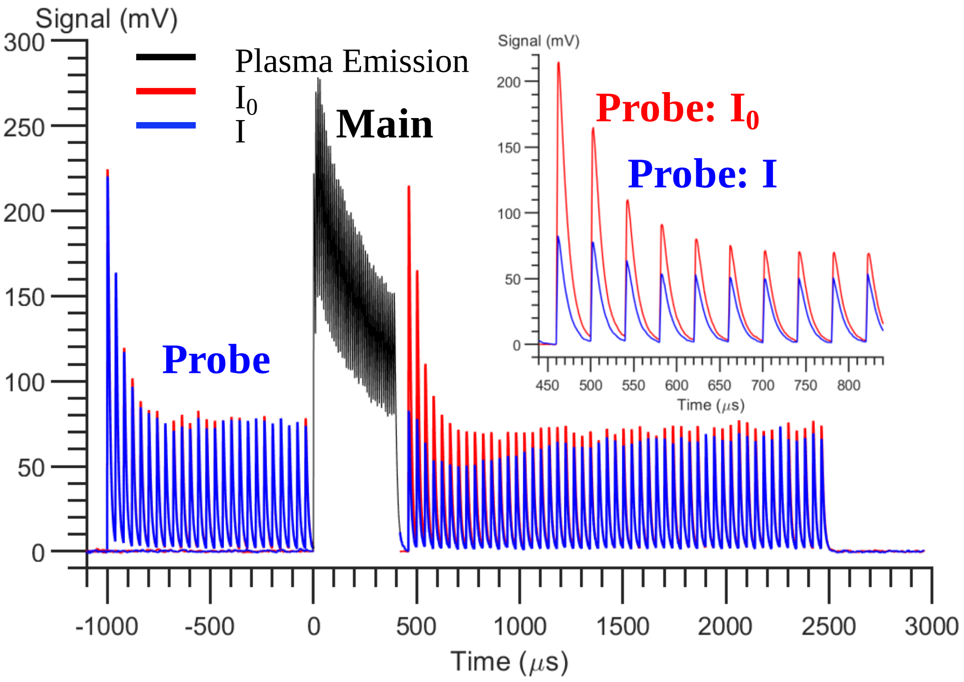
- **Use “probe” ns pulse discharge to generate Vacuum UV emission at 148 and 174 nm**
- **Measure resonance absorption in the “main” discharge afterglow**

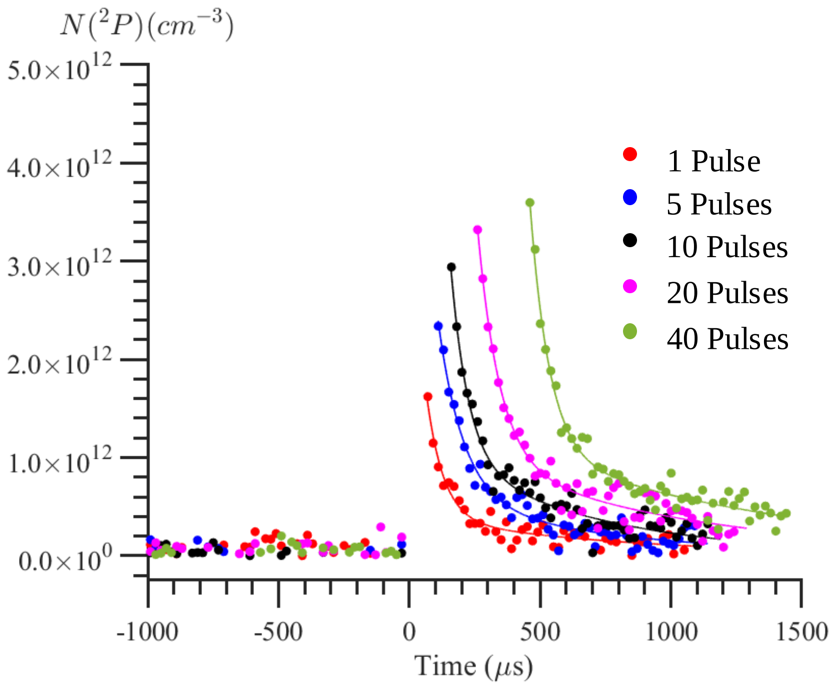


- **Infer time-resolved number densities of N(^{2}D,^{2}P) in the afterglow**
- **Use the same approach for O(^{3}P) atoms in N_2-NO plasma**

ARAS: $N(^2P)$ Population in Afterglow

N_2, P = 50 Torr, T = 800 K, emission / absorption at λ = 174.25 nm





- **Main discharge: 1-40 pulse burst at 100 kHz**
- **Accumulation of $N(^2P)$ in long bursts**
- **<u>Caution:</u> data need to be corrected for line self-absorption in probe discharge**

I. Summary

- **Heated plasma flow reactor (T_0 =300-1000 K) excited by ns pulse discharge used for time-resolved, absolute measurements of**
  - **Metastable $N_2(A^3\Sigma)$ molecules (precursor of metastable atoms)**
  - **Molecular ions, N_2^+**
  - **Metastable atoms, $N(^2D,^2P)$ (associative ionization precursors)**
- **Transient rise of N_2^+ in the afterglow is not fully understood, kinetic modeling in progress**
- **In progress: diagnostics for measurements NO^+ ions, inference of $N^* + N^* \rightarrow N_2^+ + e^-$ and $N^* + O^* \rightarrow NO^+ + e^-$ ionization rates**

