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Diagnostics and Modeling of Plasma Assisted Combustion Kinetics

Igor Adamovich and Walter Lempert

Department of Mechanical and Aerospace Engineering
Ohio State University

OSU NETL group

Igor Adamovich, Walter Lempert, Sergey Leonov, J. William Rich, and Jeffrey Sutton

Sherrie Bowman, David Burnette, Ben Goldberg, Zak Eckert, Kraig Frederickson, Suzanne Lanier, Ting Li, Munetake Nishihara, Vitaly Petrischev, Annie Pulcini, Andrew Roettgen, Ivan Shkurenkov, Caroline Winters, Zhiyao Yin

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Plasma assisted combustion: why is it needed?

- **Ignition and combustion become unstable at the following conditions:**
  - **Low fuel-air (F/A) ratios, or equivalence ratios $\phi = (F/A) / (F/A)_{stoichiometric}$: fuel economy and NO_x reduction in gas turbines, internal combustion engines, jet engines, unmanned aerial vehicles (UAV)**
  - **Low pressures in combustor (i.e. jet engines at high flight altitudes): preventing engine flameout**
  - **High flow velocities in combustor (i.e. jet engines at high flight speed, scramjet engines)**

- **Major new capability provided by nonequilibrium plasmas:**
  - **Efficient generation of a pool of highly reactive radical species**
  - **Radicals react rapidly with fuel, even at low temperatures**
  - **A wide range of plasma chemical chain branching / fuel oxidation reactions**
  - **This may “nudge” conventional combustion chemistry in the right direction, over a wide range of equivalence ratios, pressures, and flow velocities**

Nonequilibrium plasma for ignition, combustion, and flameholding: how does this work?

- High peak reduced electric field (E/N), high electron energy ($\varepsilon \sim E/N$), especially in transient plasmas (nsec pulse duration). Use of short pulse duration also improves plasma stability.
- Significant input energy fraction (tens of %) into inelastic electron impact processes, dissociation and electronic excitation: efficient generation of metastable and radical species (N_2*, O*, Ar*, O, H, OH, CH); more radicals generated during N_2*, O*, Ar* reactions
- Large pool of radicals enables fuel oxidation at low temperatures, accelerates oxidation at high temperatures
- **Effect of plasma-generated radicals on fuel-air flows (over last ~10-20 years):**
  - Reduction of ignition delay at $T_0 > T_{thermal}$ (up to 2-3 orders of magnitude, shock tubes)
  - Reduction of ignition threshold at $T_0 < T_{thermal}$ (up to 100-200 K, plasma flow reactors)
  - Increase of flame blow-off velocity (up to a factor of 2, premixed turbulent flames)
  - Reduction of lean flammability limit (up to $\Delta\phi/\phi \sim 10\%$, premixed turbulent flames)
  - Critical for tgnition and flameholding in high-speed flows
- **Critical issues / concerns:**
  - Plasma stability at high pressures (discharge filamentation = rapid thermalization)
  - Scarcity of experimental data at controlled, well-characterized plasma conditions
  - Validation of kinetic models, developing quantitative predictive capability

PAC experiments / modeling goals and approaches at NETL

Goals

- Quantitative data in well-characterized plasma assisted combustion experiments: temperature, species number densities, vibrational state populations, electric field, electron density
- Quantify the effect of plasma generated species – radicals and excited states – on fuel oxidation, ignition, combustion, and flameholding
- Elucidate detailed kinetic mechanisms, develop predictive kinetic models of nonequilibrium plasma assisted combustion processes, assess and validate the models

Approaches

- **Experimental Platform I.** Plane-to-plane, high repetition rate nsec pulse discharge: large-volume, premixed, diffuse plasma chemical fuel oxidation and ignition at near-0-D conditions.
- **Experimental Platform II.** Point-to-point, single-pulse nsec pulse discharge: kinetics of energy transfer among excited species and radicals at high energy loadings per molecule
- **Kinetic modeling.** Integrated model of electric discharge dynamics, plasma kinetics / chemistry, and "conventional" hydrogen / hydrocarbon chemistry mechanism

Kinetic modeling of nonequilibrium fuel-air plasmas: brief model overview

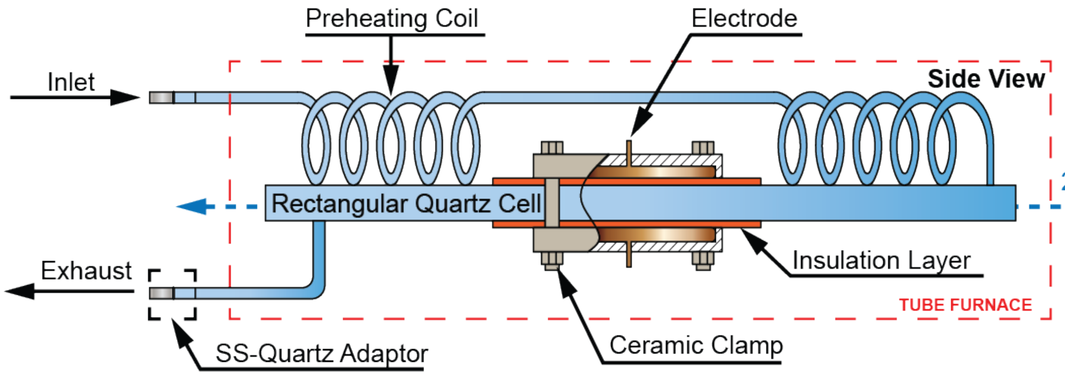
If quasi-0-D geometry is assumed:

- **Boltzmann equation** for EEDF (two-term expansion, experimental cross sections): predict rates of electron impact excitation, dissociation, and ionization processes
- **Charged species equations** (ionization, recombination, attachment, detachment processes, ion-molecule reactions): predict electron density in plasma
- **Excited neutral species equations** (electron impact excitation, non-reactive and reactive quenching): predict contribution to radical species formation
- **Master equation** for N_2 (X,v) populations; vibration-translation (V-T), vibration-vibration (V-V) processes, vibrational-chemistry (V-Chem) enhancement of reaction rates
- **Neutral species reactions:** fuel-air air chemistry, enhanced by radical production in plasma

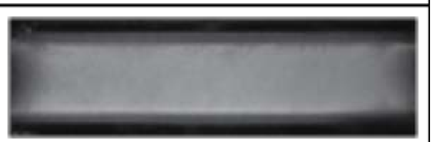
Quasi-1-D and 2-D (plane or axisymmetric) geometry adds:

