Seminar at Department of Aerospace Engineering, University of Michigan
January 30, 2020

Understanding Reactivity of Nonequilibrium Molecular Plasmas for Propulsion and Power Applications

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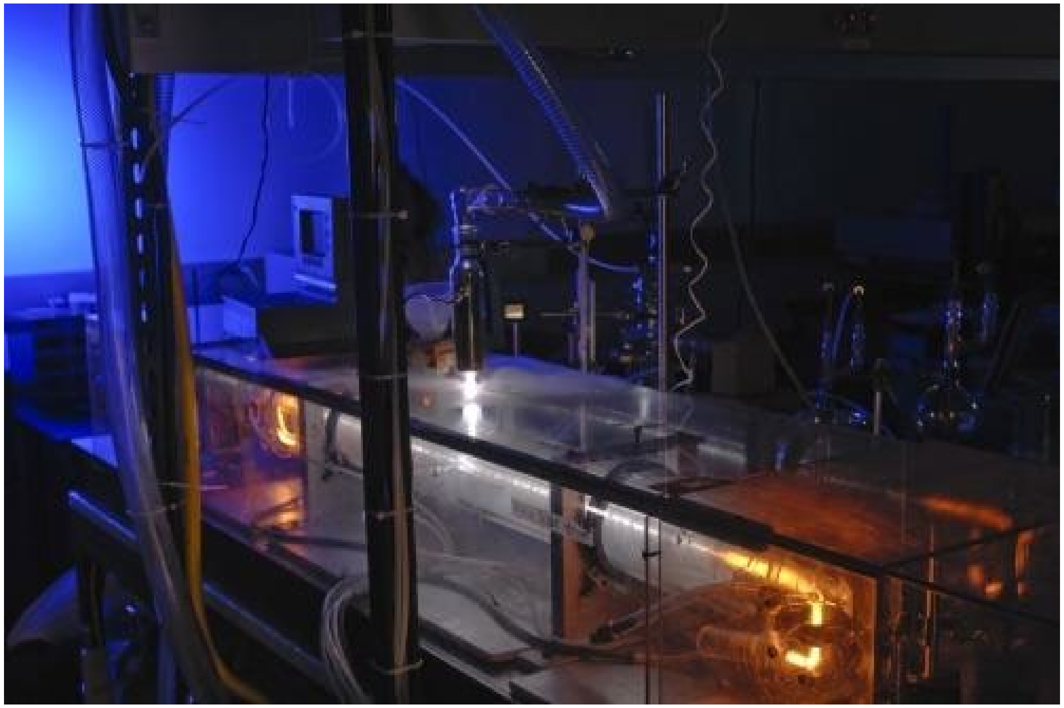


Nonequilibrium Thermodynamics Laboratory: Research Fields

- Kinetics of high-speed nonequilibrium flows and low-temperature plasmas
- Energy transfer in molecular collisions, nonequilibrium chemical reactions, emission and absorption of radiation
- Laser diagnostics of plasmas and reacting flows
- Development of new molecular gas lasers
- Applications for high-speed aerodynamics, propulsion and combustion, hypersonic flows, plasma chemical reactors, and biology

Nonequilibrium Reacting Plasmas:
Relevance for Aerospace Applications

- High-speed flow (formation of coherent structures) is affected by localized heating in pulsed plasmas: plasma flow control

- Excited species and radicals enable low-temperature reaction pathways in reacting flows: plasma-assisted combustion

- Excited species and radicals control UV / visible emission from nonequlibrium flows: hypersonic flight, atmospheric reentry

- Energy partition in the plasma (vibrational and electronic excitation, dissociation, radical generation), and temperature rise are controlled by the electric field

- Quantitative insight requires non-intrusive diagnostics of electric field, excited species, and radicals:

    - In laboratory environments

    - At pulsed high-enthalpy flow facilities

Electric Field in Pulsed Plasmas:

Understanding High-Speed Plasma Flow Control

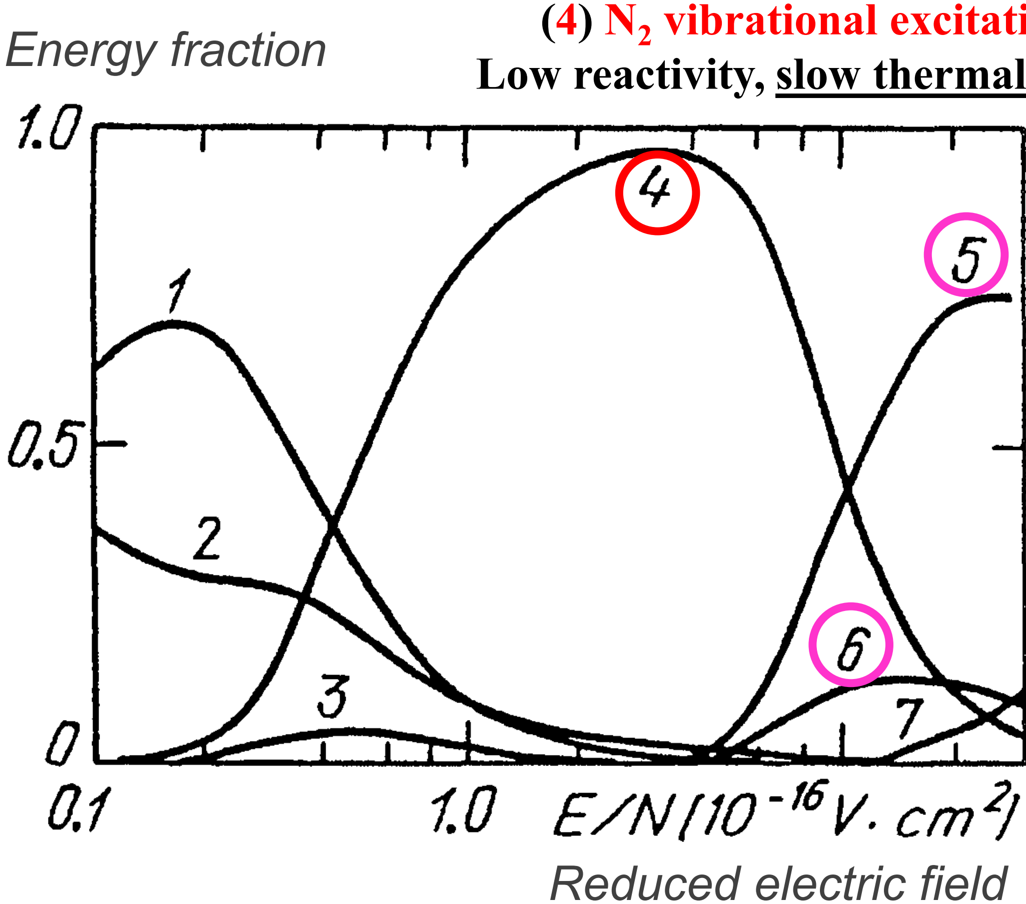
Energy Partition in Air Plasma vs. Electric Field

Yu. Raizer, Gas Discharge Physics, Springer, 1991

Quasi-steady-state discharges: low E/N

(4) N_2 vibrational excitation:

Low reactivity, slow thermalization



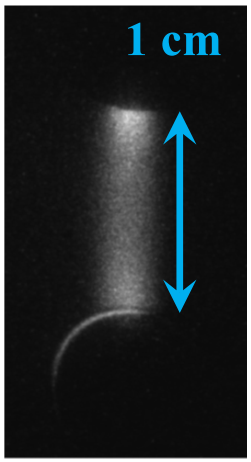
Pulsed discharges: high E/N

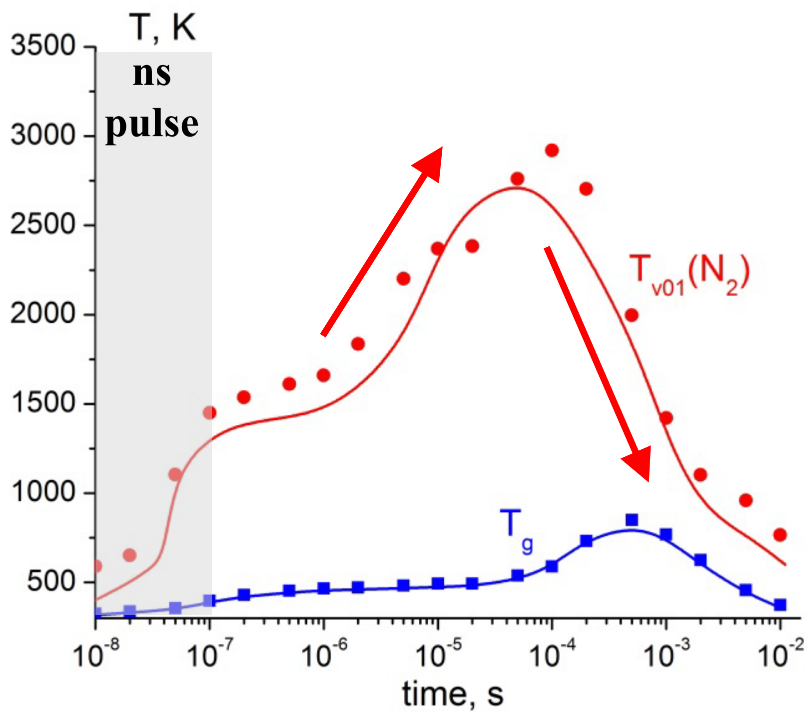
(5,6) N_2, O_2 electronic excitation, dissociation,

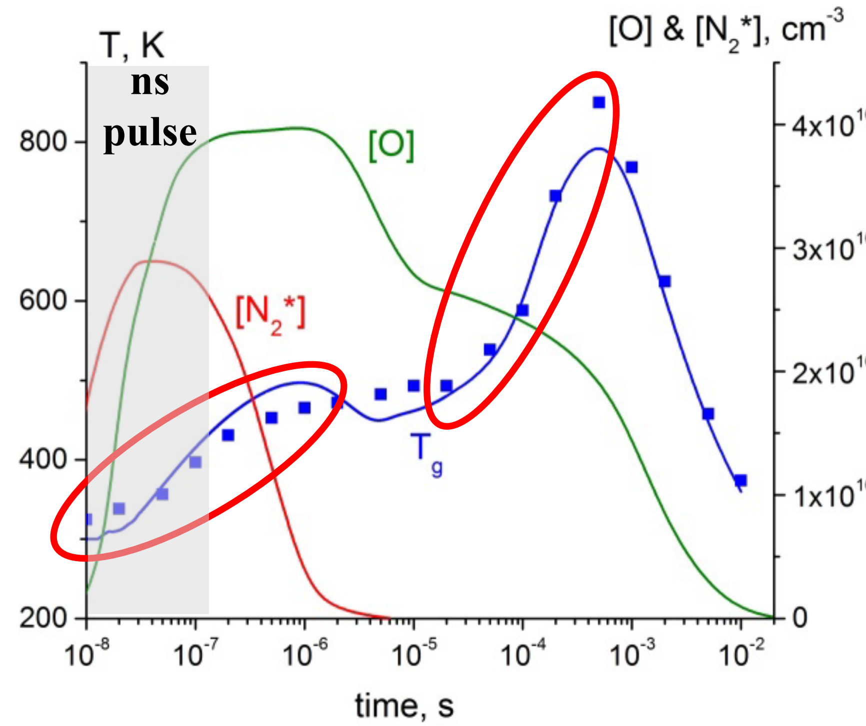
High reactivity, rapid thermalization

- *E/N* controls species generated in the plasma and the rate of temperature rise

Effect of Excited Species on Temperature Rise: Ns Pulse Discharge in Air, 100 Torr



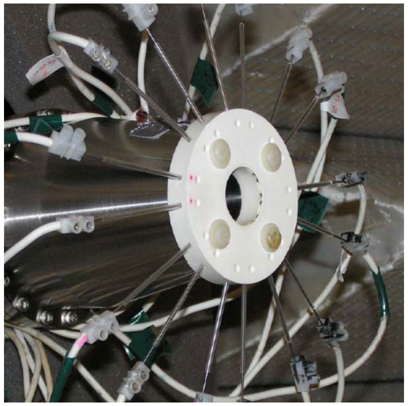


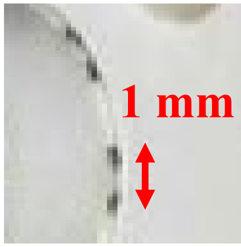


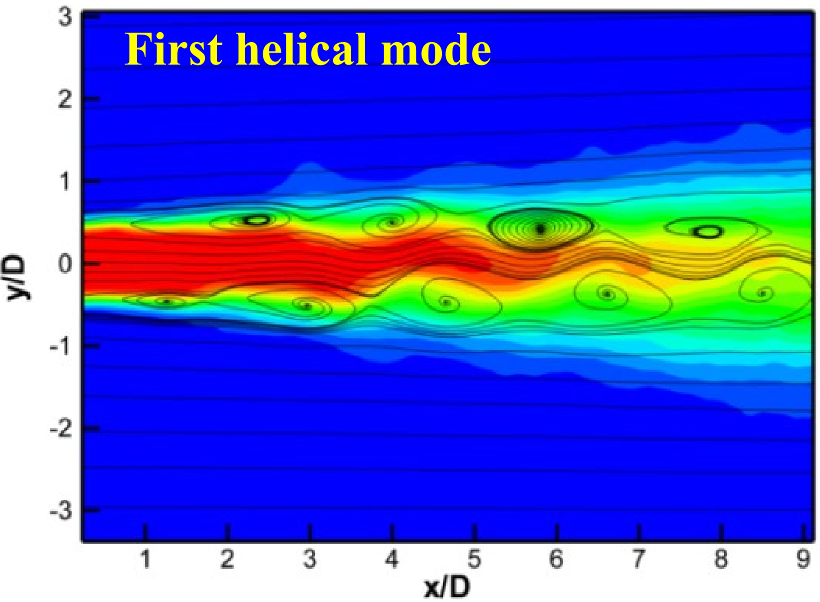
- T_v rise: V-V exchange, $N_2(v) + N_2(v=0) \rightarrow N_2(v-1) + N_2(v=1)$
- T_v decay: V-T relaxation, $N_2(v) + O \rightarrow N_2(v-1) + O$
- "Rapid" heating: quenching of N_2 electronic states, $N_2^* + O_2 \rightarrow N_2 + O + O$
    - Compression wave formation
- "Slow" heating: V-T relaxation, $N_2(v) + O \rightarrow N_2(v-1) + O$
    - Formation of coherent structures in the flow