S. Raskar, AIAA Paper 2024-1825, AIAA Paper 2025-0990 (manuscript in preparation)

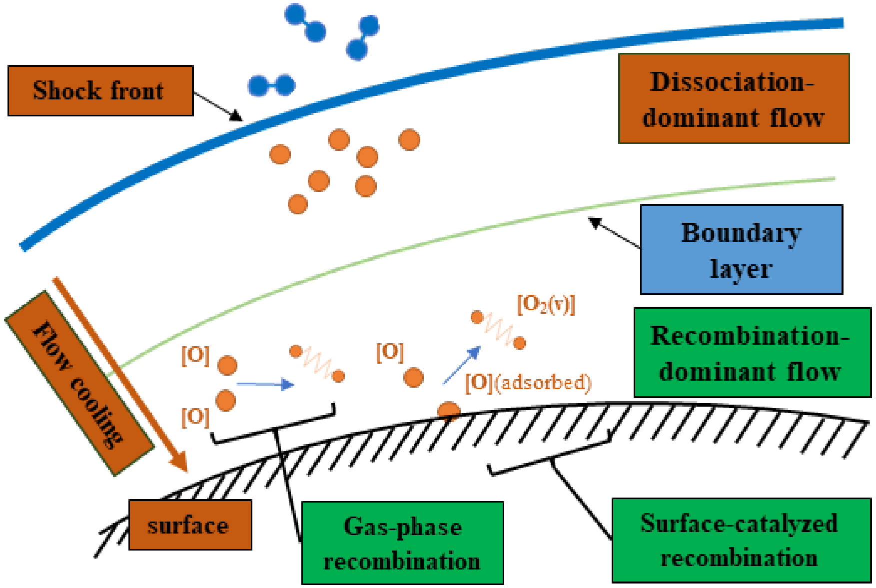
II. Kinetics of O Atom Recombination in Partially Dissociated O_2-Ar

Motivation:

- O atoms generated during atmospheric reentry recombine in boundary layer,

$$O + O + M \longrightarrow O_2(v) + M$$

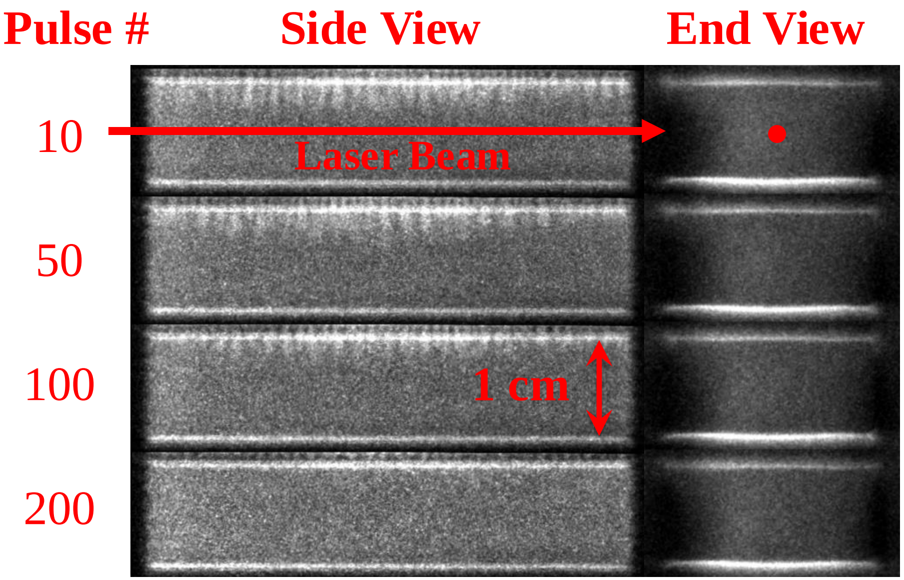
- Energy stored in $O_2(v)$ vibrational mode controls surface heat flux

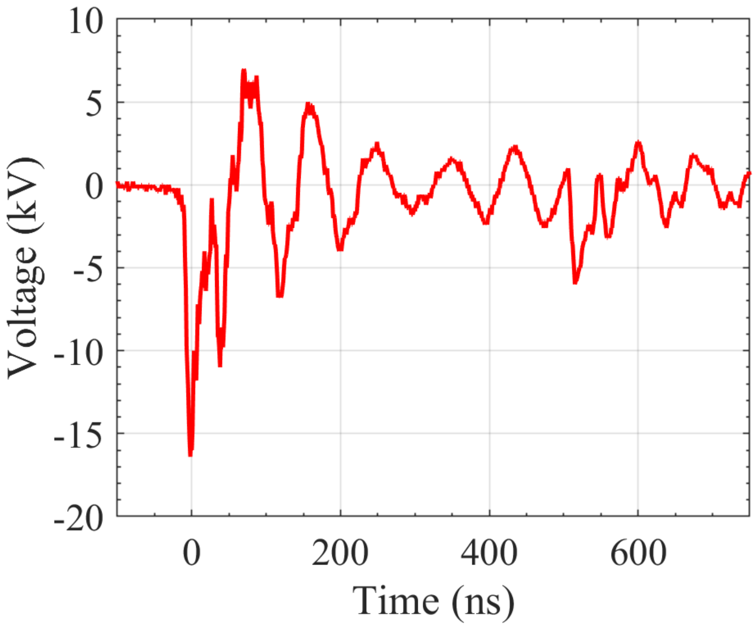


Objectives:

- Measure O atoms generated in a ns pulse discharge, $O_2 + e \longrightarrow O + O + e$
- Measure vibrational populations of recombination products, $O_2(v)$
- Quantify the effect of ozone reactions on O atom recombination kinetics
- Compare results with kinetic modeling, infer state-specific recombination rates

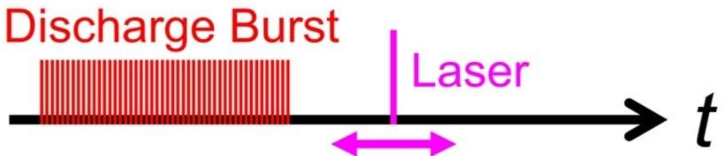
Discharge Waveforms and Plasma Images





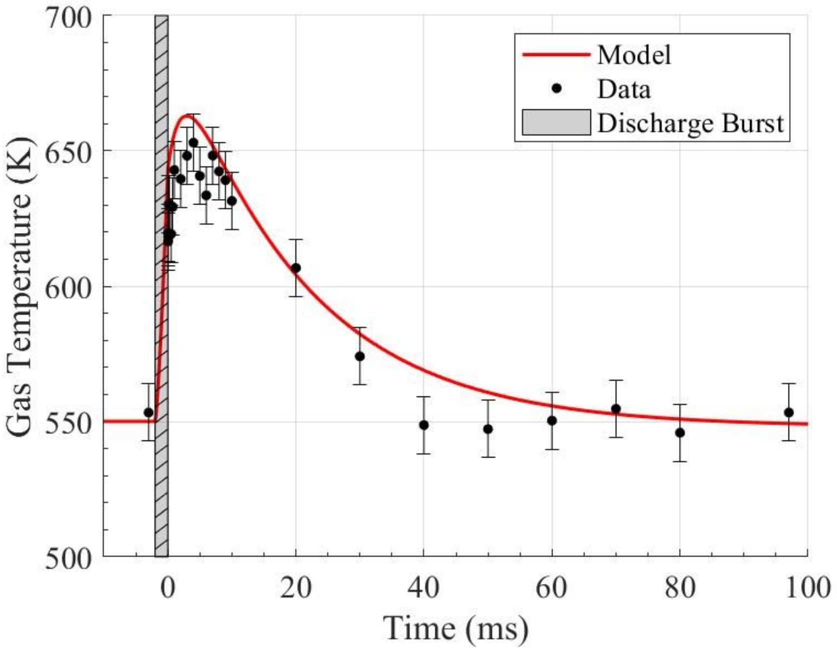
- Single shot plasma images
- 20% O_2 - Ar
- P=200 Torr, T_0=600 K