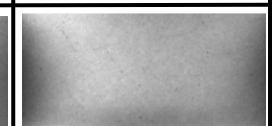
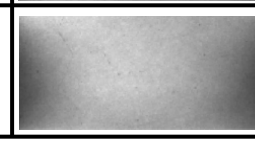
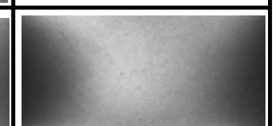
- **Poisson equation** for the electric field: predict electric field in plasma, cathode voltage fall
- **Coupling between chemistry, transport processes** (diffusion, conduction), and flow
- Nonequilibrium plasma model / code used as a starting point: non-PDPSIM (M. Kushner), widely used in low-temperature plasma community, well-documented

Experimental Platform I:
premixed, mildly preheated H_2-air, CH_4-air, C_2H_4-air, C_3H_8-air



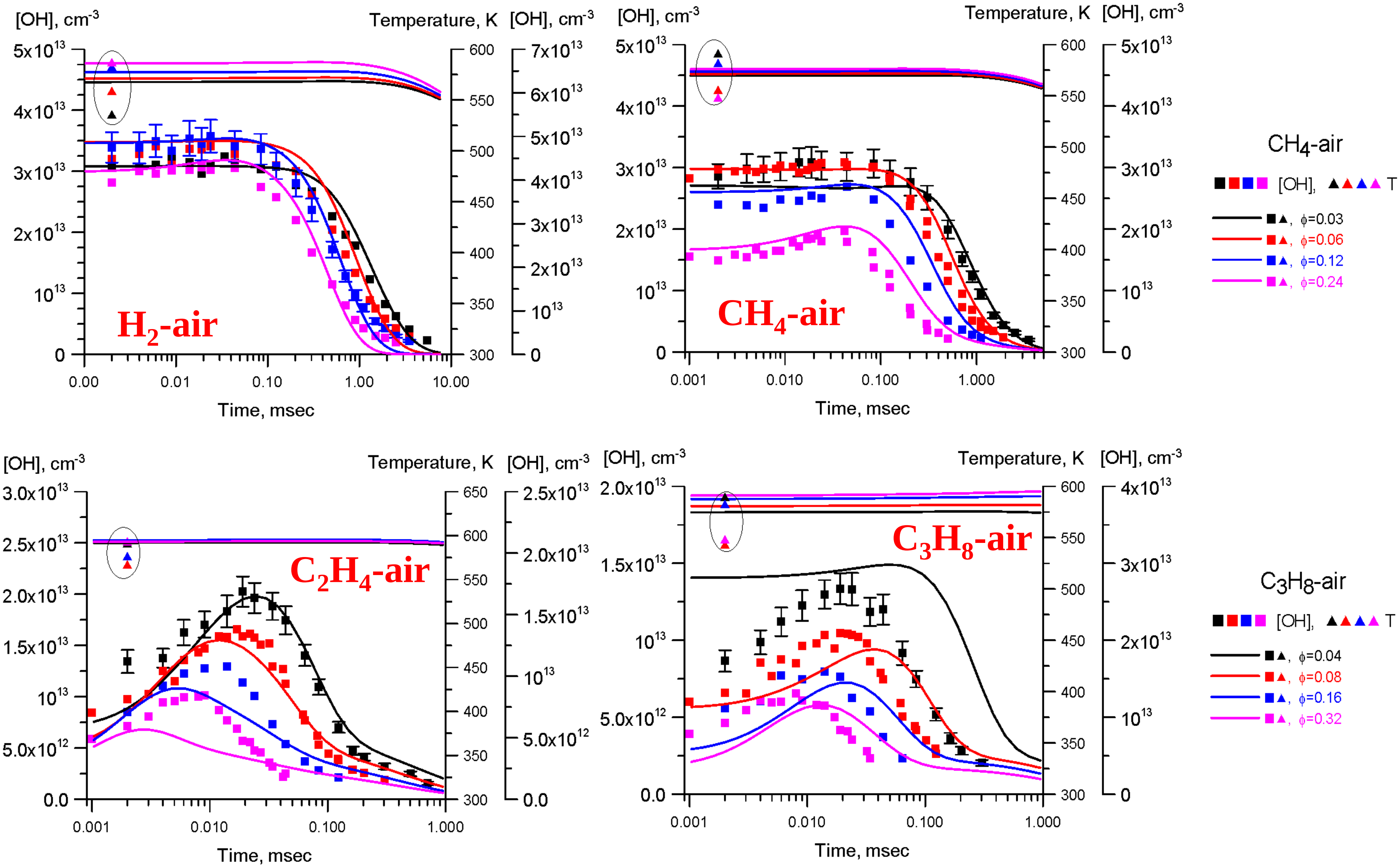
- Discharge dimensions **1 cm x 2 cm x 6 cm**
- Entire cell placed inside a tube furnace
- Diffuse, volume filling plasma
- Large-volume ignition (no propagating flame)
- "Near 0-D" conditions

Pressure (torr)	H_2-air , pulse #10
100	
300	
500	

	Pulse #10	Pulse #100
H_2 – air, ϕ=0.3 T_0=500 K, P=100 torr		
C_2H_4 – air, ϕ=0.3 T_0=500 K, P=100 torr		

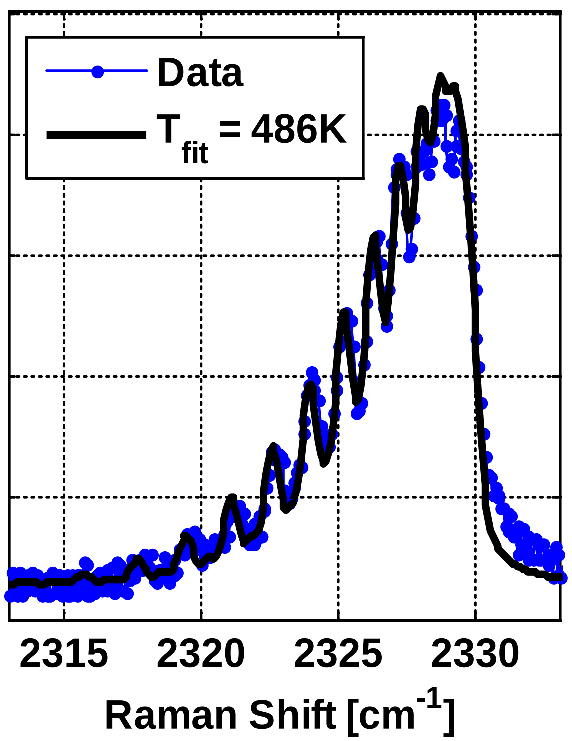
- H_2-air, C_2H_4-air, CH_4-air, and C_3H_8-air at T_0= 100-300° C, P=50-500 torr, ϕ=0.03-1.2
- Repetitive nanosecond pulse "bursts": 20-25 kV peak, ~10-50 nsec, ν=10-40 kHz, 50-100 pulses
- Ample optical access (LIF, Two-Photon LIF, psec CARS) for species and temperature measurements
- OH LIF absolute calibration: adiabatic burner in Hencken burner, Rayleigh scattering