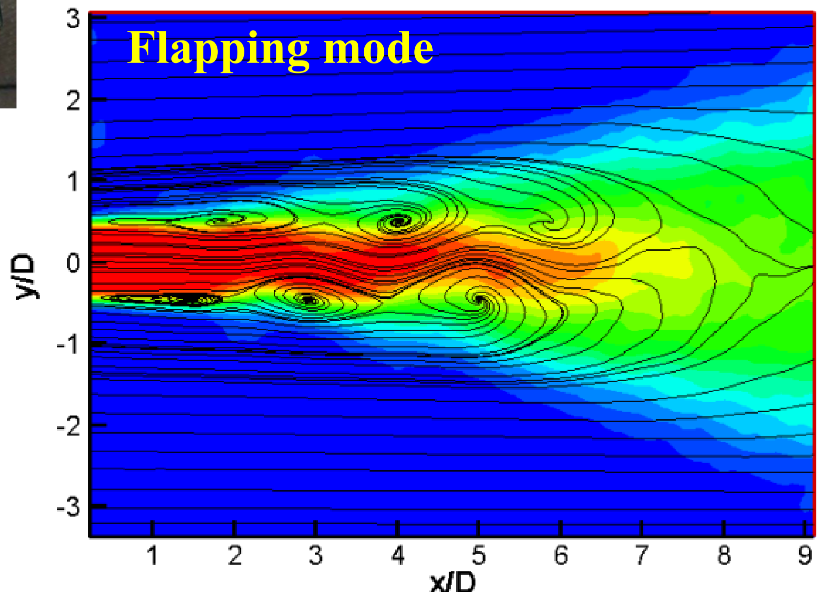
Shkurenkov et al, PSST, 2016

Localized Arc Filament Plasma Flow Actuators M=0.9 Circular Jet





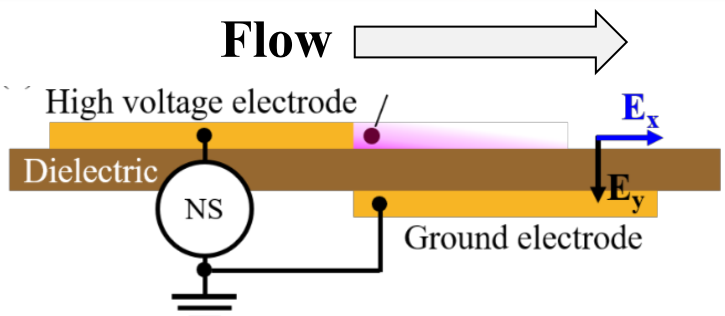




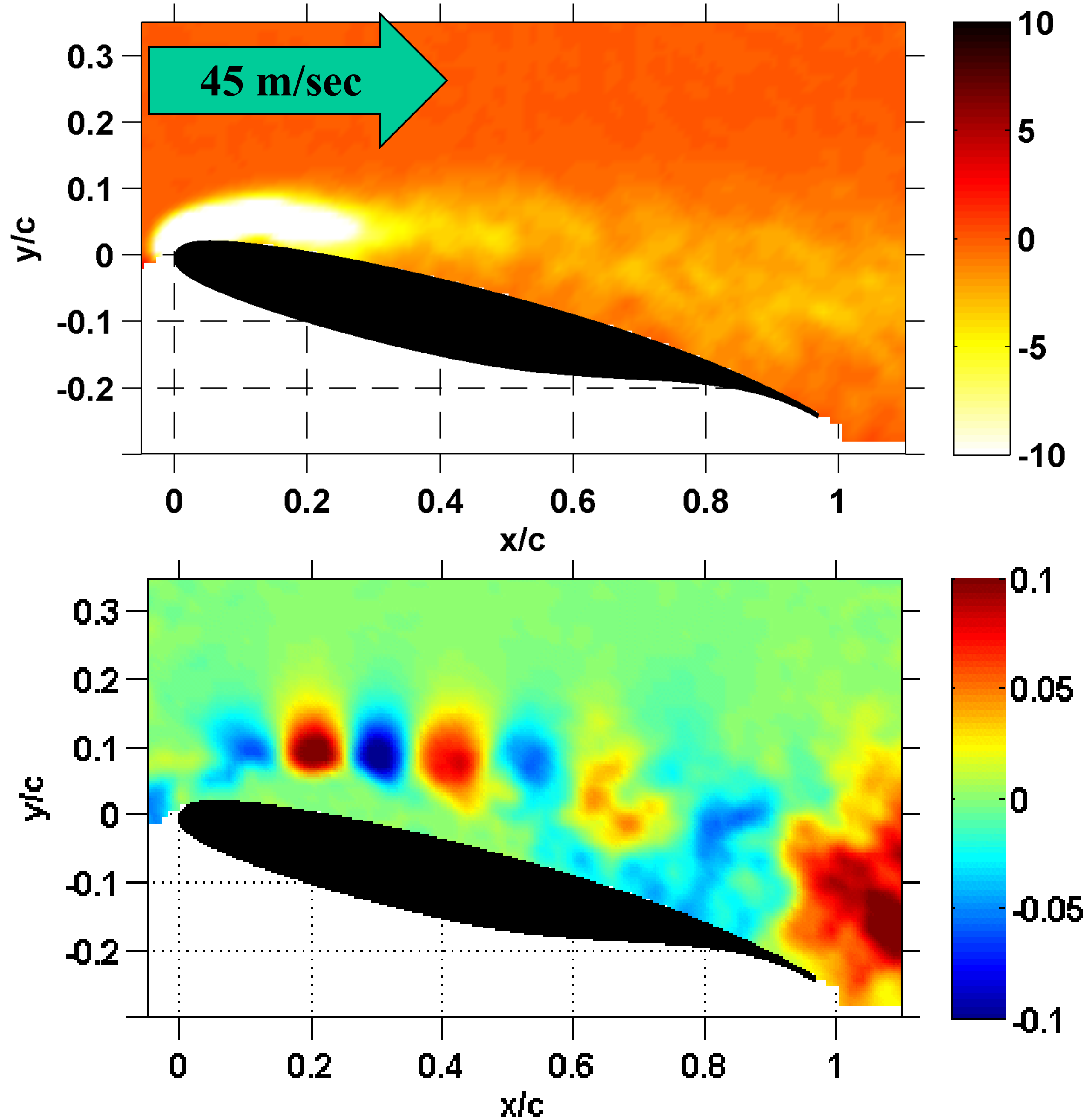
- High amplitude perturbations (localized heating in arc filaments)
- Every discharge pulse results in a vortex formation
- Flow responds to forcing near instability frequency
- Mixing enhancement, jet noise reduction

Kim et al, Expts. Fluids, 2010

Ns Pulse Surface Plasma Flow Actuators: Boundary Layer Reattachment (M=0.2-0.3)

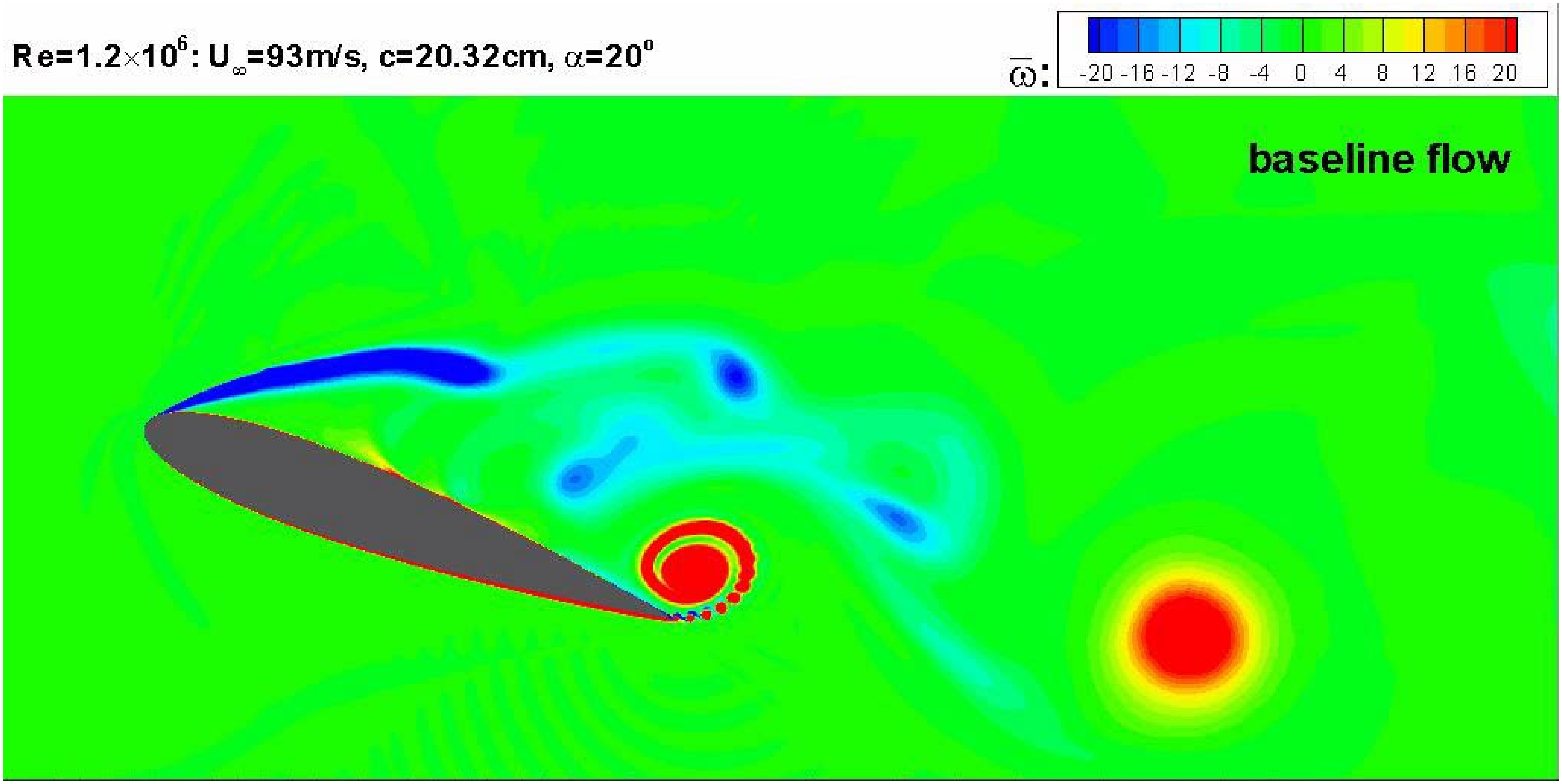


- Every ns discharge pulse produces a spanwise "vortex tube"
- Enhanced mixing with free stream, boundary layer reattachment
- Effect detected up to u=96 m/s



Little et al, AIAA J., 2012

Surface Plasma / CFD Modeling Predictions
Baseline and forced flows



- **Vortex formation controlled by localized heating in plasma layer**
- **Need to know time-resolved electric field, *E(t)*, to predict flow field accurately**

Zheng et al, Phys. Rev. Fluids, 2016

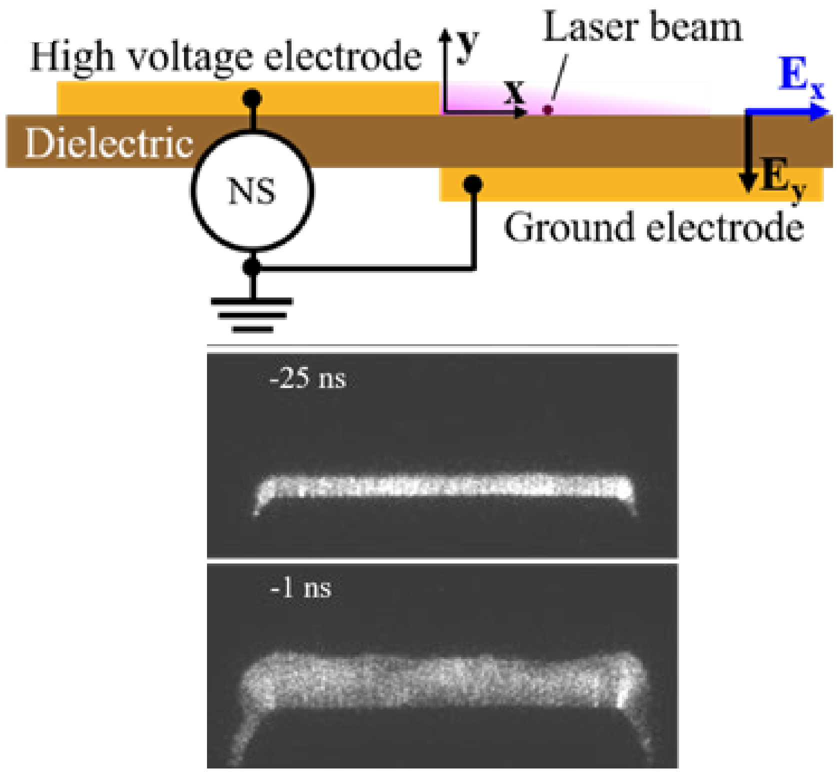
Electric Field Induced Second Harmonic Generation (E-FISH)