- Ns pulse discharge burst: 100-200 pulses @ 100 kHz, burst repetition rate 10 Hz

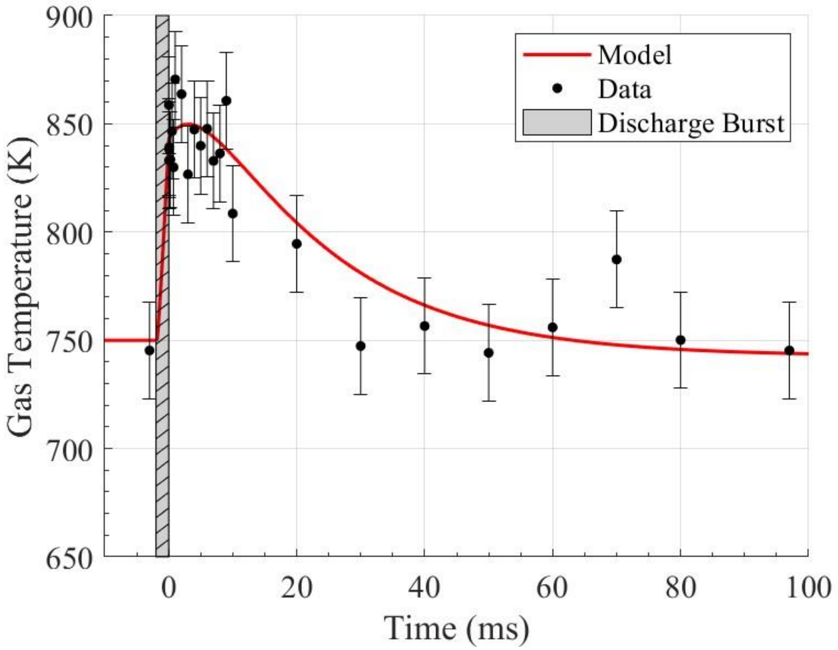


Temperature: Rayleigh Scattering at 355 nm

T_0 = 600 K



T_0 = 800 K

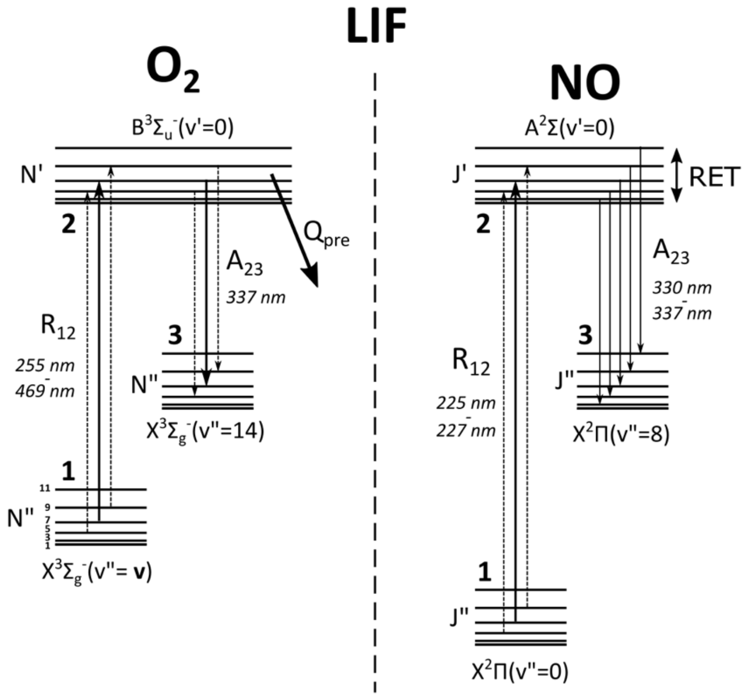


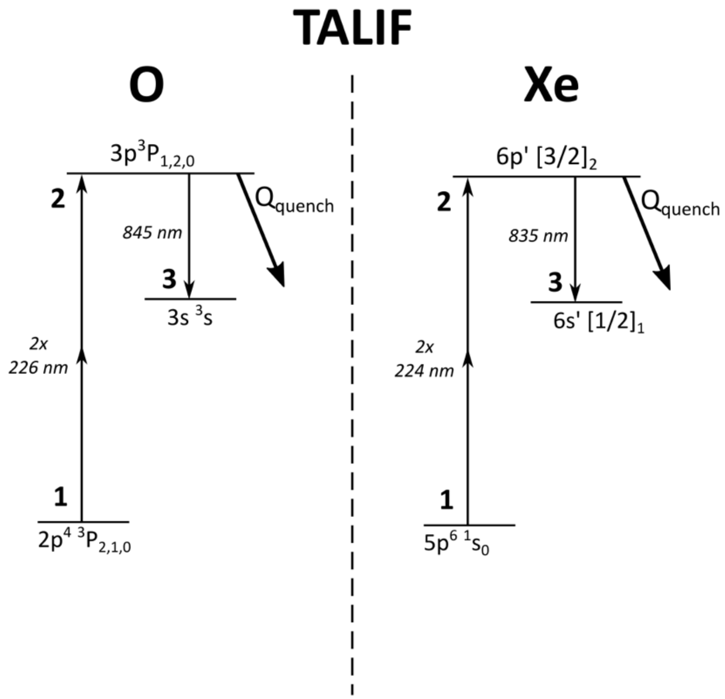
- **Discharge heats the flow by up to ΔT=100 K**
- **Temperature reduced in the afterglow, due to convection, wall diffusion**