[OH] on centerline after a 50-pulse burst, T_0=500 K, P=100 torr: comparison with 0-D kinetic modeling (A. Konnov mechanism)

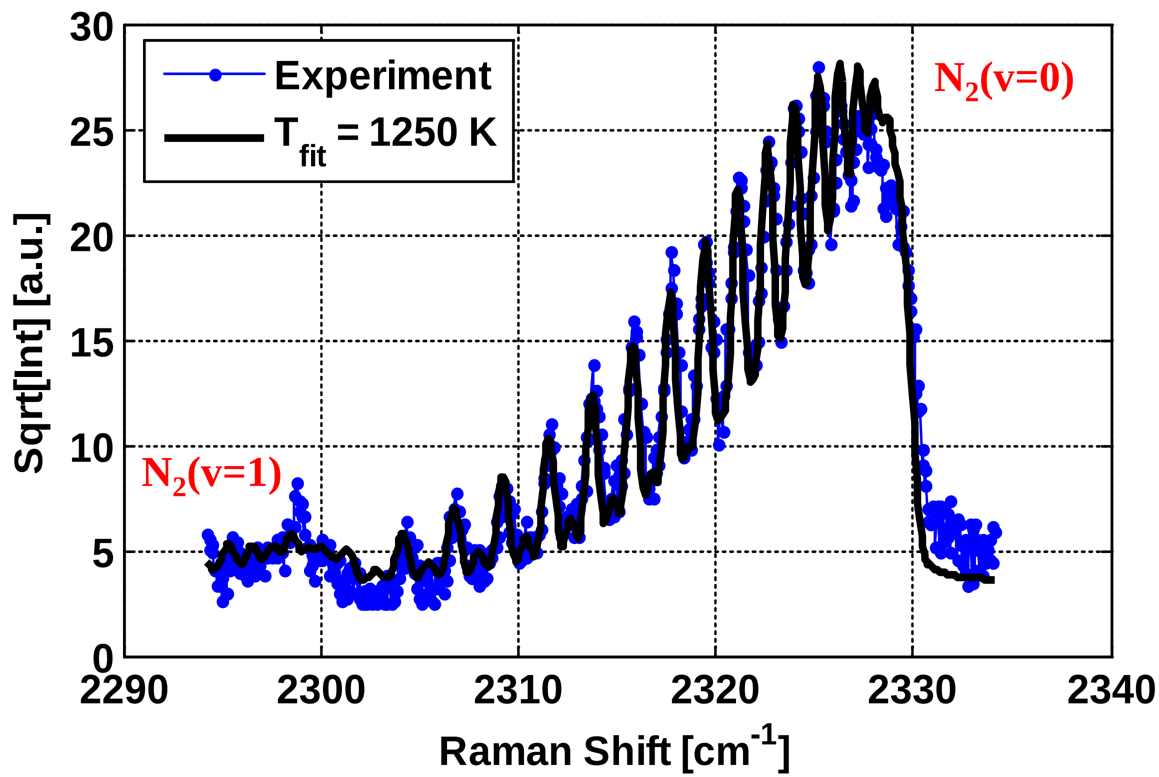


Good agreement for simple fuels, worse for more complex hydrocarbons

Typical N_2 psec CARS spectra and best fit T_{rot} in air and H_2-air



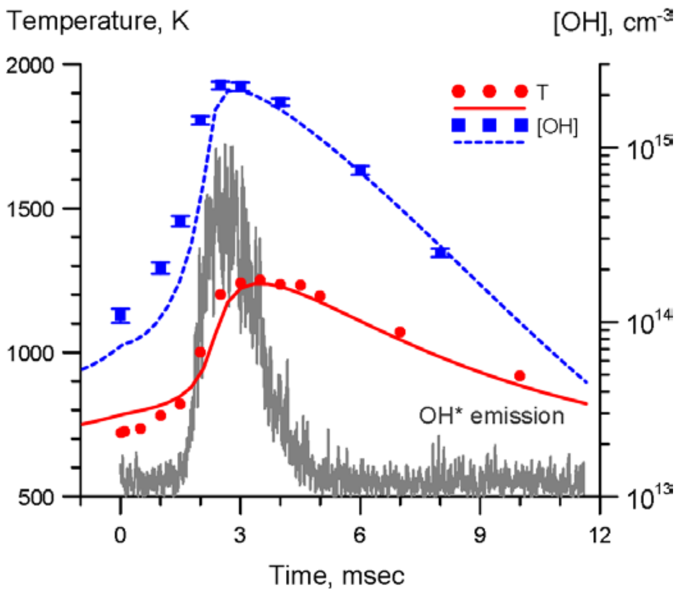
100-shot accumulation spectrum
in 100 torr air, T_0 = 500 K,
95% confidence interval ~15 K



100-shot accumulation spectrum
in 92 torr H_2 –air during ignition, T_{peak}= 1250 K

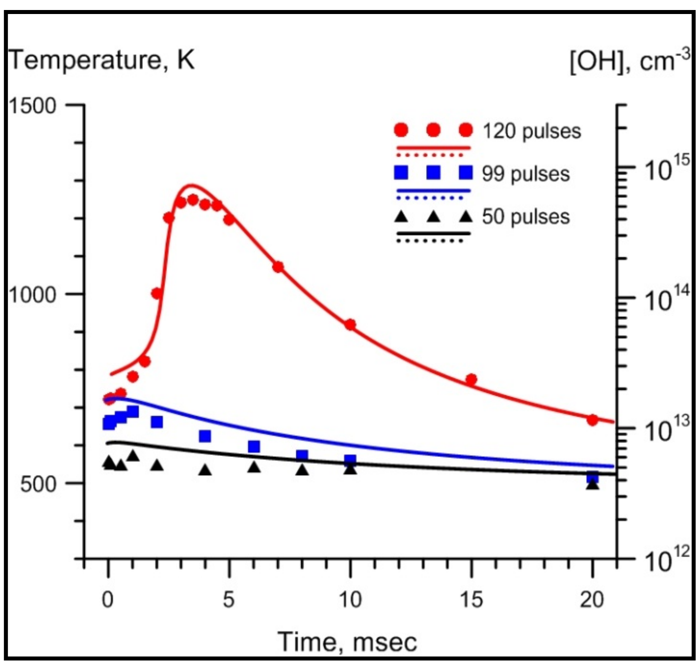
Also yields N_2(v=1) level population, N_2 vibrational temperature