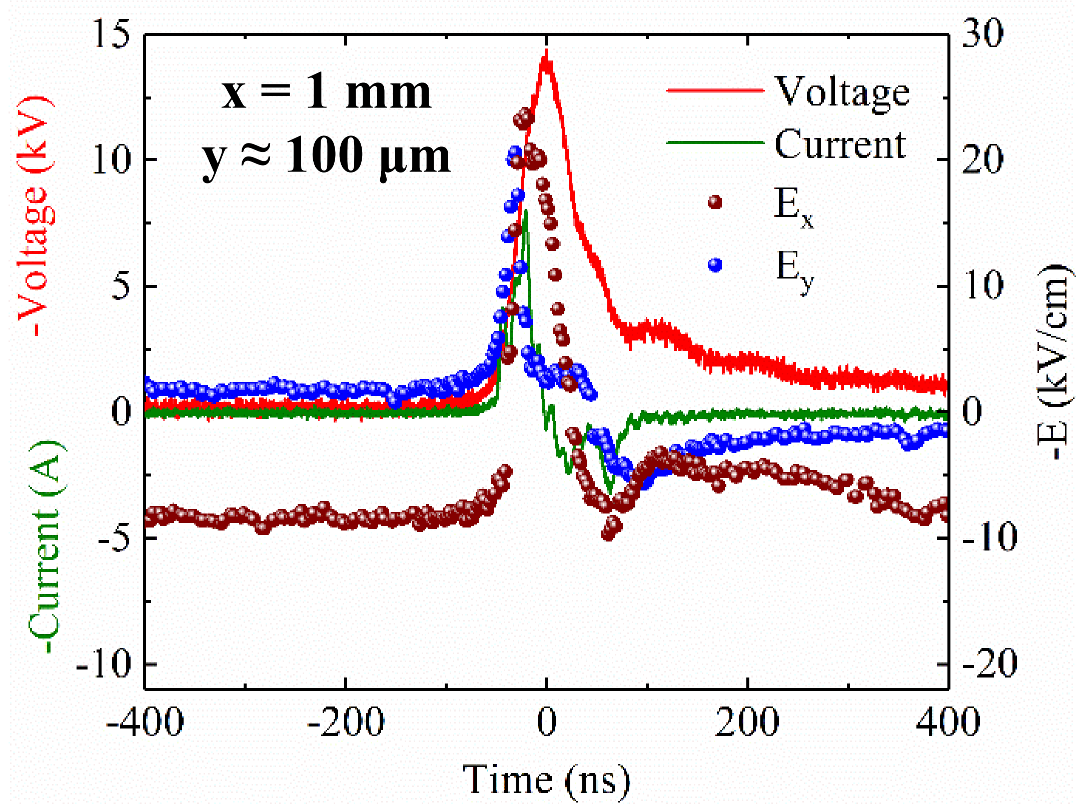
- Electric field in the plasma, E, induces a dipole moment in molecules or atoms
- Pulsed laser beam (fs, ps, or even ns) passes through the plasma
- Laser field, I_{ω}, generates coherent oscillating polarization of the dipoles
- Oscillating dipoles launch a coherent 2nd harmonic signal beam, $I_{2\omega} \sim \left[\chi^3 I_{\omega} E L\right]^2$ ($\chi^{(3)}$ – nonlinear susceptibility, L – interaction length)
- Straightforward signal isolation and detection, sub-ns time resolution
- Signal polarization same as field direction: E_x, E_y can be measured separately
- Simplest experiment ever, great for a student laser diagnostics lab
- **Goal:** determine effect of discharge pulse waveform on the flow field

Dogariu et al, Phys. Rev. Applied, 2017

Goldberg et al, Appl. Phys. Lett, 2018

Electric Field
In Ns Pulse Surface Plasma Actuator

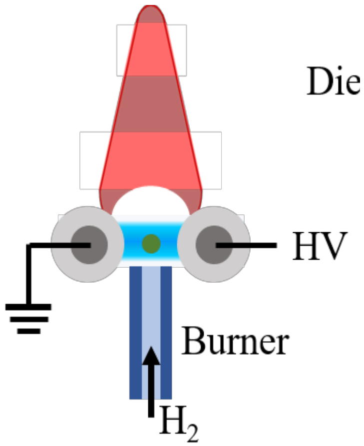


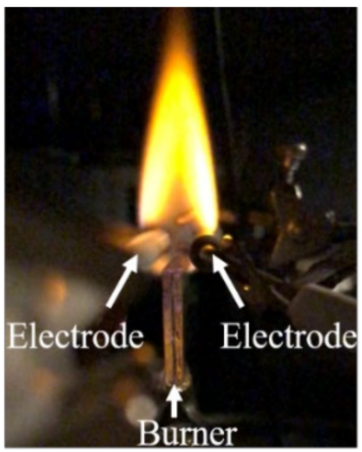


- 150 ps Nd:YAG pulse, 2 mJ at 1064 nm
- Field offset: surface charge accumulation from previous discharge pulse
- Field rises with applied voltage, drops after breakdown (plasma self-shielding)
- *E(t)/N* controls temperature rise, vortex formation in the flow

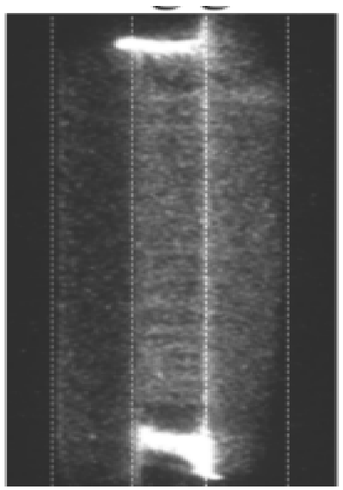
Simeni Simeni et al., PSST, 2018

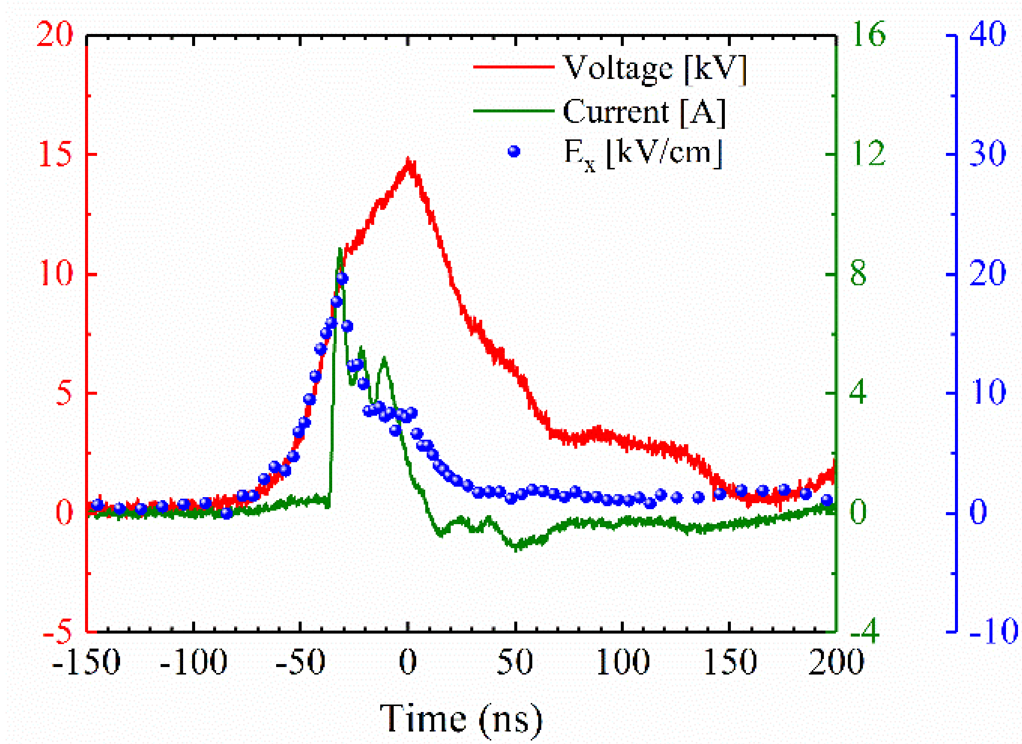
Electric Field
In H_2 Diffusion Flame with Ns Pulse Discharge





Top view





- **Electric field measured in H_2 plasma at T=370 K**
- **Energy coupled at *E* = 9-19 kV/cm (*E/N* = 50-100 Td): efficient H atom generation**
- ***E/N(t)* is critical for quantifying effect of plasma on combustion**

Simeni Simeni et al., Comb. Flame, 2018

Simeni Simeni et al., Comb. Flame, 2019

“Dark” Metastable Species in Hypersonic Flows: Understanding UV Radiation Mechanism

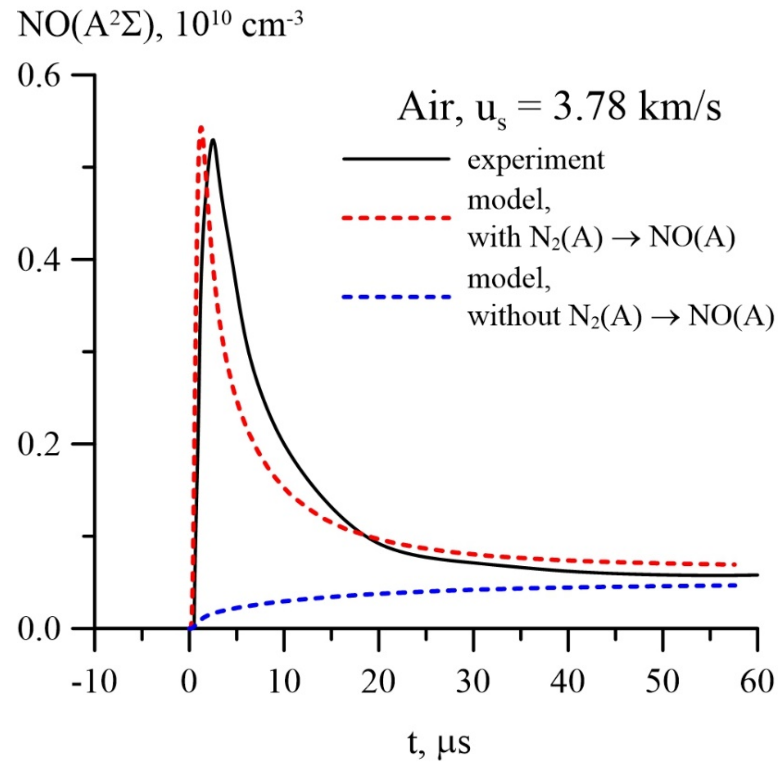
UV Emission from Strong Shock Waves in Air

- Shock tube data, modeling (CUBRC, 1991): NO UV radiation controlled by energy transfer from $N_2(A^3\Sigma)$

$$N_2 + N \rightarrow N_2(A^3\Sigma) + N$$

$$N_2(A^3\Sigma) + NO \rightarrow N_2 + NO(A^2\Sigma)$$

$$NO(A^2\Sigma) \rightarrow NO + h\nu \quad (\gamma\ bands)$$

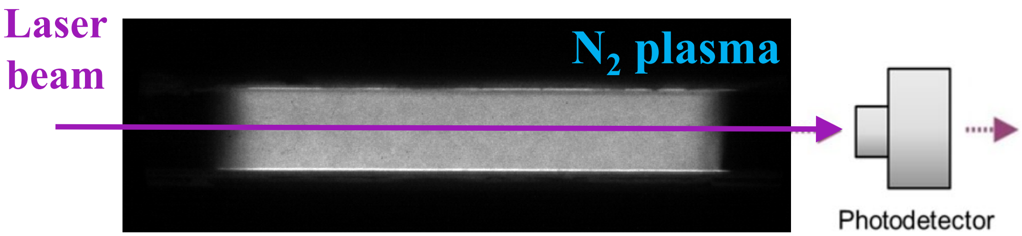


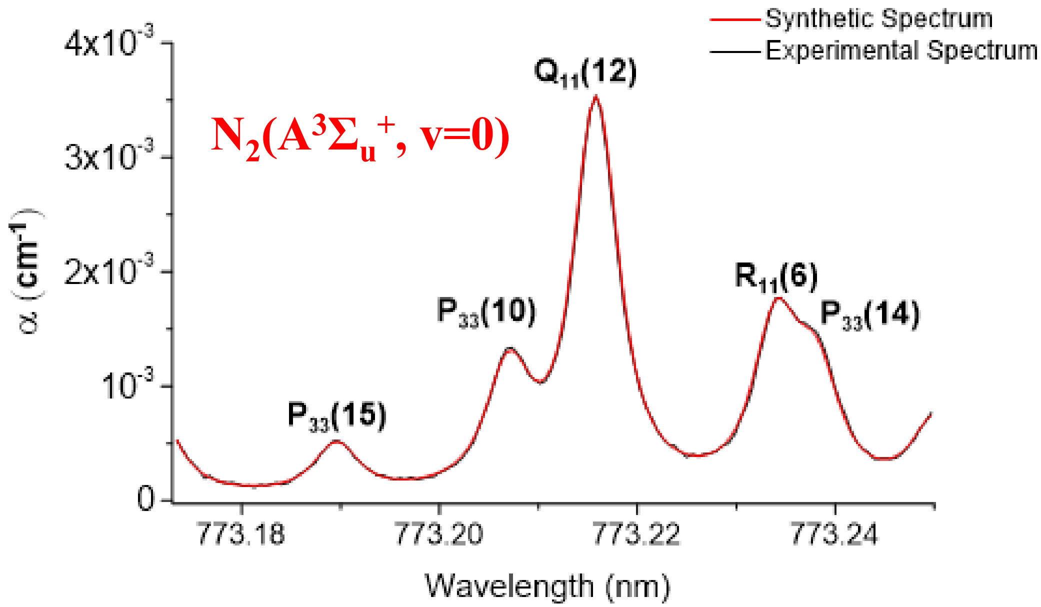
NO UV emission, Mach 11 normal shock in air