O_2(v) and O Atoms: Laser Induced Fluorescence

- **LIF: excitation, fluorescence on Schumann-Runge bands: O_2(v = 8-13, 17-20)**
- **Calibration by NO LIF**

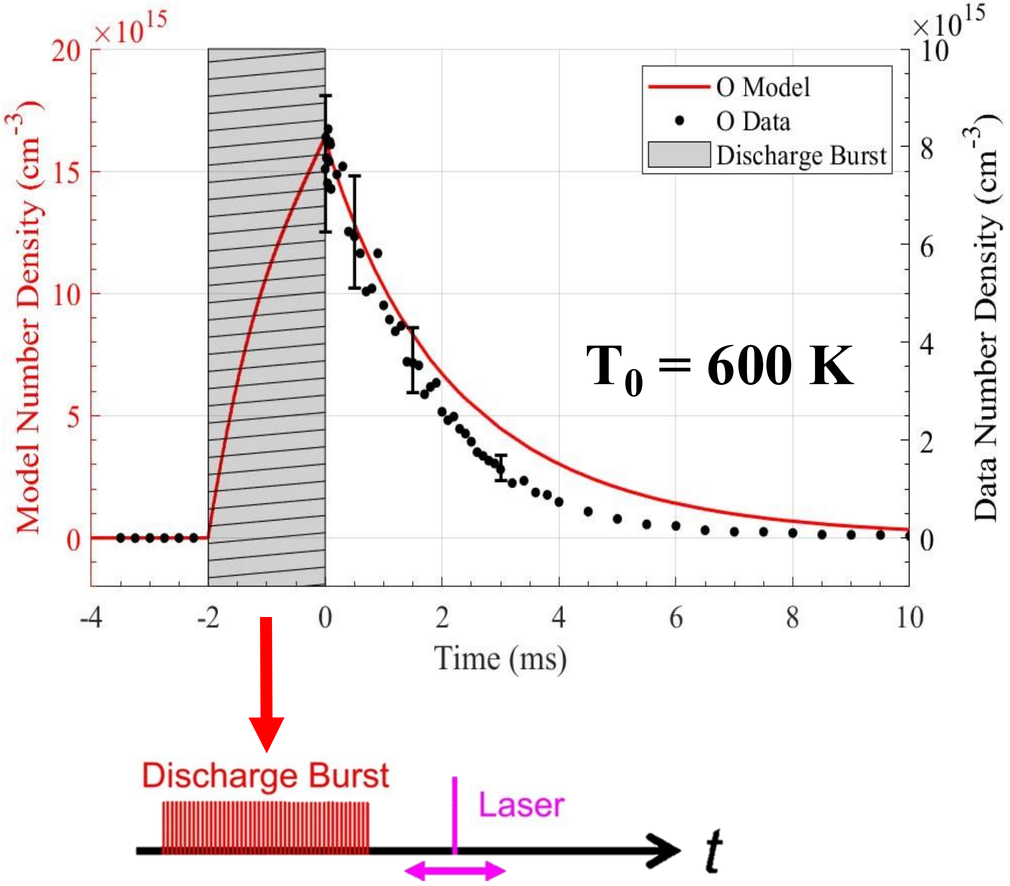
- **TALIF: two-photon excitation**
- **Calibration in Xe**





- **Absolute calibration: need better laser output stability, accuracy of LIF spectroscopic model**

O Atom Decay: Kinetic Mechanisms



- **Generated by electron impact, quenching of Ar*:**

  $O_2 + e \longrightarrow O + O + e$

  $Ar + e \longrightarrow Ar^* + e$

  $Ar^* + O_2 \longrightarrow Ar + O + O$

- **Recombination pathways:**

  $O + O + M \longrightarrow O_2(v) + M$

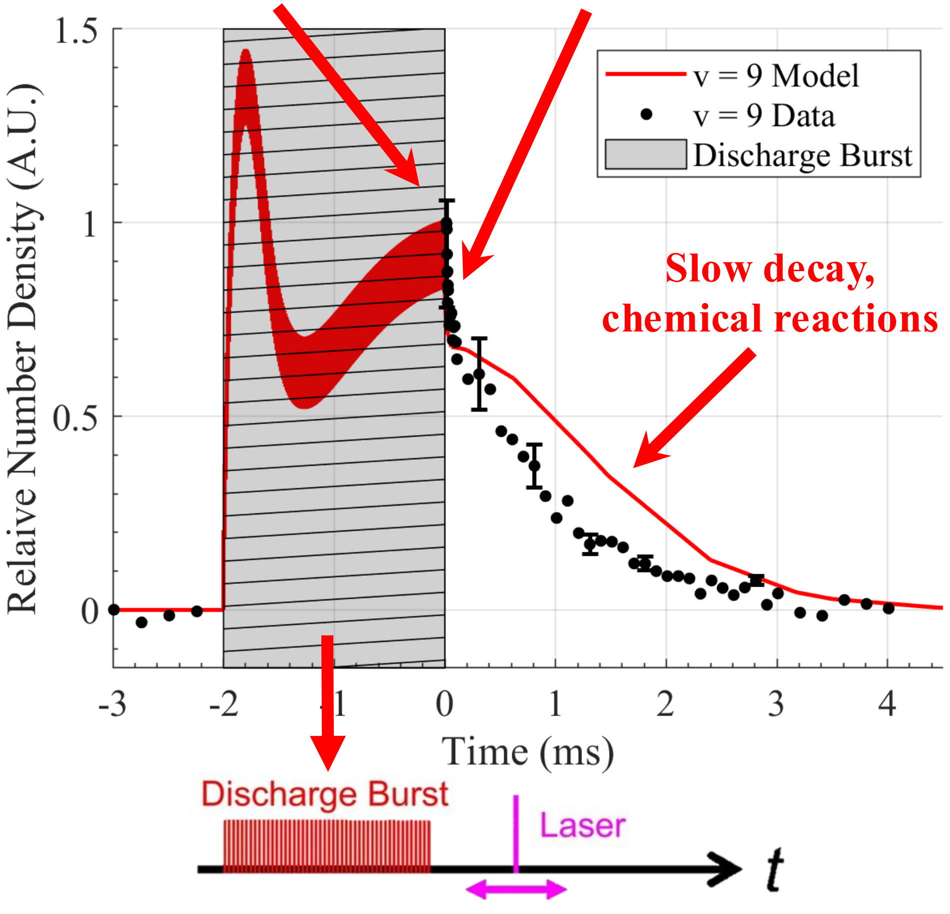
  $O + O_2 + M \longrightarrow O_3 + M$

  $O + O_3 \longrightarrow O_2(v) + O_2(w)$

- **Modeling predictions consistent with O atom data**

$O_2(v)$ Time Evolution: Kinetic Mechanisms

$O_2(v=9)$ relative population at T_0 = 400 K, P = 200 Torr



Initial population, electron impact

Rapid decay, V-T and V-V processes

Slow decay, chemical reactions

Dominant Processes:

Electron Impact (During the Burst)

$O_2 + e \longrightarrow O_2(v) + e$

Vibrational Relaxation (Rapid)

$O_2(v) + O \rightleftarrows O_2(v-\Delta v) + O$

$O_2(v) + O_2(0) \rightleftarrows O_2(v-1) + O_2(1)$

Chemical Reactions (Slow)

$O + O + M \rightleftarrows O_2(v) + M$

$O_2 + O + M \rightleftarrows O_3 + M$

$O_3 + O \rightleftarrows O_2(v) + O_2(w)$

Similar behavior for $O_2(v=8\text{-}21)$, T_0 = 400-800 K

II. Summary

- **Heated plasma flow reactor used for time-resolved measurements of O, O_2(v)**

- **Heating improves plasma stability, suppresses ozone formation**

- **O_2(v=8-13,17-21) detected on time scale much longer than V-T and V-V relaxation, comparable to O atom decay time**

- **Kinetic modeling: dominant generation and decay processes for O and O_2(v)**

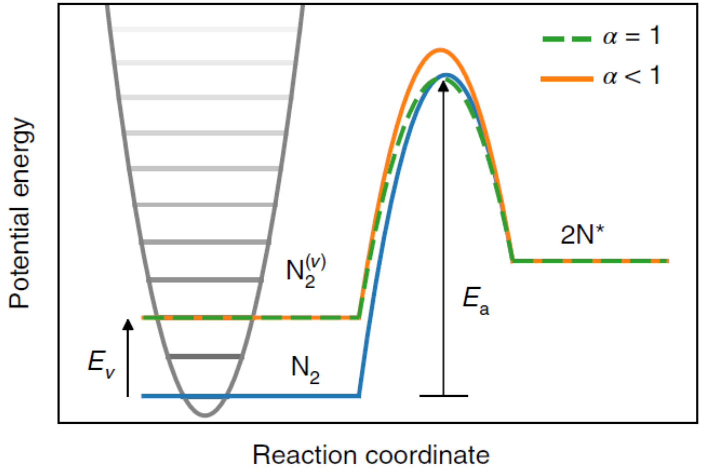
- **Results indicate O_2(v) generation in chemical reactions, $O_3 + O \rightarrow O_2(v) + O_2(w)$**

- **Isolating $O + O + M \rightarrow O_2(v) + M$ reaction: need complete O_2 dissociation in the discharge (lower O_2 mole fraction)**

- **Need better absolute calibration of O_2(v)**

K. Orr, PSST 34 (2025) 015002

III. Kinetics of Plasma Catalytic Ammonia Synthesis in N_2-H_2



P. Mehta, Nature Catalysis 2018

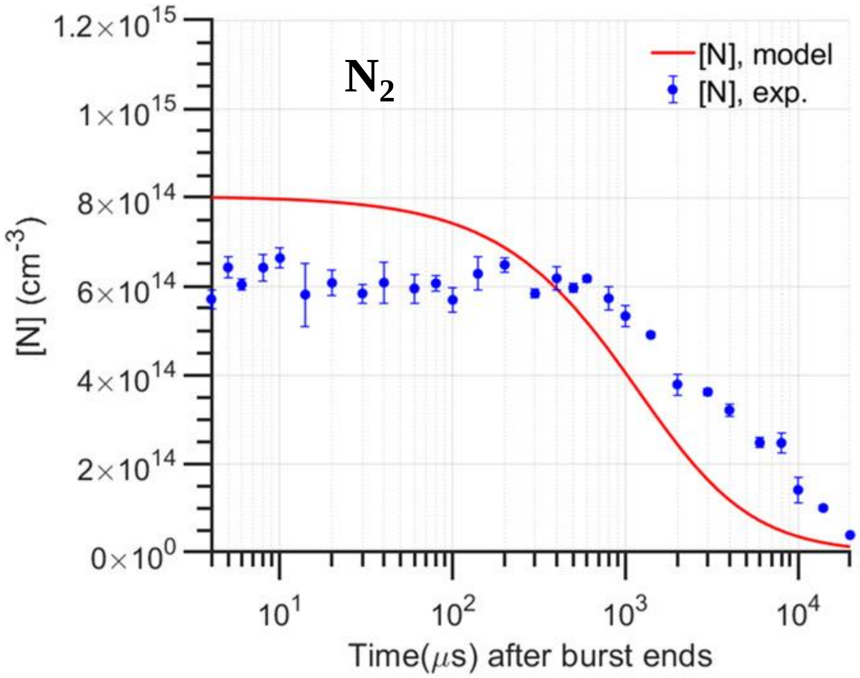
Motivation:

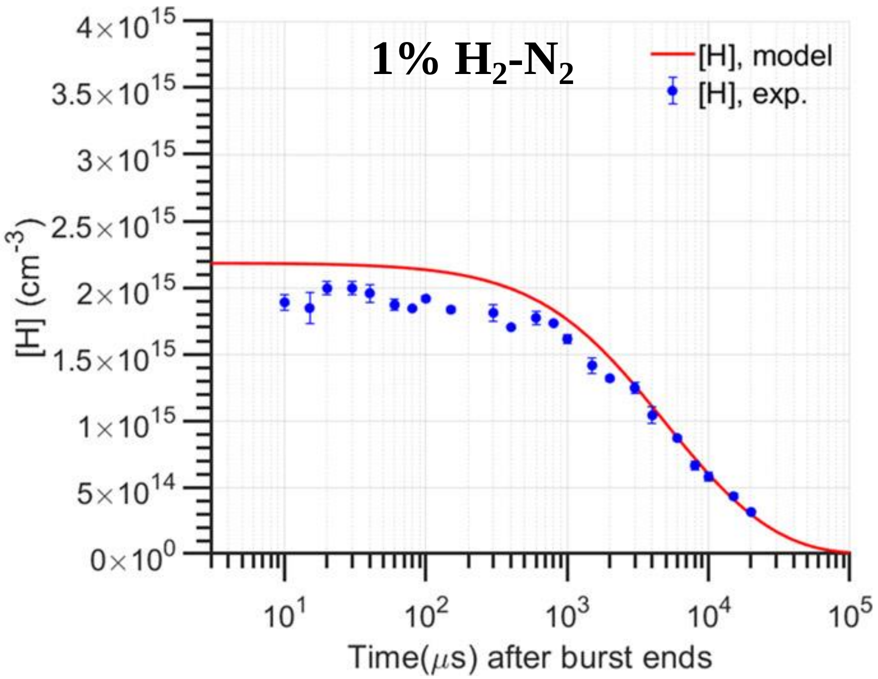
- Isolate kinetic mechanisms of plasma catalytic ammonia generation
- Previous work suggests contribution of $N_2(v)$ dissociation on catalyst surface
- $N_2(v)$ data not entirely convincing (OES)

Objectives:

- Generate atomic species (N, H) and $N_2(v)$ molecules selectively, in a "hybrid" ns pulse / RF discharge
- Isolate effect of $N_2(v)$ from that of N, H atoms on NH_3 generation
- Isolate effect of $N_2(v)$ from that of N, O atoms on NO generation

Previous Work: N and H atoms in Ns Pulse Discharge

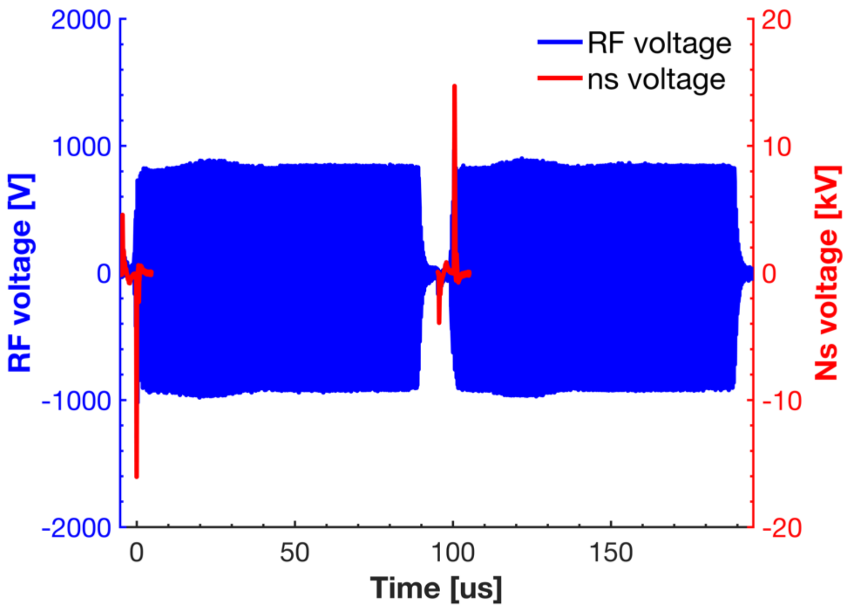


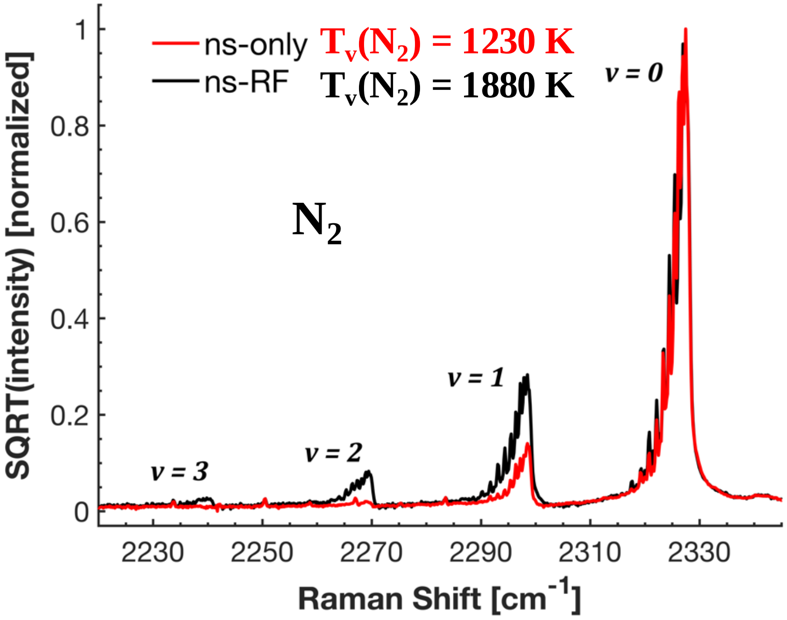


X. Yang, PSST 31 (2022) 015017

- **Time-resolved, absolute [N] and [H] in N_2-H_2 plasmas (without catalyst)**
- **Dominant reactants for plasma catalytic NH_3 generation, generated efficiently**
- **Kinetics are well understood**