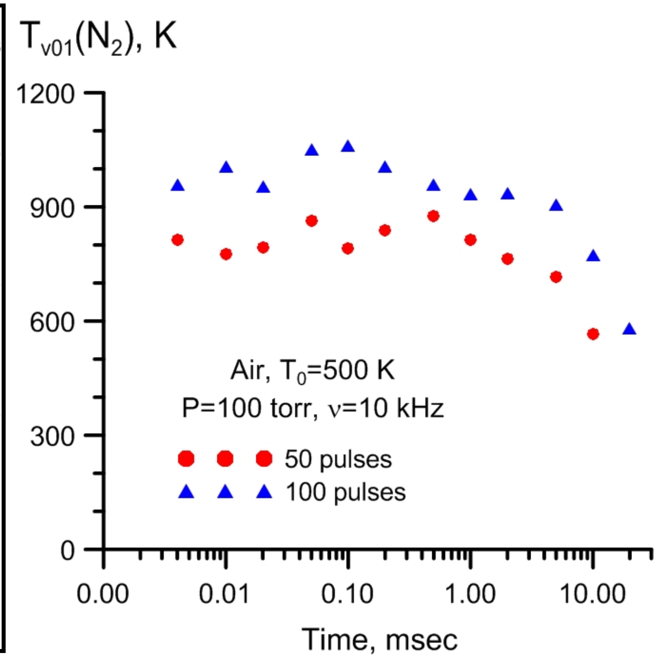
[OH] (LIF) and psec CARS (T, T_v (N_2)) measurements during plasma assisted ignition of H_2-air



T_0=500 K, P=92 torr, ϕ=0.4, ν=10 kHz, 120 pulses

- **[OH] by OH LIF (Proc. Comb. Symp. 2013)**
  - 0-D model: good agreement with measured [OH] at the end of the burst, during ignition
- **T, T_v (N_2) by psec CARS (Comb. Flame 2013)**
  - Measured temperature in excellent agreement with 0-D model predictions from previously published work





- Threshold ignition temperature T_f ~ 700 K, lower than autoignition temperaure, T_a ~ 900 K
- N_2 vibrational temperature remains quite low
- Use pin-to-pin discharge to enhance energy loading
- This provides far more stringent test of the model

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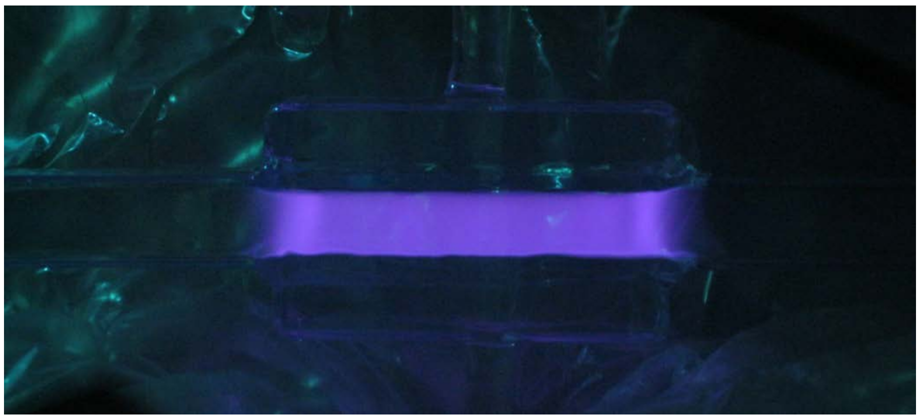
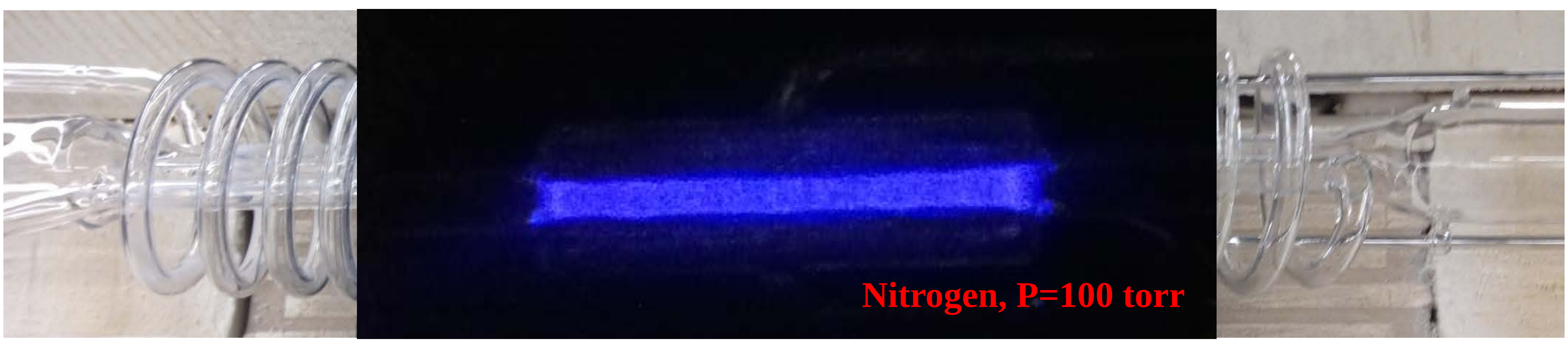
On-going high-pressure (~1 bar) experiments: use of liquid metal electrodes (Ga-In-St) in a "Wolverine" cell

- Electrodes are fully encapsulated in quartz cells
- No corona outside the channel, no damage of dielectric layers
- No discharge pulse energy reduction and / or "drifting"



Discharge test with salt water electrodes
(cells on top and bottom of the channel)
P=40 torr, air, ν=10 kHz

Discharge channel, electrode cells filled with liquid metal (galinstan)