- No one ever detected $N_2(A^3\Sigma)$ in a hypersonic flow – it is a "dark" metastable state
- <u>Goal:</u> diagnostics of "dark" states such as $N_2(A^3\Sigma)$ and $O_2(a^1\Delta)$ at high-enthalpy test facilities, isolate UV radiation and O_2 dissociation mechanisms

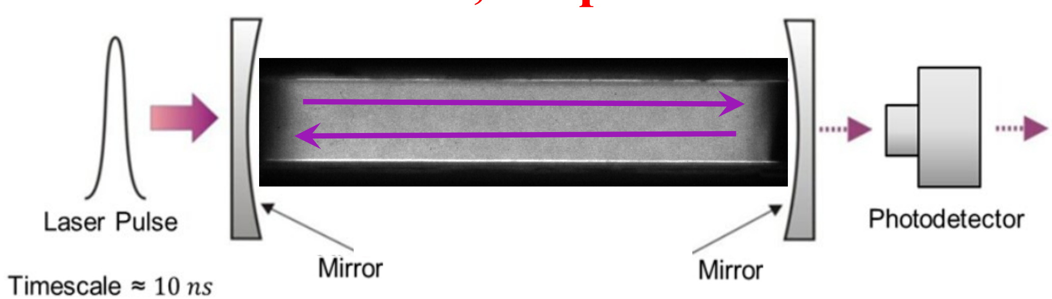
How to Measure Species That Do Not Want to Be Detected

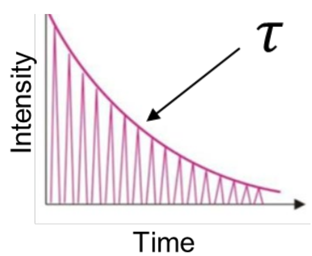
Tunable Diode Laser Absorption Spectroscopy (TDLAS) – single pass



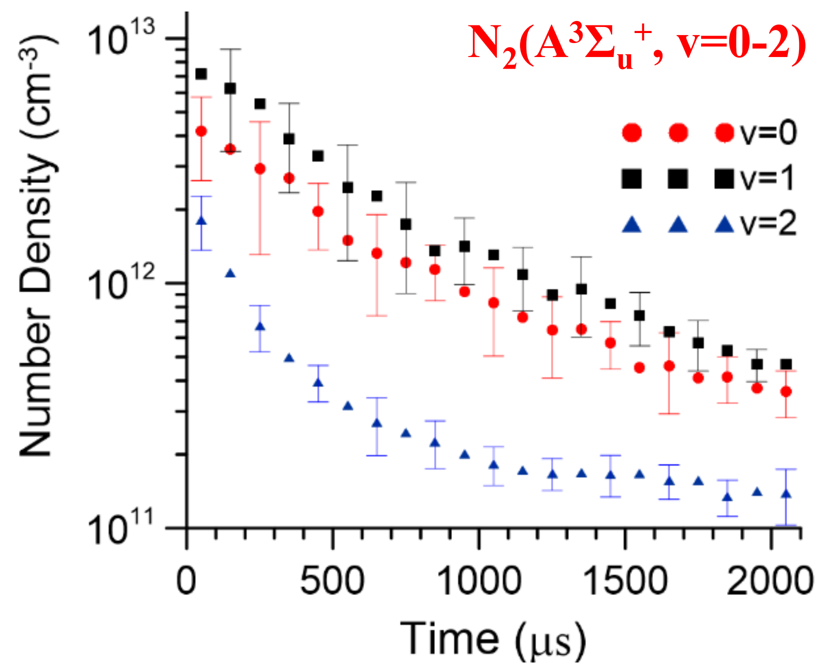


Cavity Ring Down Spectroscopy (CRDS) ~ 10,000 passes



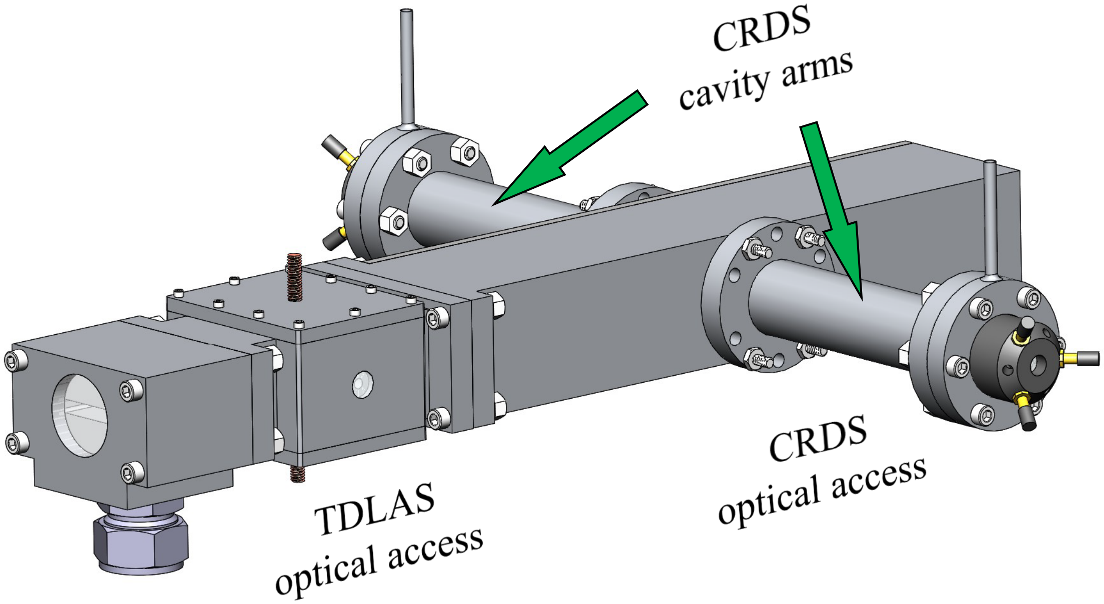


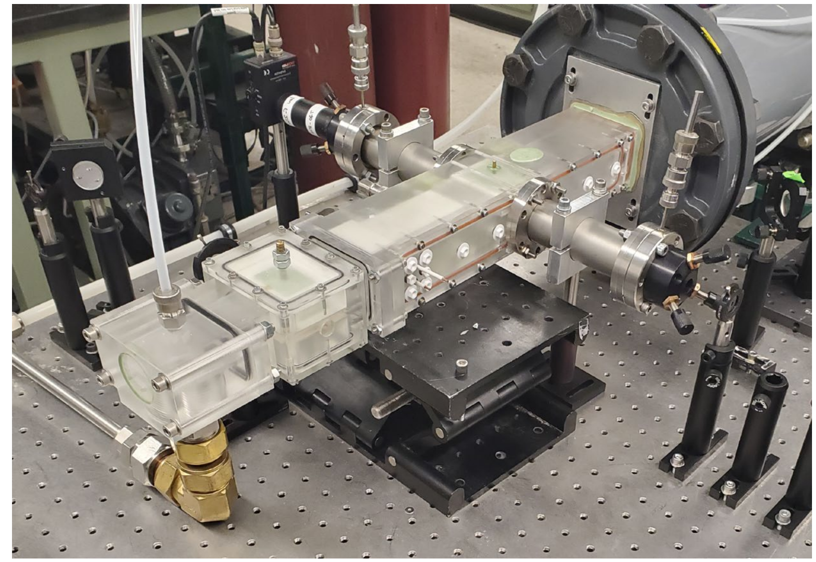
$$N = \frac{1}{c\sigma}\left(\frac{1}{\tau} - \frac{1}{\tau_{empty}}\right)$$

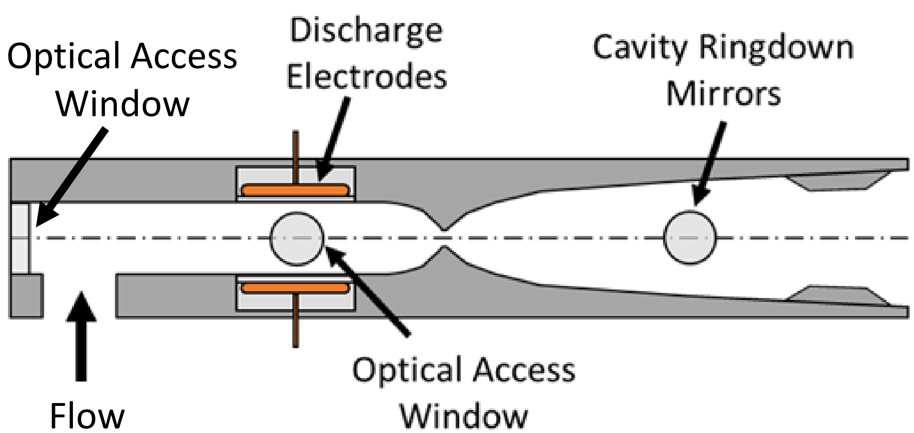


Jans et al, J. Molecular Spectroscopy, 2019

Nonequilibrim Flow Mach 5 Wind Tunnel

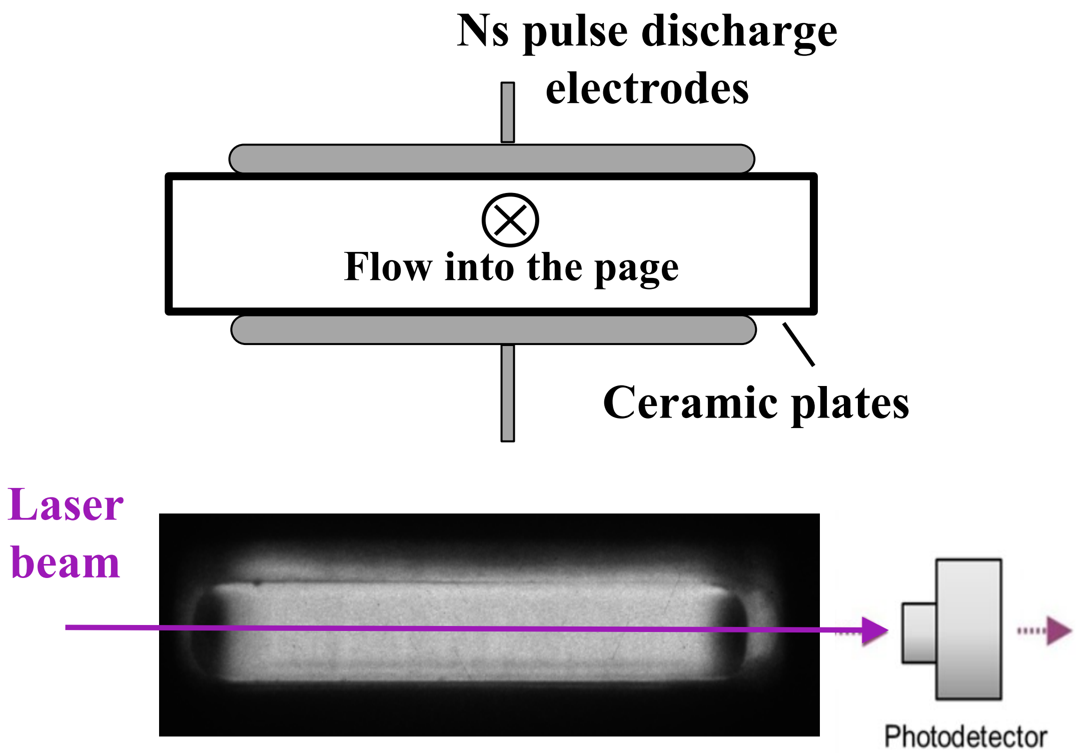


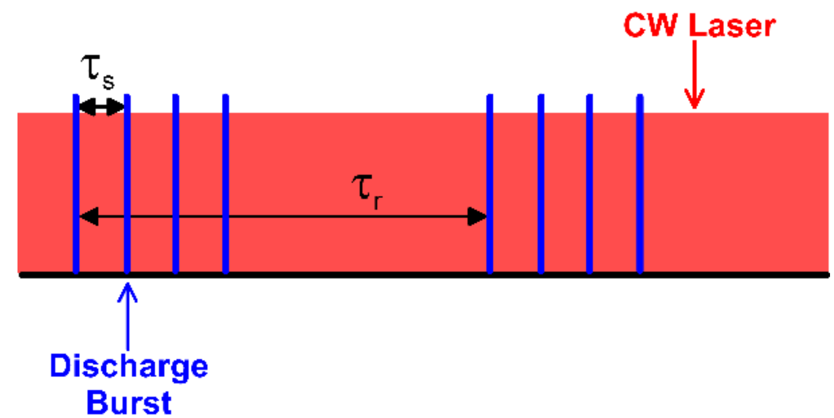




- **Blowdown wind tunnel, $P_0 = 0.3 – 1.0$ atm, Mach 4 – 5, run rime 10 s**
- **N_2(A) generated by discharge in plenum**
- **Measurements by TDLAS (in plenum) and CRDS (in supersonic flow)**