Previous Work: RF Excitation Enhances N_2 Vibrational Populations

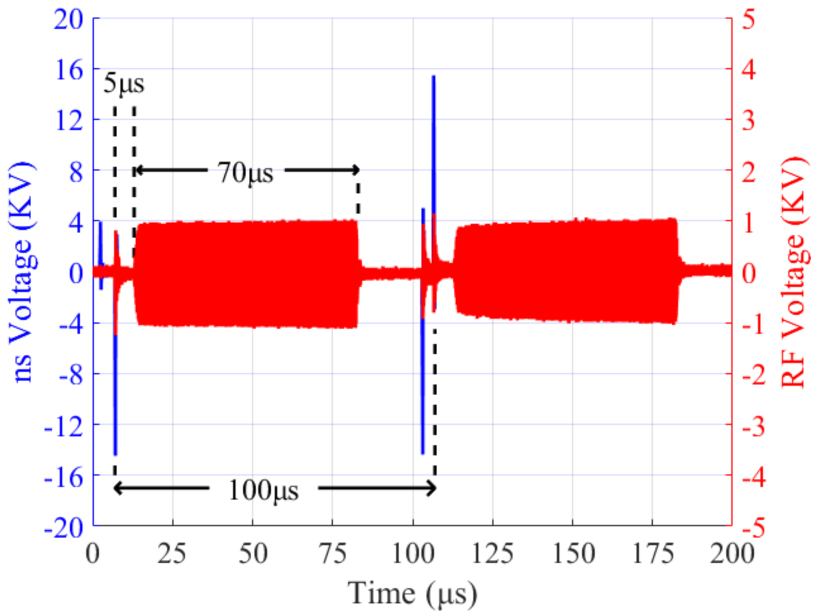


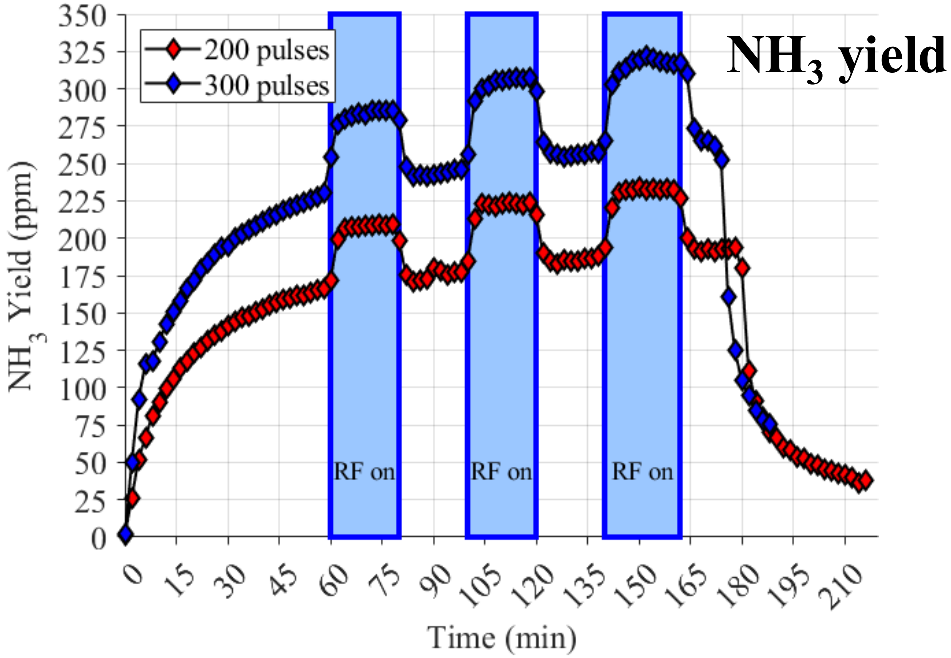


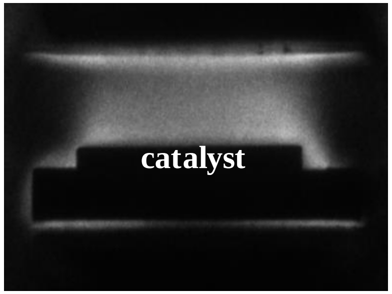
I. Gulko, PSST 29 (2020) 104002

- **RF excitation heats the electrons, enhances N_2 vibrational temperature**
- **<u>Independent</u> control of vibrational excitation**
- **Kinetics are well understood**

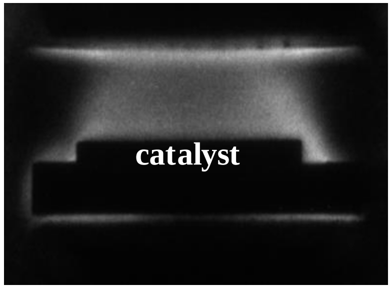
NH_3 Yield in Ns-RF Discharge: Higher Than in Ns Discharge Alone