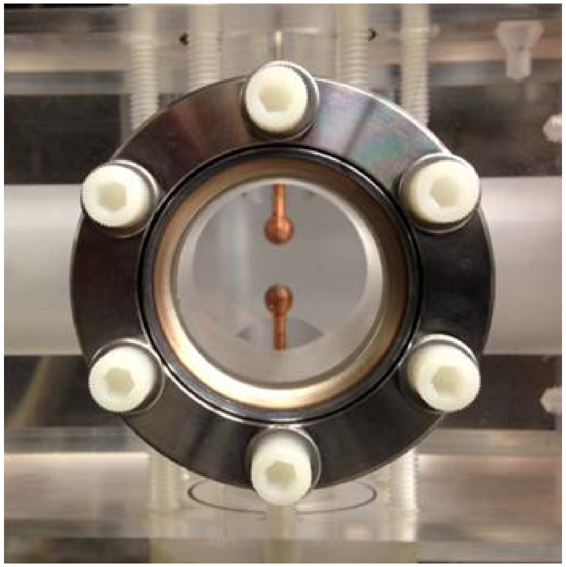


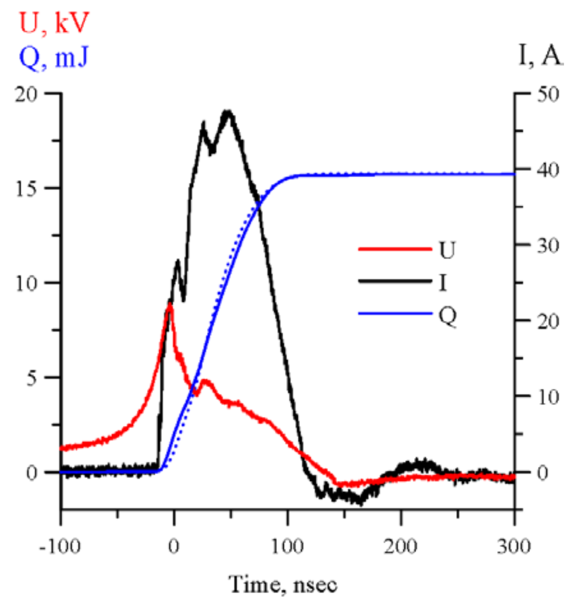
New high-pressure discharge channel, with electrode cells and preheating coil shown, gap L=5 mm

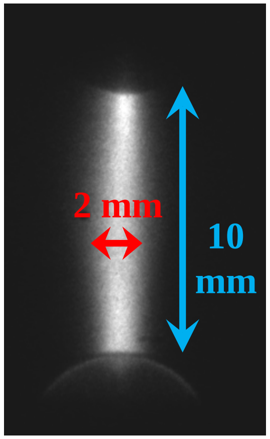
Experimental platform II:

N_2, air, H_2-air, C_2H_4-air, initially at room temperature

Air, P=100 torr, 16 mJ/pulse







- **<u>No dielectric barrier:</u> stable, diffuse, single filament discharge (~10 mm gap, ~2-3 mm diameter) at P=0.1-0.2 atm**
- **<u>With dielectric barrier</u>: volume-filling discharge (~1-2 mm gap, ~10 mm diameter) at P=0.5-1.0 atm**
- **High peak electric field (~10 kV/cm), electron density (~10^{14} - 10^{15} cm^{-3}), electron temperature (~5 eV)**
- **High energy loading per molecule (up to ~ 0.2-0.3 eV/molecule), strong vibrational excitation, high concentrations of radical species (N_2(X,v) molecules, N, O, H atoms, OH, NO …)**
- **Spatially resolved temperature, vibrational level populations, species concentrations measurements**
- **"Test bed" to study vibrational and electronic energy transfer, plasma chemical reactions in high energy loading, highly transient plasmas**

Optical diagnostics data
for insight into air and fuel-air plasma chemistry

Key plasma parameters controlling coupled energy and its partition among different channels (elastic, vibrational, electronic, dissociation, ionization):

- **Electric field (CARS / 4-wave mixing)**
- **Electron density (Thomson scattering)**
- **Electron temperature (Thomson scattering)**

Estimating E, n_e, and T_e from voltage and current results in significant uncertainty

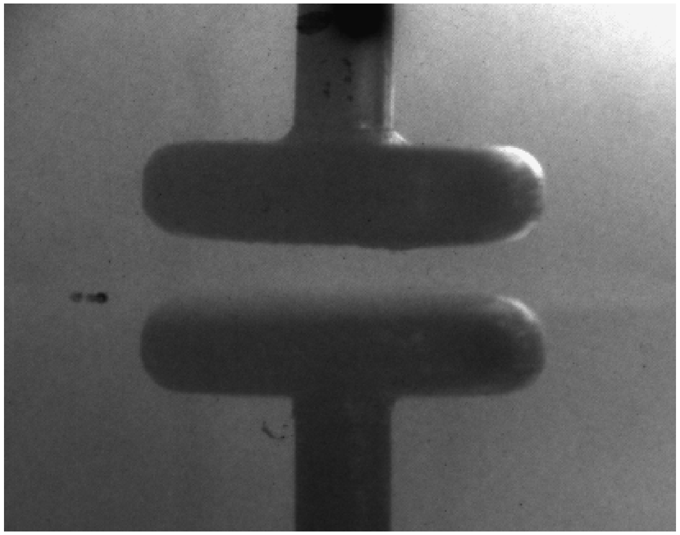
Kinetic models need to predict them accurately, given applied voltage waveform

Key plasma parameters affecting plasma chemistry:

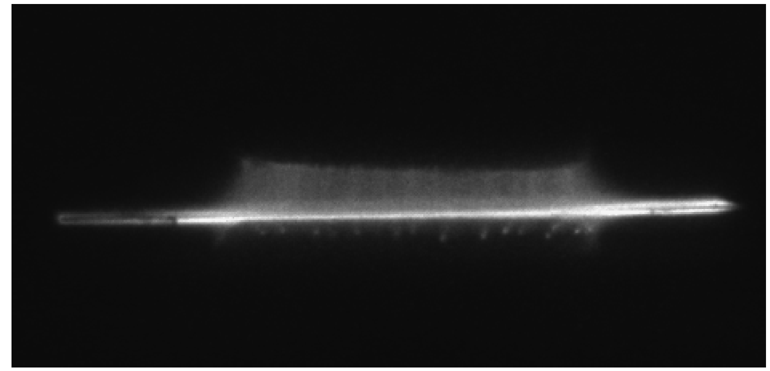
- **Temperature and vibrational level populations (psec vibrational and rotational CARS, Rayleigh scattering, spontaneous Raman scattering)**
- **Radical species number densities (LIF, TALIF), including 1-D and 2-D imaging**

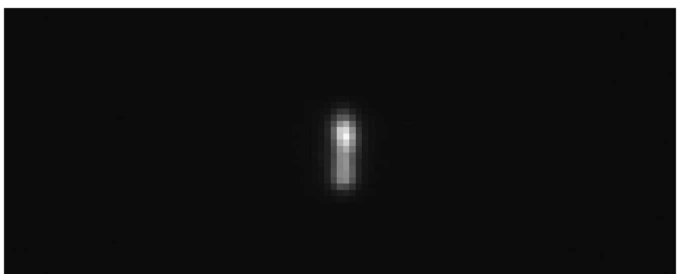
Time-resolved and spatially-resolved data are highly desirable

Electric field measurements, plane-to-plane nsec pulse discharge in H_2 (psec CARS / 4-wave mixing)