TDLAS Measurements in Plenum

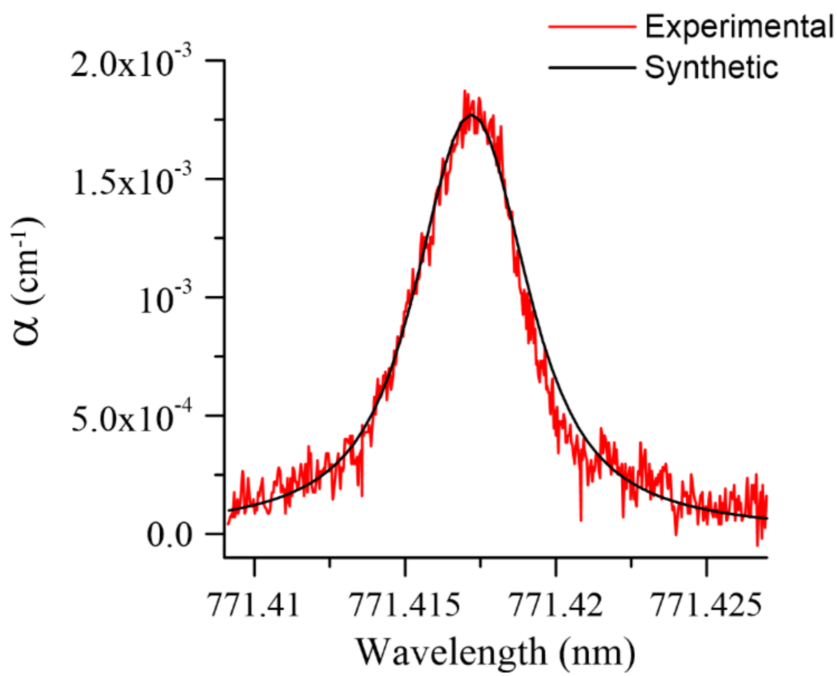


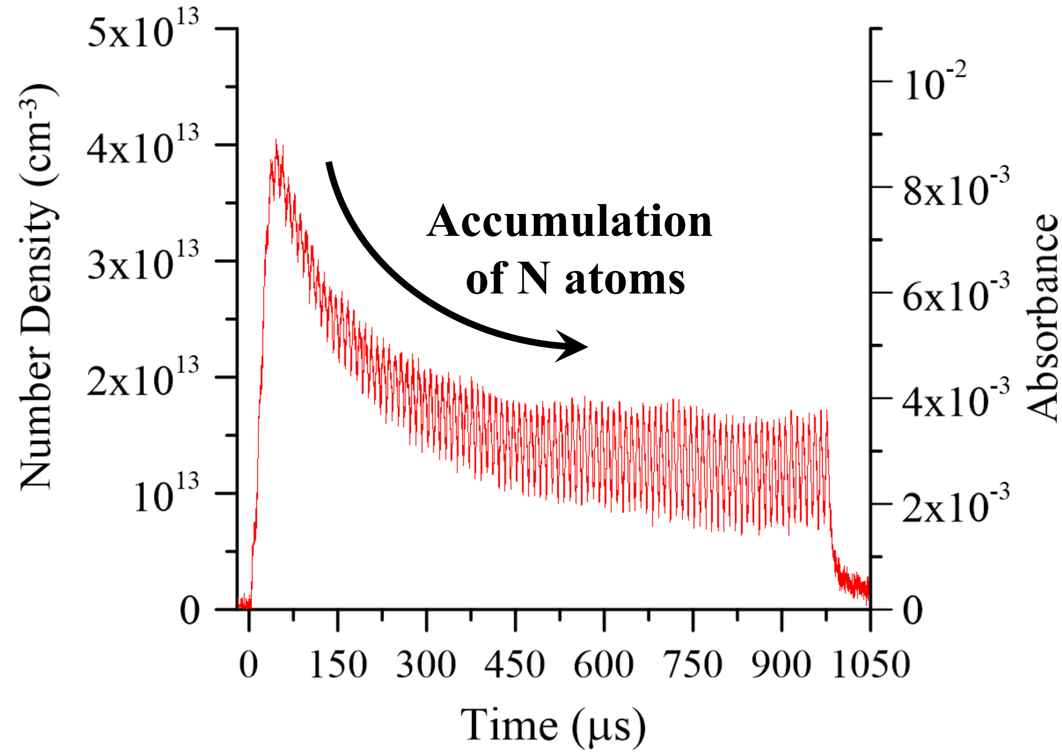


- N_2(A) generated in a repetitive ns pulse discharge
- Diffuse, uniform plasma fills entire flow cross section
- Laser is scanned across absorption line or "parked" at the line center
- Same approach can be used in a shock tube (O atom measurements at Stanford, laser scan takes 1-2 μs)

TDLAS Measurements in Plenum

- **Nitrogen, $P_0 = 250$ Torr, $T_0 = 320$ K, discharge pulse rep rate ν=100 kHz, 100 pulse burst**





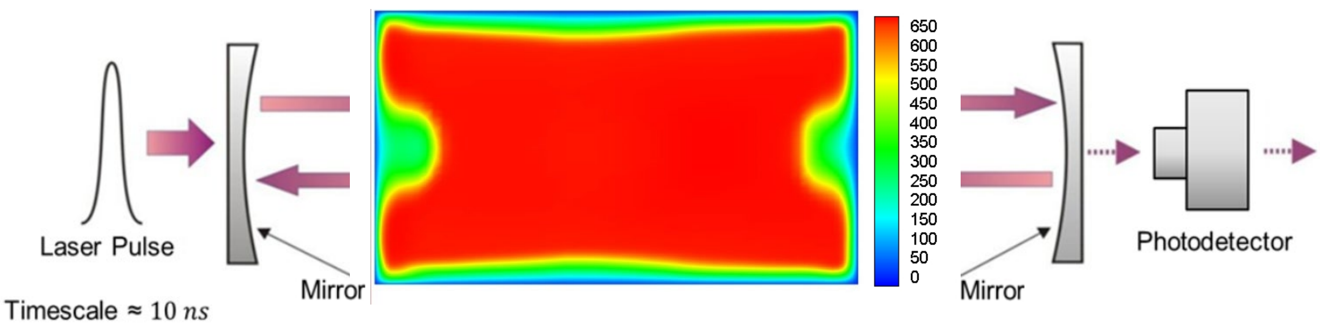
- **N_2(A) generated by electron impact:** $N_2 + e \rightarrow N_2(A^3\Sigma, B^3\Sigma, C^3\Pi) + e \rightarrow N_2(A^3\Sigma) + e$

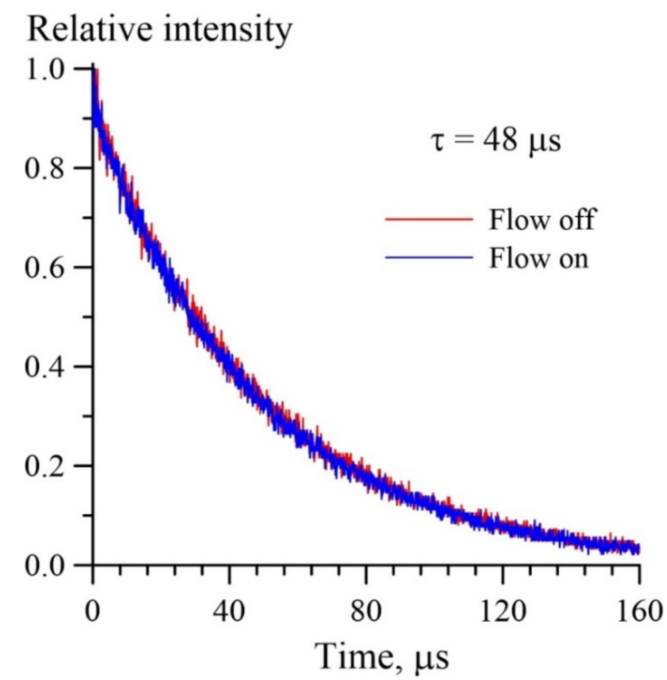
- **Quenching dominated by N atoms:** $N_2(A^3\Sigma) + N \rightarrow N_2 + N$

- **Behind the shock, excitation of N_2 by N atoms is the dominant N_2(A) generation process**

CRDS Measurements in a Supersonic Flow: Can It Be Done?

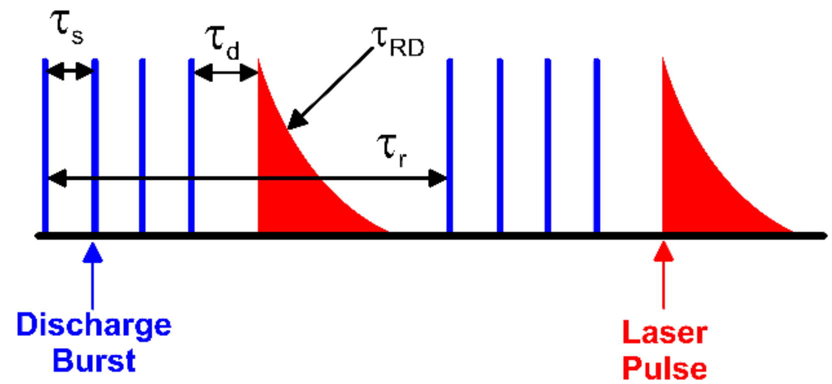
Velocity in a Mach 4 test section, CFD predictions (flow into the page)



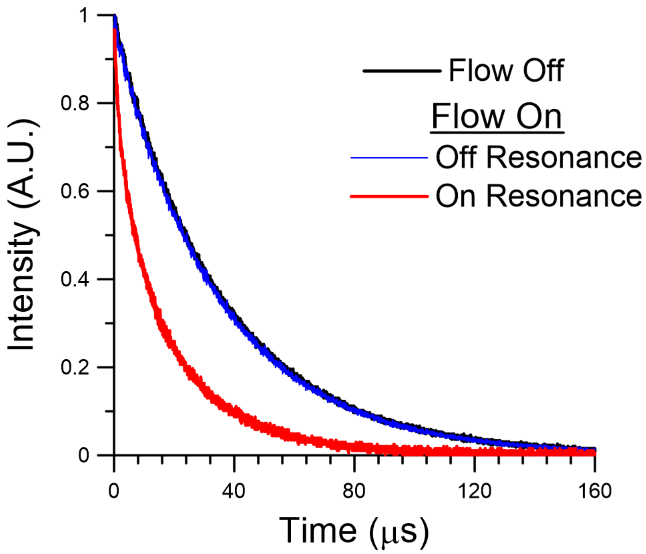


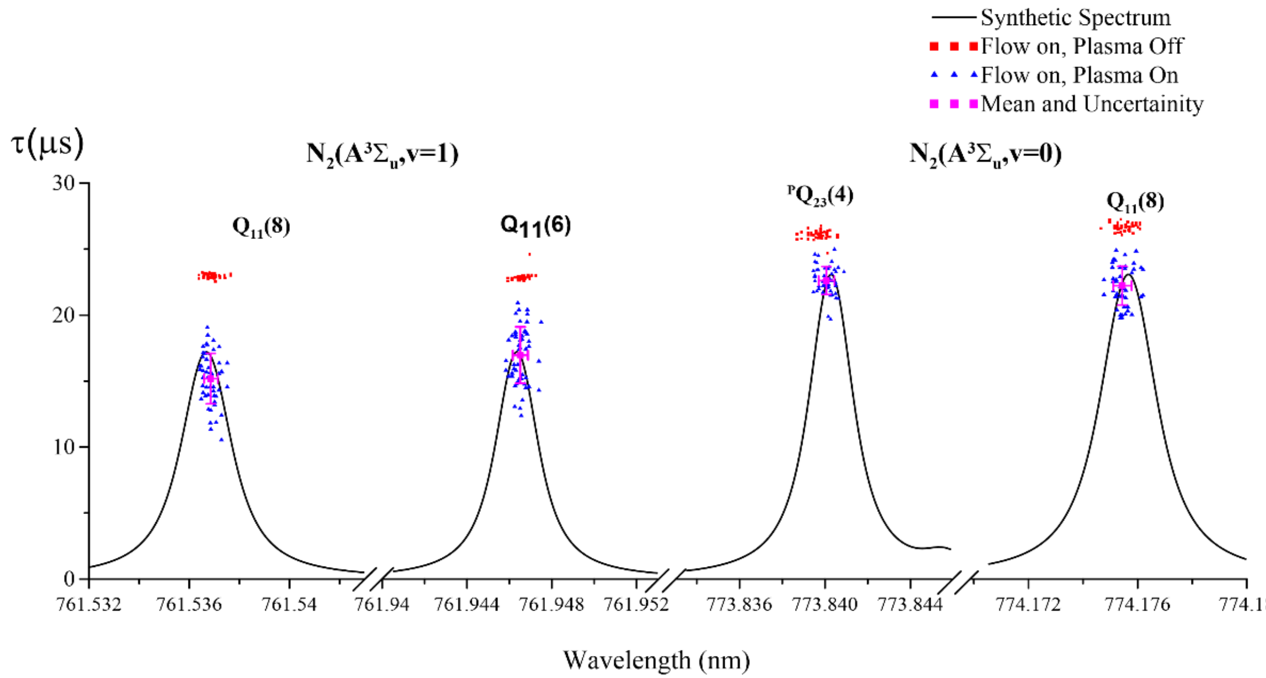
Would side wall boundary layers cause beam steering?