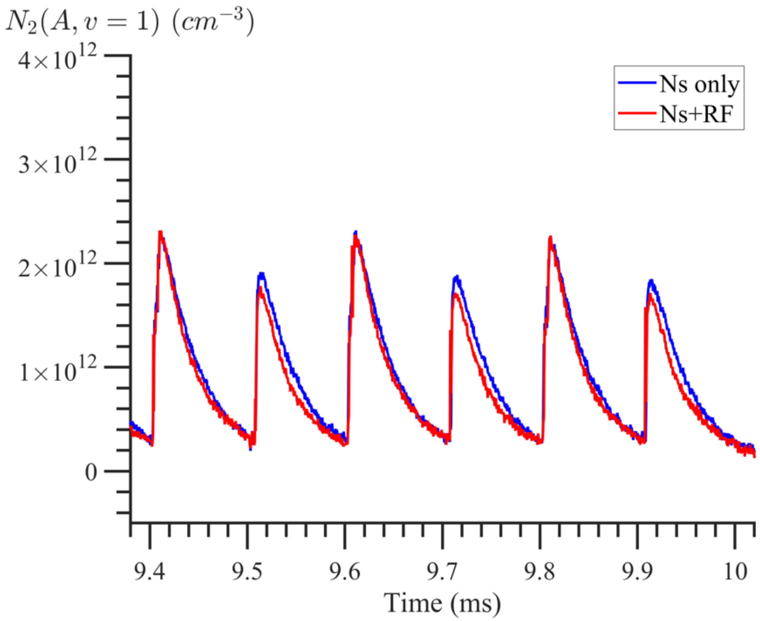
Ns pulse train only



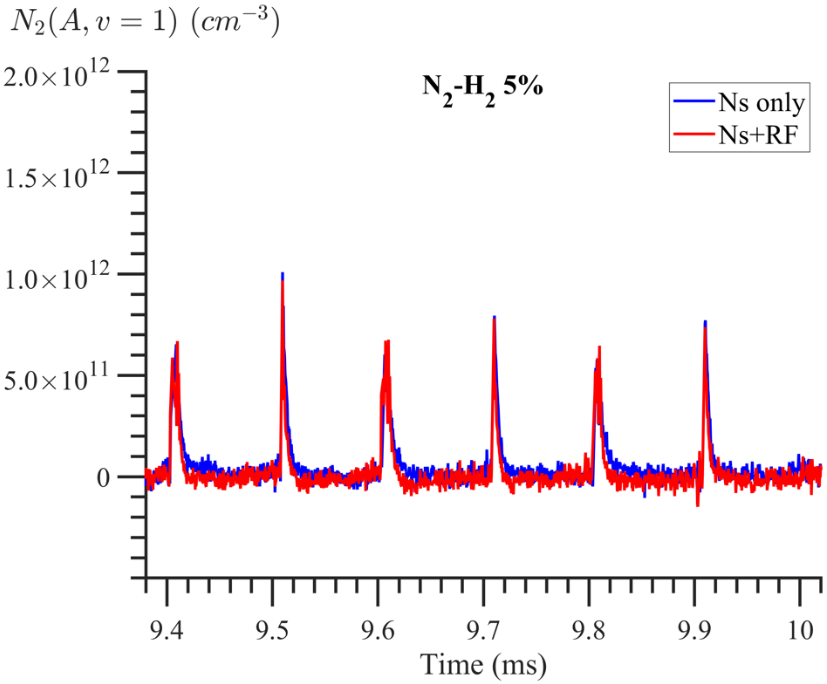
Ns pulse train + RF waveform

- **20% H_2 in N_2, 190 Torr, 573 K**
- **25% yield increase in Ns-RF on Ru catalyst**
- **RF effect scales with number of ns pulses**
- **Surface-dominated process**
- **Similar effect on Ni and Rh catalysts**

Ns-RF Discharge Does NOT Produce Additional N, H Atoms (also NH_3 Reactants)



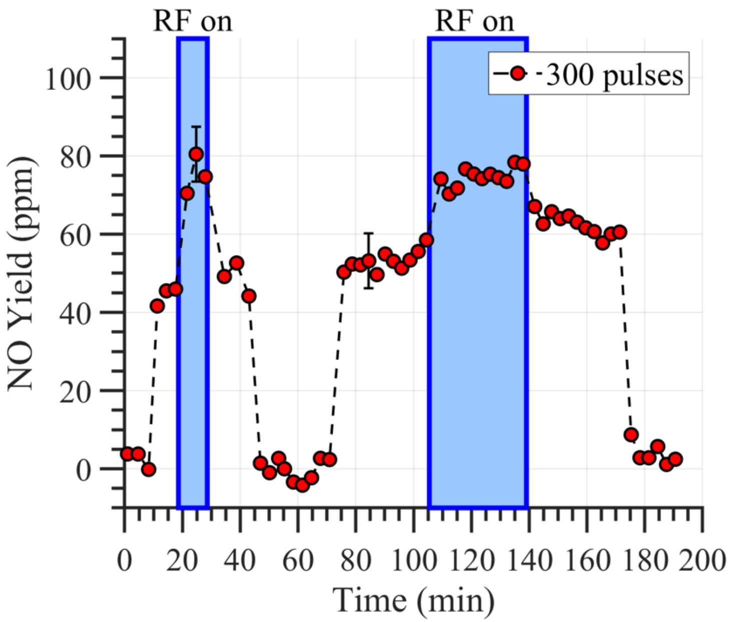
N_2, 190 Torr, 573 K

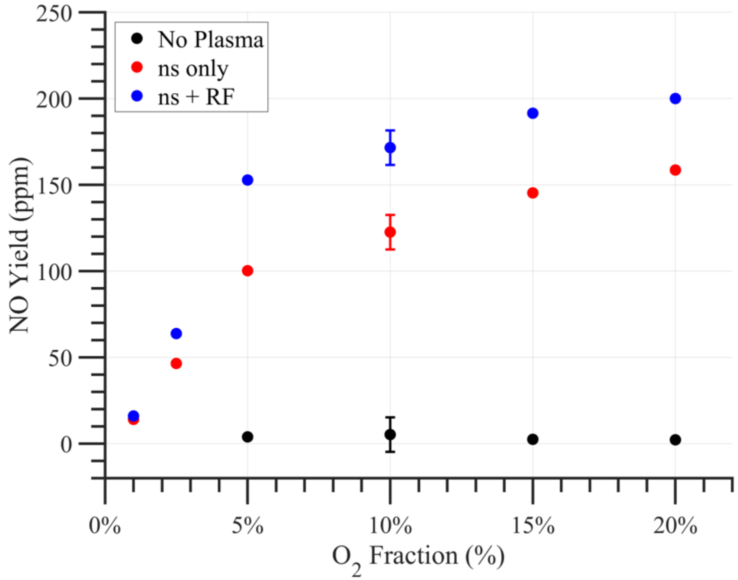


5% H_2 in N_2, 190 Torr, 573 K

- **$N_2(A^3\Sigma,v=1)$ peak population, decay rate in Ns pulse, Ns + RF discharges are the same**
- **No evidence of additional generation of N and H atoms (both rapid $N_2(A)$ relaxers)**

Additional Evidence:
NO Generation in Hybrid N_2-O_2 Plasmas





5% O_2 in N_2, 190 Torr, 573 K

1-20% O_2 in N_2, 190 Torr, 573 K

- **NO yield enhancement 30-50%**
- **Consistent with known NO generation kinetics:**

$$N_2(A^3\Sigma_u^+) + O \rightarrow NO + N \quad \text{(ns pulse train only)}$$

$$N_2(X^1\Sigma_g^+, v \geq 12) + O \rightarrow NO + N \quad \text{(ns + RF)}$$

III. Summary

- **Plasma-catalytic NH_3 generation in ns pulse discharge with sub-breakdown RF**

- **RF excitation leads to reproducible ammonia yield enhancement in a surface-dominated process, on several catalysts (Ni, Ru, Rh)**

- **RF excitation DOES increase N_2(v) populations, does NOT increase N and H number densities**

- **Suggests contribution of N_2(v) molecules to plasma-catalytic NH_3 generation**

- **RF excitation also enhances NO yield in N_2-O_2 plasmas, likely via the vibrationally stimulated Zel'dovich reaction, $\boldsymbol{N_2(X^1\Sigma_g^+, v) + O \rightarrow NO + N}$**

- **Additional verification needed: simultaneous measurements of N, H, N_2(v) in hybrid ns + RF plasmas**

M. Berry, AIAA 2024-1826 (manuscript under review)

Acknowledgements

US Department of Defense / Office of Naval Research MURI "Development of Validated Hypersonic Plasma Kinetics Models Including Atomic Excitation"

US Department of Energy Center for Plasma Interaction with Complex Interfaces (PICI)

US Department of Energy Collaborative Center for Plasma Assisted Combustion and Catalysis (PACC)