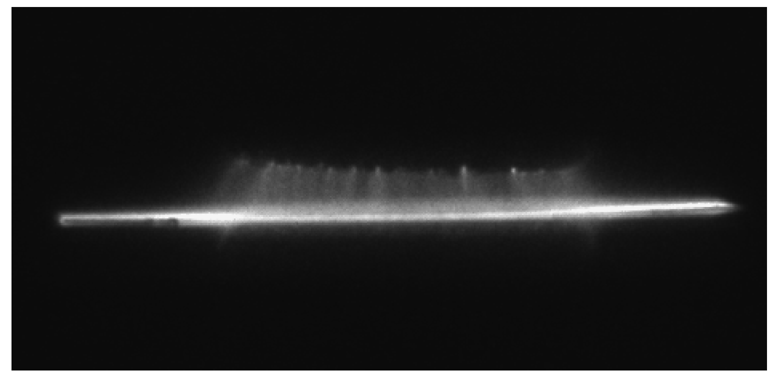


H_2, 430 torr
Dielectric barrier:
100 μm glass plate



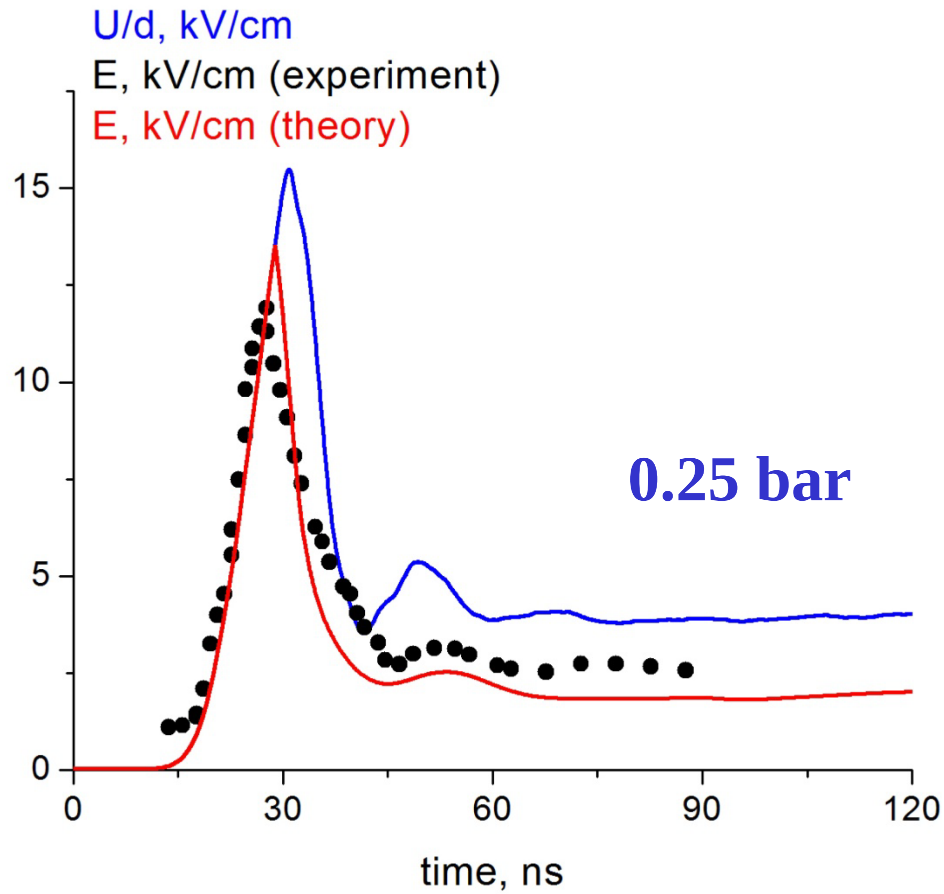


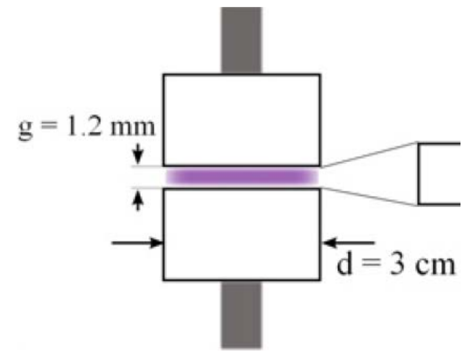
H_2, 220 torr, no dielectric barrier



- H_2, P=0.2-1.0 bar, discharge between two plane electrodes, 1 mm gap, pulse repetition rate 100 Hz
- With or without dielectric barrier (glass plate 100 μm thick on one of the electrodes)
- Without dielectric: single filament discharge; with dielectric: diffuse volume-filling discharge
- Time resolution 0.2 nsec
- Calibration: electrostatic field between two planes

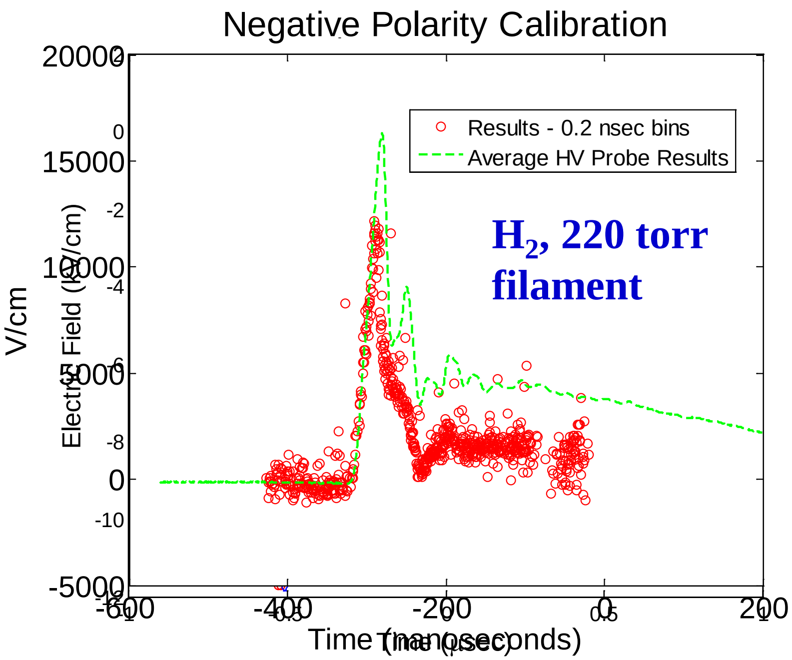
Experimental (RUB) and predicted (OSU) electric field in a plane-to-plane nsec pulse discharge in N_2