- Nitrogen, P_0 = 227 torr, M = 4.2
- Robust optical setup: no effect of building or wind tunnel vibrations
- No effect of flow on empty cavity ring down time
- Next, turn on discharge bursts in plenum:

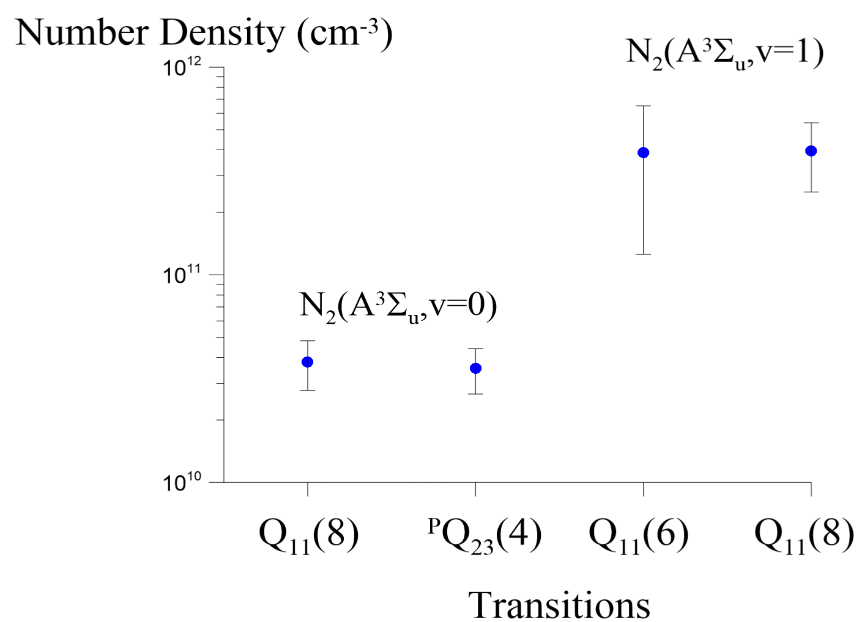


CRDS Measurements in a Mach 4 Flow

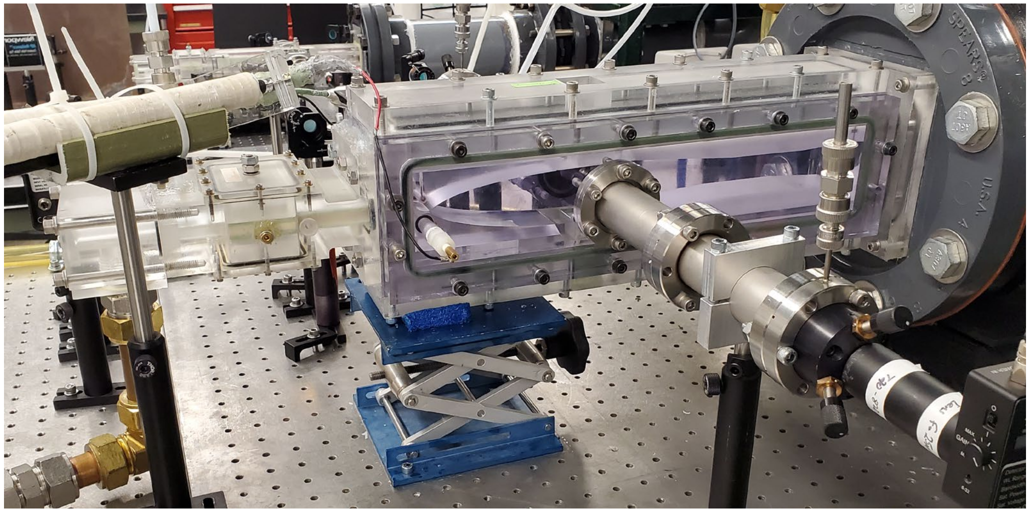


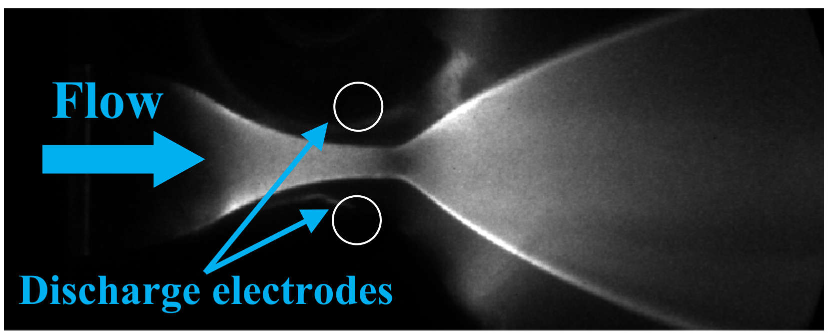


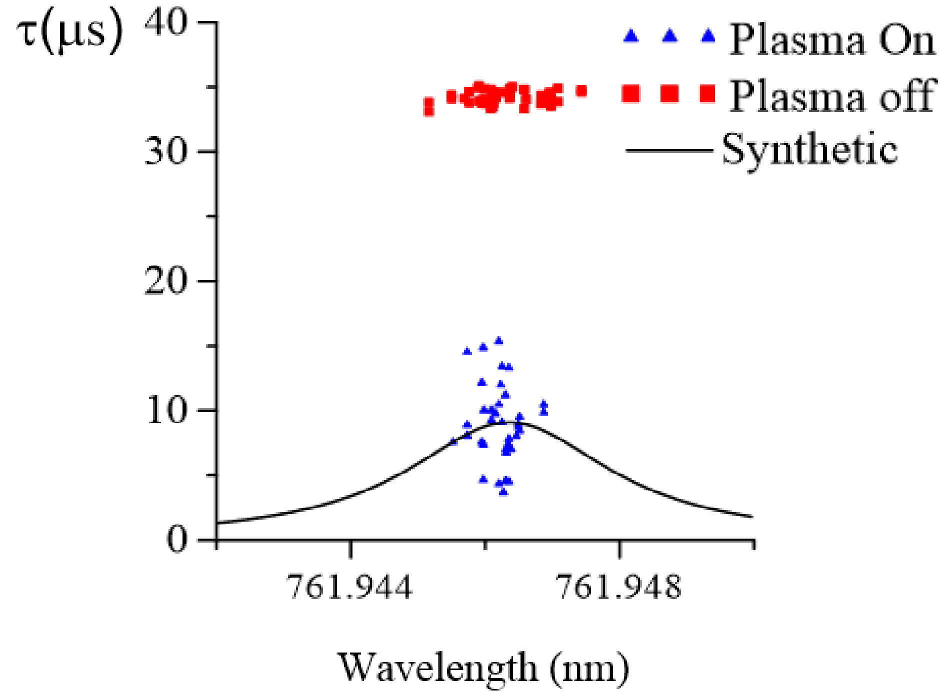
- P_0 = 227 torr, P=2.0 Torr (M = 3.7)
- ν=100 kHz ns pulse discharge <u>in plenum</u>
- Single-shot CRDS traces, 50 laser shots
- Ring down time with plasma on is shorter
- [$N_2(A^3\Sigma_u^+$,v=0,1)] are measured
- Detection limit ~ 10^{10} cm^{-3}

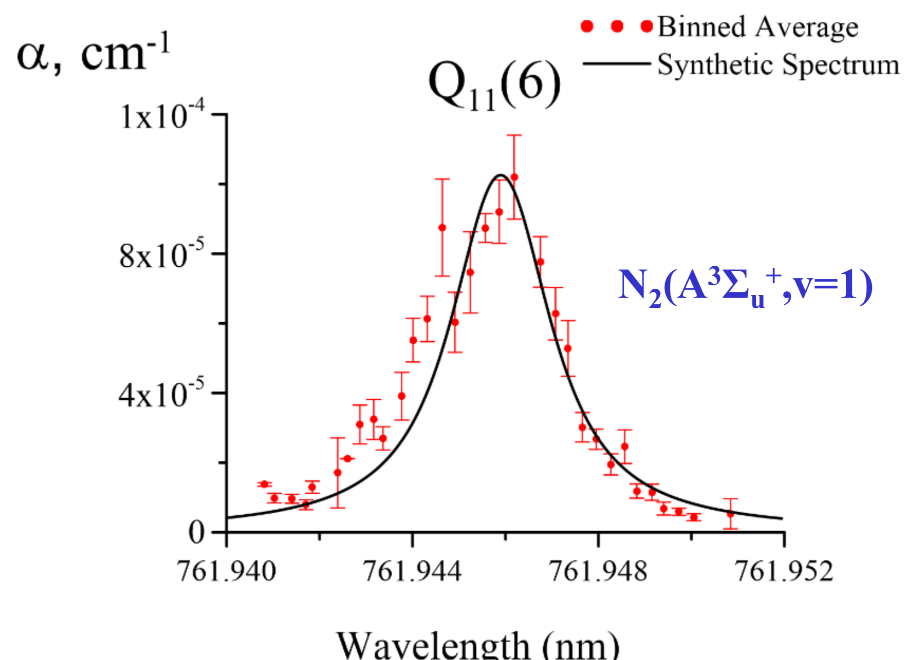


CRDS Measurements in a Mach 5 Flow









- **N_2, P_0 = 250 Torr, P=1.1 Torr (M = 4.3)**
- **ν=100 kHz discharge <u>at the nozzle throat</u>**
- **50 single-shot CRDS traces**
- **$[N_2(A^3\Sigma_u^+, v=0)] = 2\cdot10^{11}$ cm^{-3}, T = 70 K**

Hybrid Plasmas:

Understanding Plasma Chemistry and Plasma Catalysis Mechanisms

"Hybrid" Plasmas

- Separate waveforms for ionization and main energy loading
  - Ionization and energy addition are uncoupled, stable plasmas at high pressures
  - Previously used for efficient molecular lasers (CO_2, CO, e-COIL)

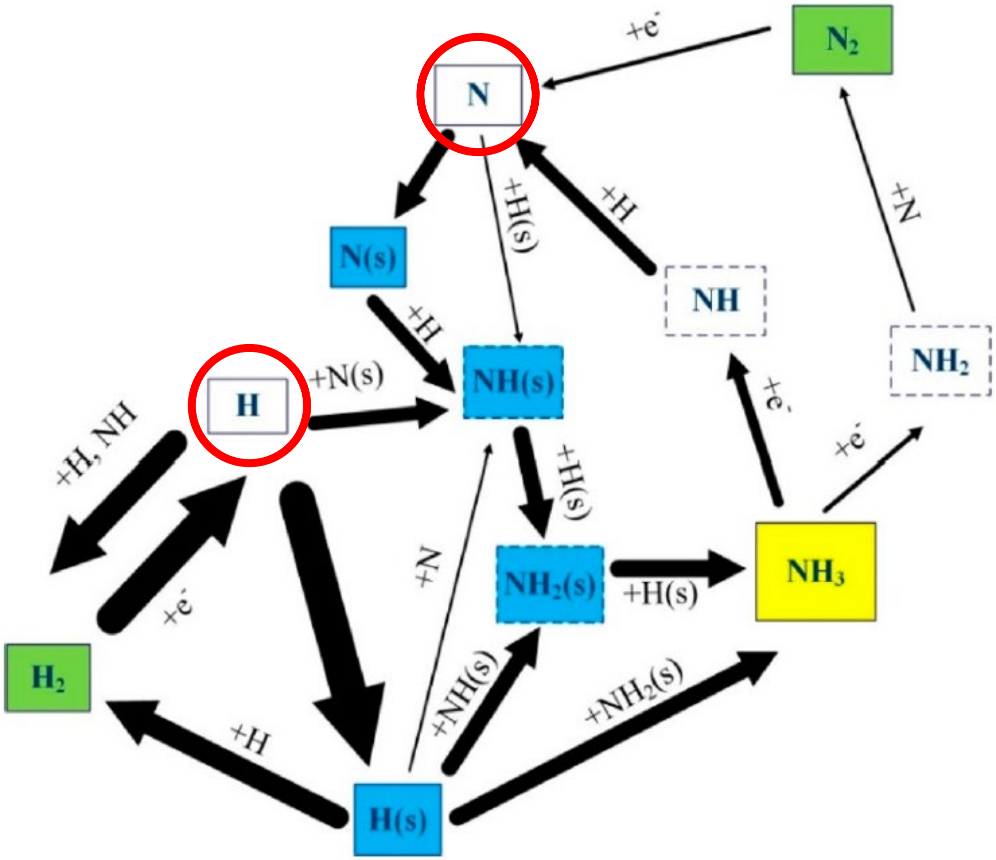
- High peak E/N ns pulses:
  - Sustain ionization
  - Generate electronically excited species, e.g. $N_2(A^3\Sigma_u^+)$, and atoms (N, H, O)

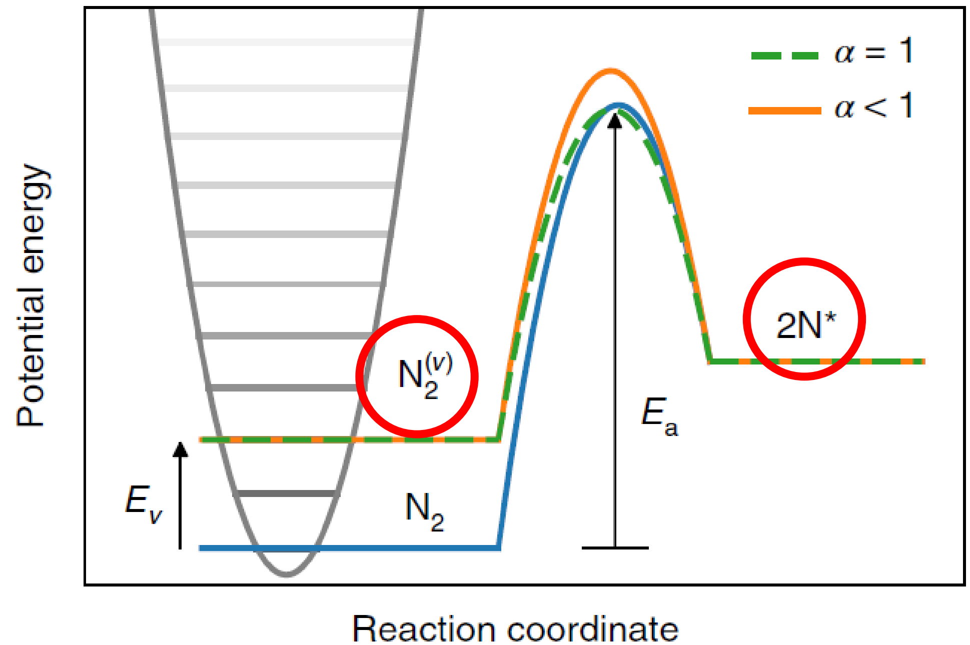
- Main energy loading waveform (DC or RF):
  - Generate vibrationally excited molecules, e.g. $N_2(v)$, $H_2(v)$, CO(v), $CO_2(v_1,v_2,v_3)$