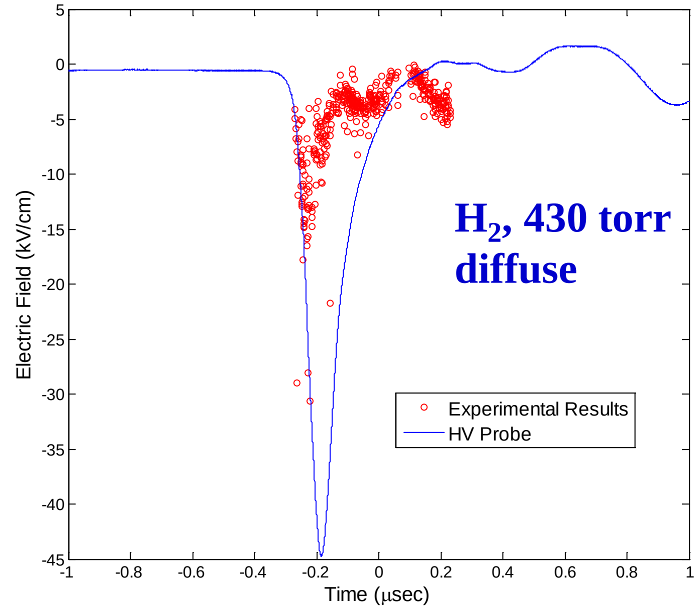


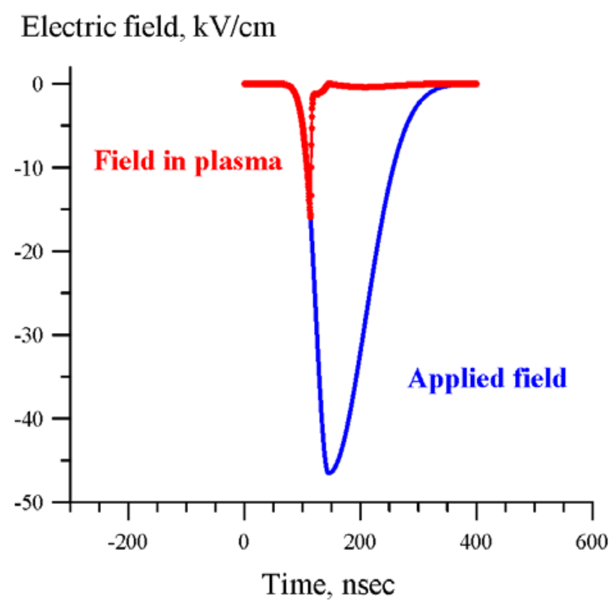


- Experiment (Ruhr Universität Bochum, Germany, nsec pulse 4-wave mixing): N_2, P=0.25 bar, 1.2 mm gap, pulse repetition rate 2 kHz
- Field in plasma before breakdown follows applied voltage, E=U/d
- Field in plasma after breakdown is significantly lower, significant cathode voltage fall
- Model predictions for time-resolved E-field, pulse current: good agreement with experiment

Preliminary results: psec CARS E-field in a nsec pulse discharge between two plane metal electrodes

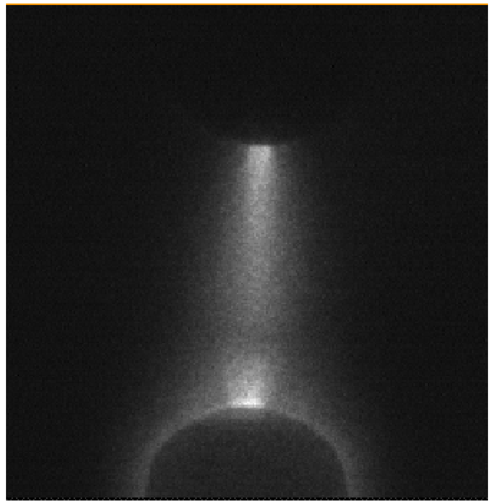


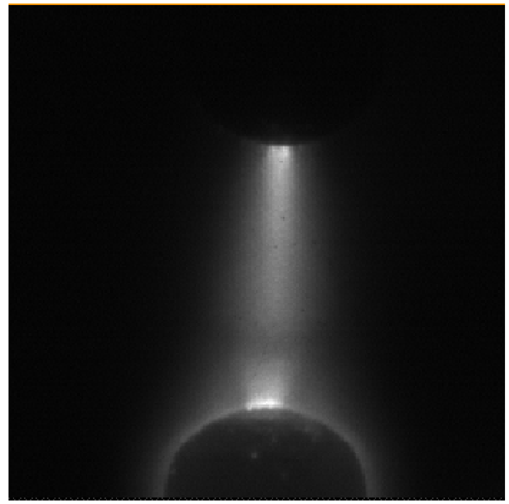




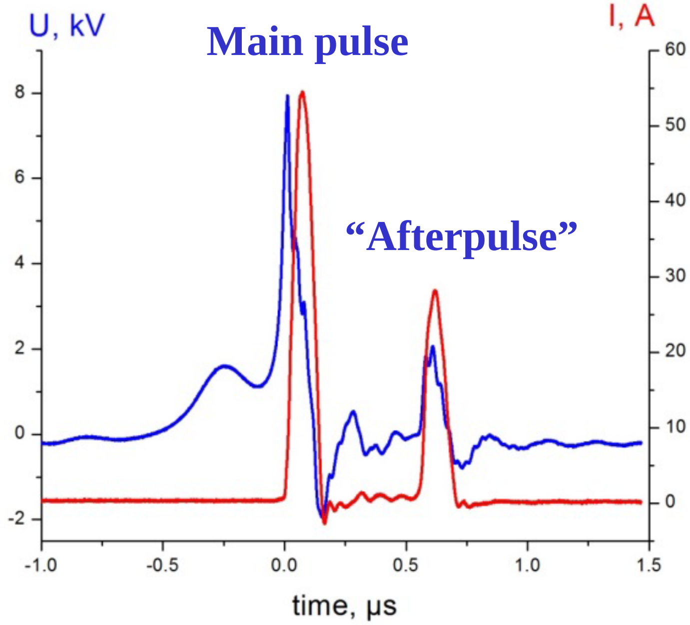
- H_2, discharge between two plane electrodes, 1 mm gap, pulse repetition rate 10 Hz
- With or without dielectric barrier (glass plate 100 μm thick on one of the electrodes)
- Without dielectric: single filament discharge
- With dielectric: diffuse volume-filling discharge
- Time resolution 0.2 nsec (0.2 nsec “time bins” are used)
- Absolute calibration: electrostatic field between two planes
- Kinetic modeling calculations are underway