- <u>Goal:</u> isolate the effect of atoms / radicals <u>and</u> vibrationally excited species on plasma chemistry and plasma catalysis

- <u>Goal:</u> develop efficient plasma chemical syntheses at atmospheric pressure

Plasma Catalytic Synthesis of NH_3: Reaction Pathways





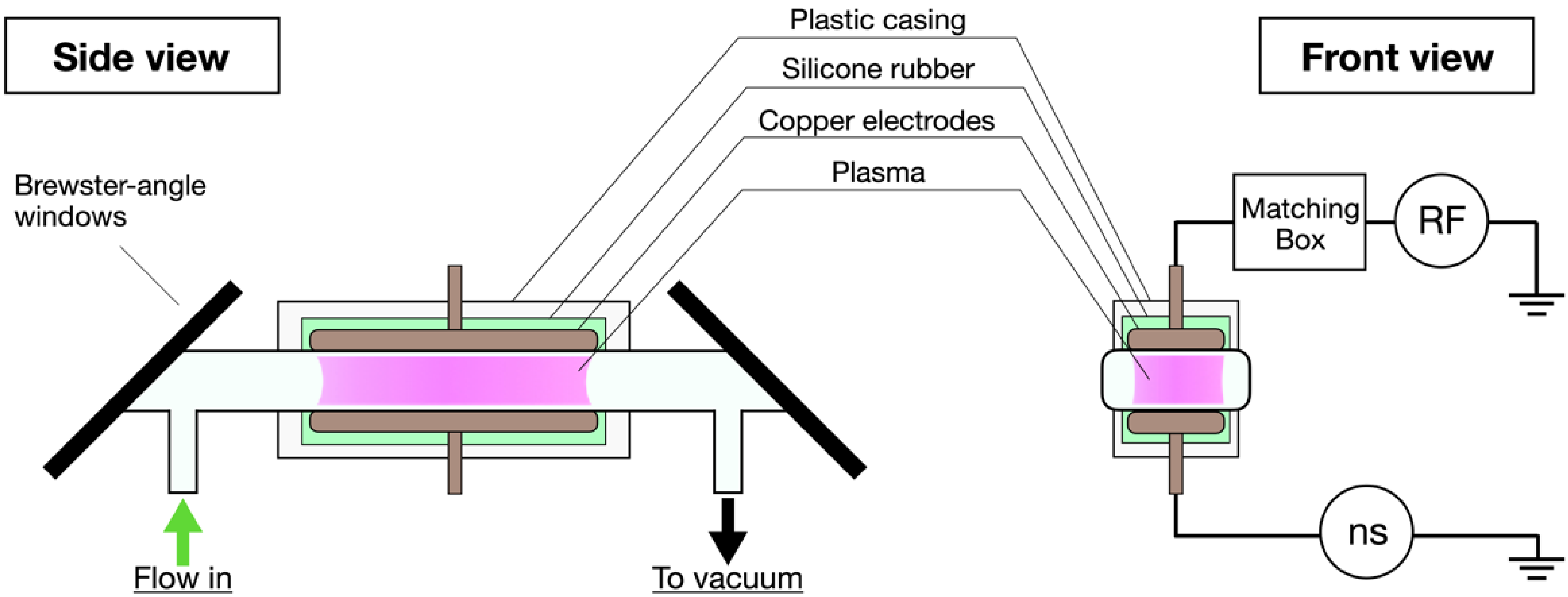
- Process dominated by surface reactions of **N** and **H** (generated by electron impact)
- Vibrational excitation of N_2 reduces barrier for surface dissociation reaction (?)

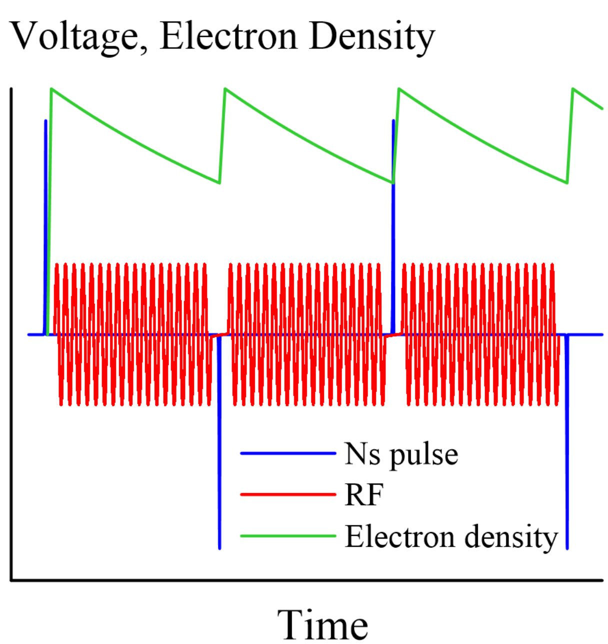
J. Shah et al, ACS Appl. Energy Mater. 2018

P. Mehta et al., Nature Catalysis 2018

N / H or N_2(v)? It is difficult to generate them independently

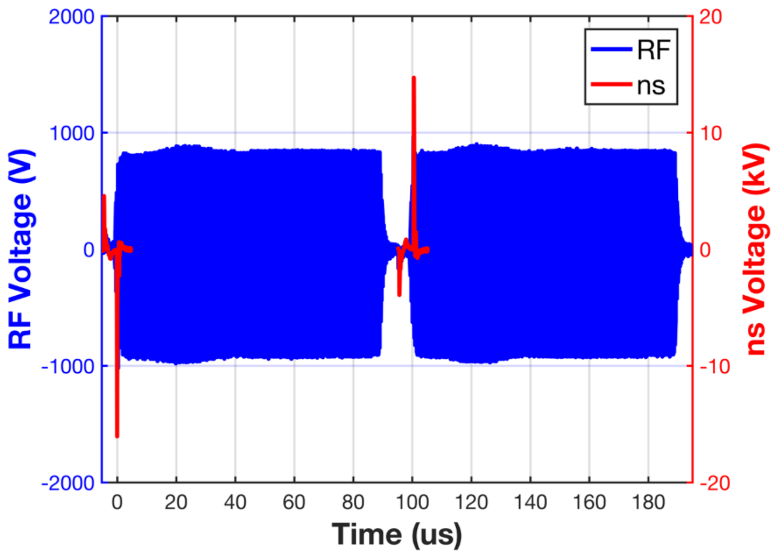
Ns Pulse / RF Hybrid Plasma



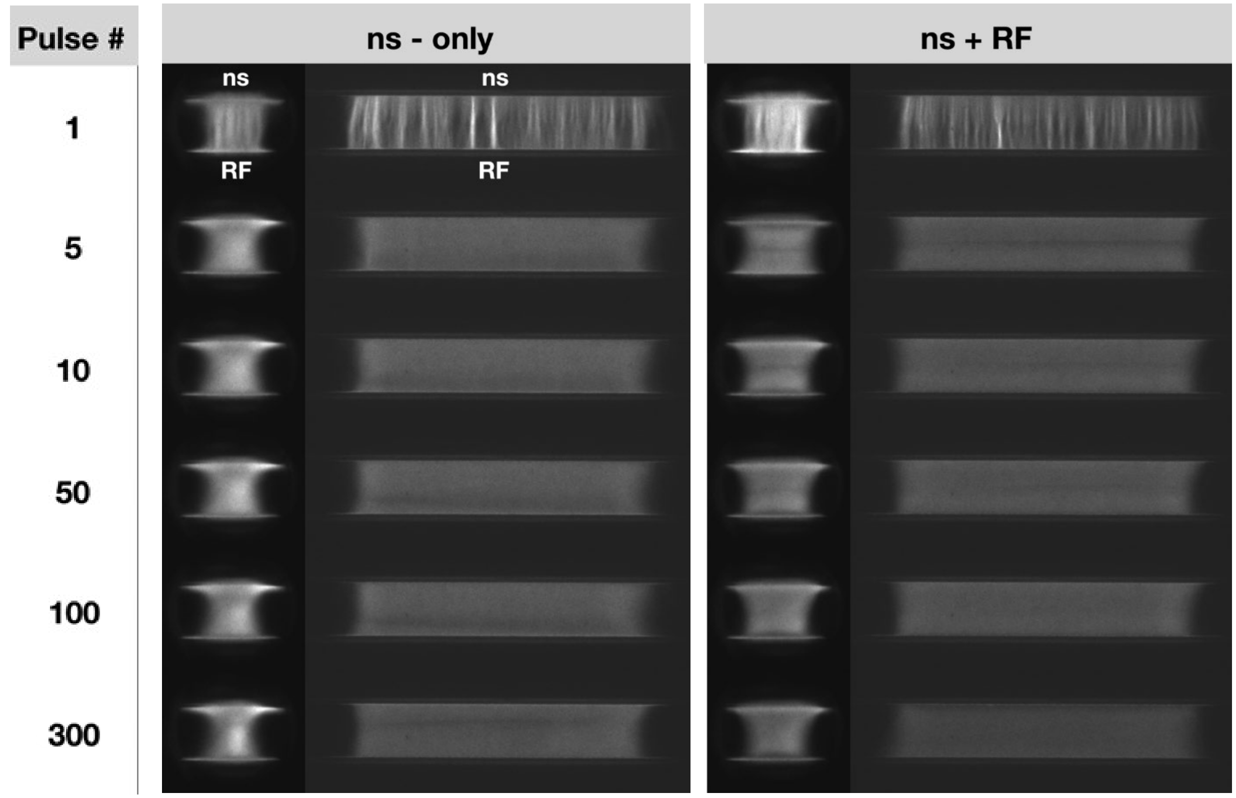


- **Single pair of electrodes, external to the reactor**
- **Ns pulses and RF bursts are separated in time**
- **RF voltage couples energy to electrons generated by the pulses**

Discharge Waveforms and Plasma Images

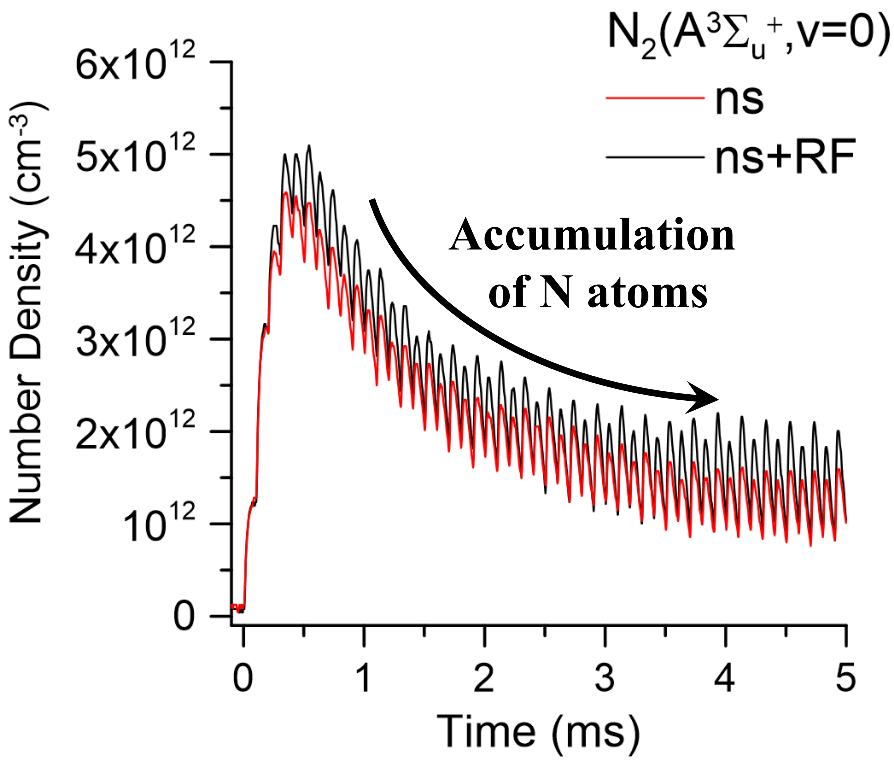


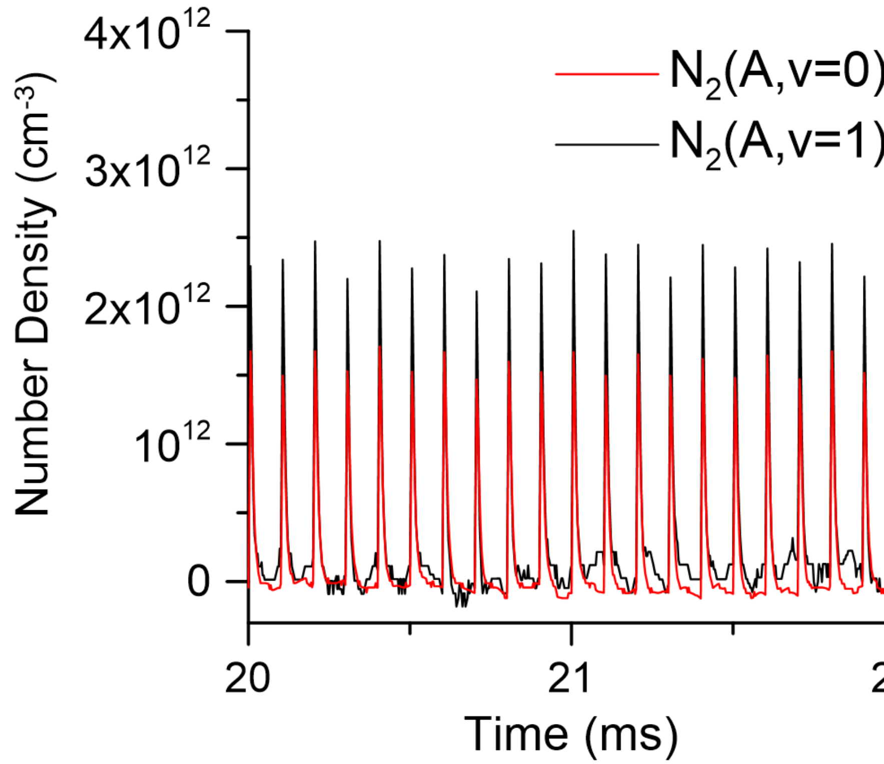
Ns pulse / RF voltage waveforms



- 100 Torr N_2, ν=10 kHz, diffuse plasma during entire burst
- RF-induced electron oscillations improve plasma uniformity
- Similar behavior up to P=1 atm and ν=100 kHz

Ns Discharge:
Generation of $N_2(A^3\Sigma_u^+)$, N, and H atoms





- $[N_2(A,v=0)]$ in 100 Torr of **nitrogen**, with and without RF
- $[N_2(A,v=0,1)]$ in 100 Torr of **1% H_2-N_2**, without RF

- Almost no effect of RF voltage on $[N_2(A)]$
- Quenching by N atoms,

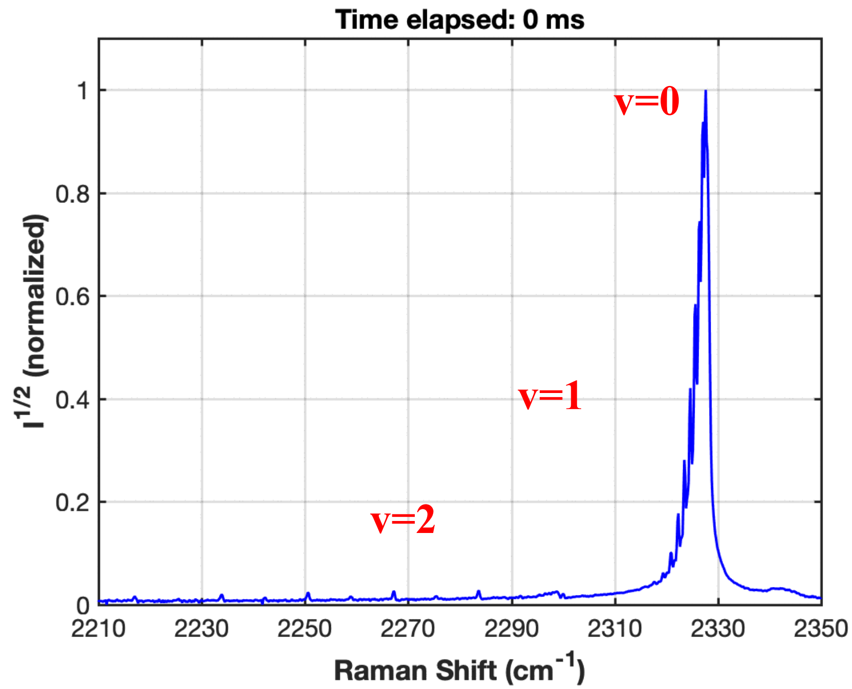
$N_2(A) + N \rightarrow N_2(X) + N$

- Rapid decay between the pulses
- Quenching by N <u>and</u> H atoms,

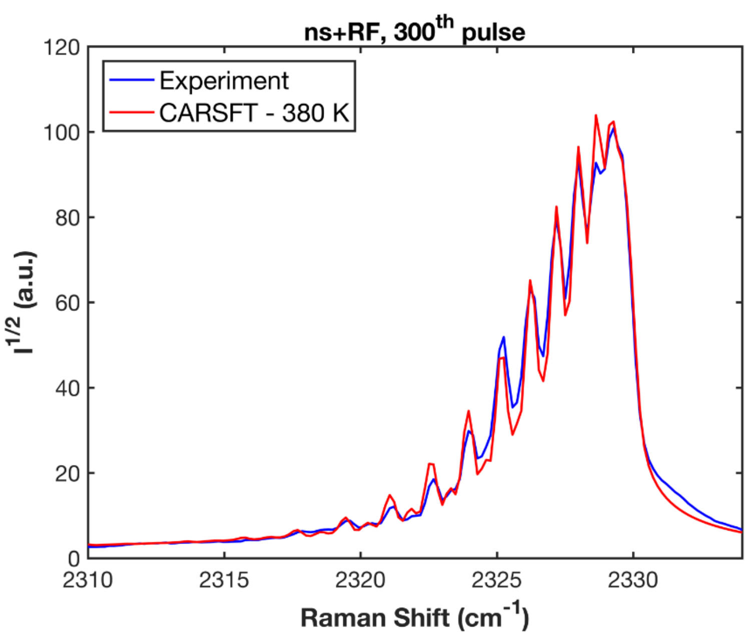
$N_2(A) + H \rightarrow N_2(X) + H$

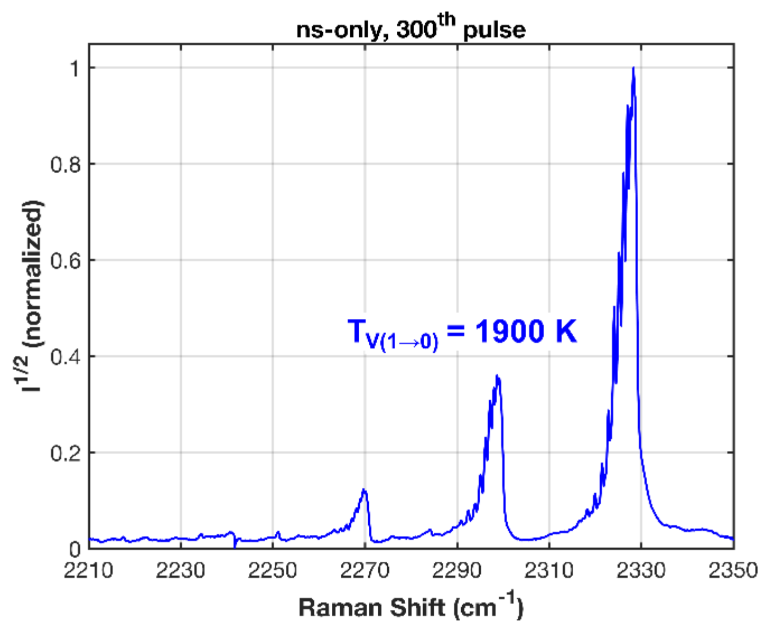
Ns / RF Discharge: N_2 Vibrational Excitation

- **Nitrogen, P=100 Torr, pulse rep rate 10 kHz**
- **Ns / RF bursts (30 ms on, 70 ms off)**
- **Animation N_2 CARS spectra**



- **Strong nonequilibrium: T_v=1900 K, T=380 K**
- **Ns and RF: selective generation of excited species**





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Summary

- Electric field in pulsed plasmas: flow control *via* quenching of excited species, localized heating, coherent structure formation
- Field measured in plasma flow actuators, H_2-air plasmas (ps EFISH): quantification of plasma flow control, plasma-assisted combustion
- $N_2(A^3\Sigma)$, "dark" species controlling NO UV emission behind shock waves: measured in Mach 4-5 nonequlibrium flows (TDLAS and CRDS)
- TDLAS and CRDS: potential for $N_2(A^3\Sigma)$ and $O_2(a^1\Delta)$ measurements in shock tubes and shock tunnels, to understand NO UV radiation and O_2 dissociation
- Hybrid plasmas: selective generation of excited species and radicals, potential for isolation of plasma chemistry and catalysis mechanisms
- $N_2(A)$ and $N_2(v)$: generated selectively and measured in hybrid ns / RF plasmas (TDLAS, CARS). N, H, product species measurements are underway

Acknowledgments

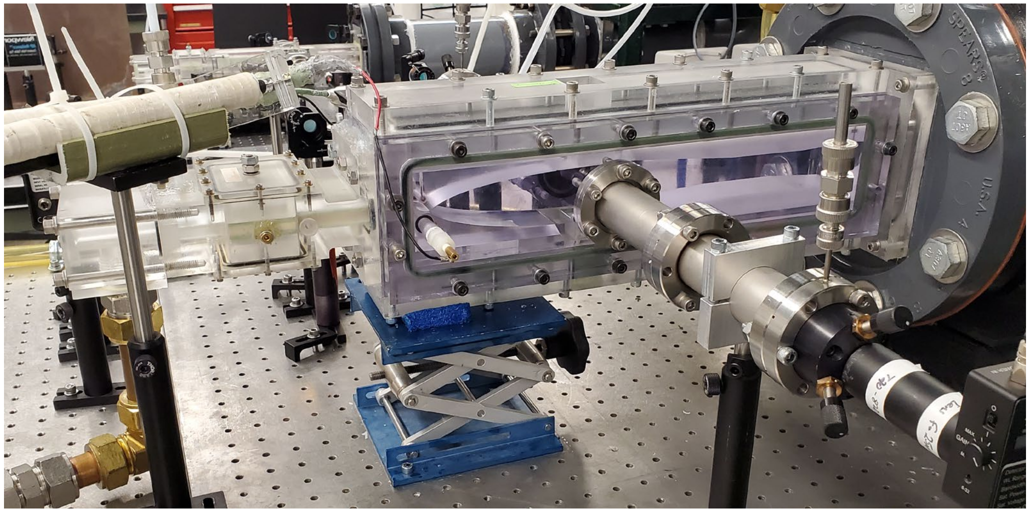
<u>Students and *Colleagues*:</u>

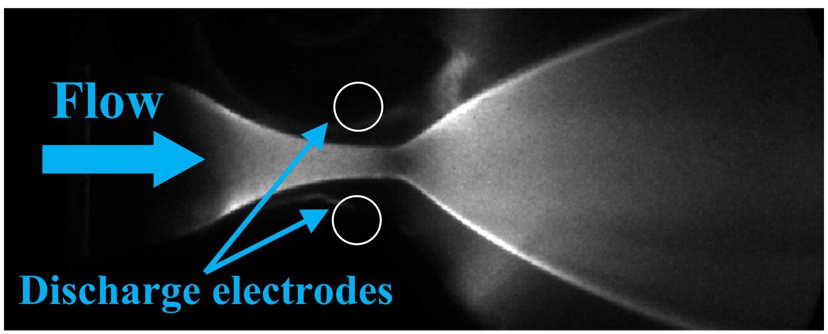
- **Ben Goldberg (OSU / Princeton U. / Sandia Livermore), Marien Simeni Simeni (OSU / U. Minnesota), Tang Yong (OSU / Tsinghua U.), Elijah Jans (OSU), Kraig Frederickson (OSU / US Navy), Ilya Gulko (OSU), *Bill Rich (OSU), Walter Lempert (OSU), Mo Samimy (OSU), Terry Miller (OSU Chemistry)***

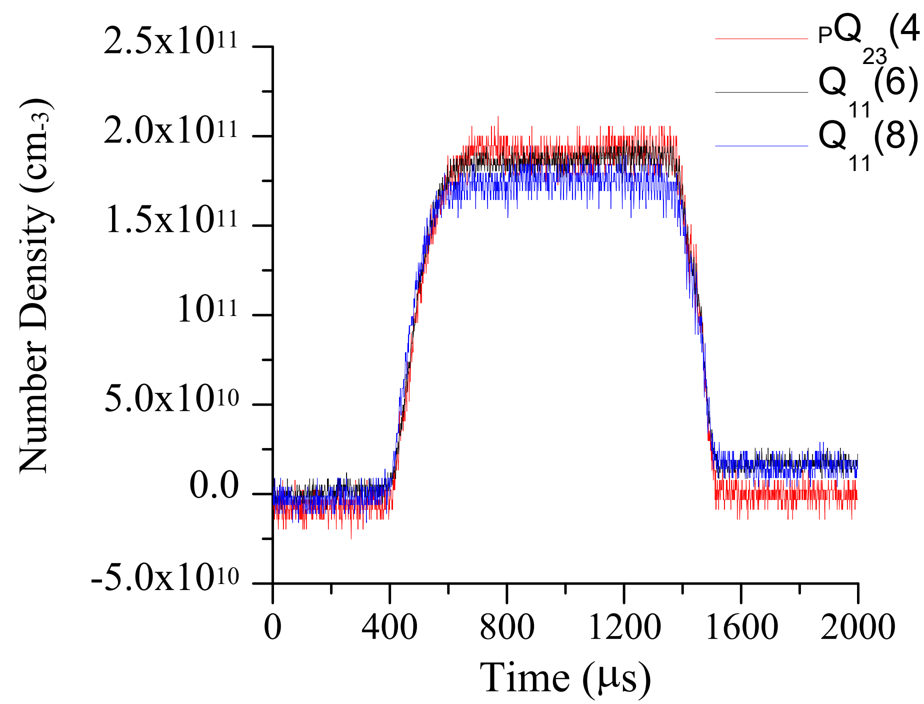
<u>Sponsors:</u>

- **AFOSR "Energy Transfer Processes in Nonequilibrium Hypersonic Flows"**
- **US DOE Plasma Science Center "Predictive Control of Plasma Kinetics: Multi-Phase and Bounded Systems"**
- **NSF "Fundamental Studies of Accelerated Low Temperature Combustion Kinetics by Nonequilibrium Plasmas"**
- **US DOE PSAAP-2 Center "Exascale Simulation of Plasma-Coupled Combustion"**
- **US DOE Collaborative Research Center for Studies of Plasma-Assisted Combustion and Plasma Catalysis**
- **US DOE Center for Low Temperature Plasma Interactions with Complex Interfaces**

This Just In: $N_2(A^3\Sigma_u^+)$ TDLAS in a Mach 5 Flow







- N_2, P_0 = 250 Torr, P=1.1 Torr (M = 4.3)
- ν=100 kHz discharge at the nozzle throat, discharge burst 1 ms long
- $[N_2(A^3\Sigma_u^+, v=0)] = 1.7 \pm 0.1 \cdot 10^{11}$ cm^{-3}, T = 66 ± 8 K
- Results consistent with CRDS measurements at the same conditions

Backup