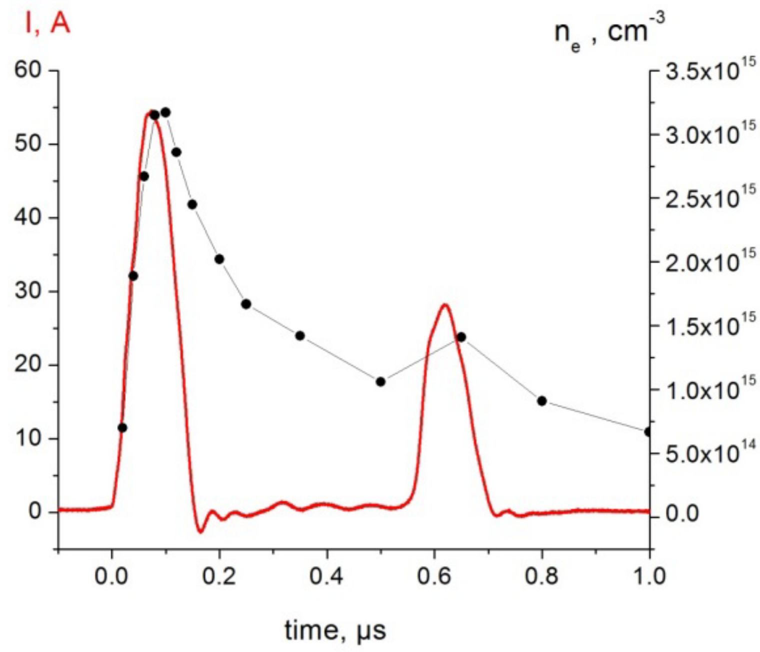
Thomson scattering electron density measurements in diffuse filament discharges in He, H_2-He, O_2-He



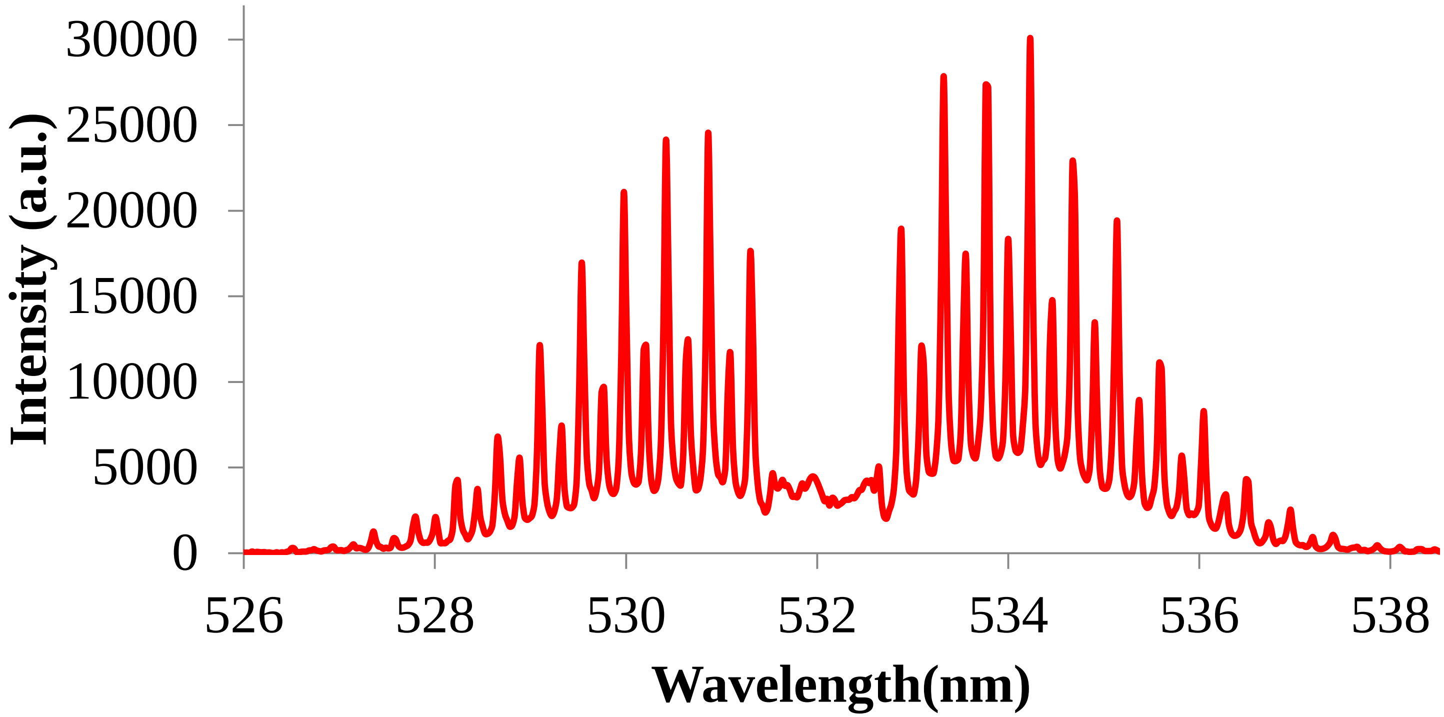


Helium, 200 torr, 10 mm gap, camera gate 150 nsec
Left: single pulse; right: 100-pulse average





Absolute calibration of Thomson scattering data using N_2 rotational Raman spectra



No discharge

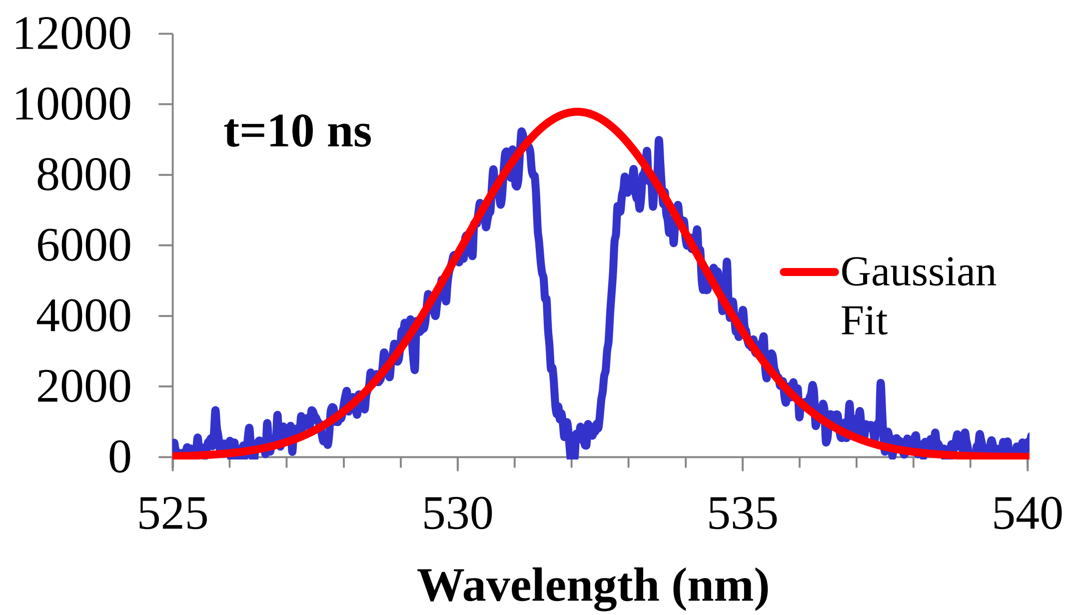
Used for Thomson scattering calibration

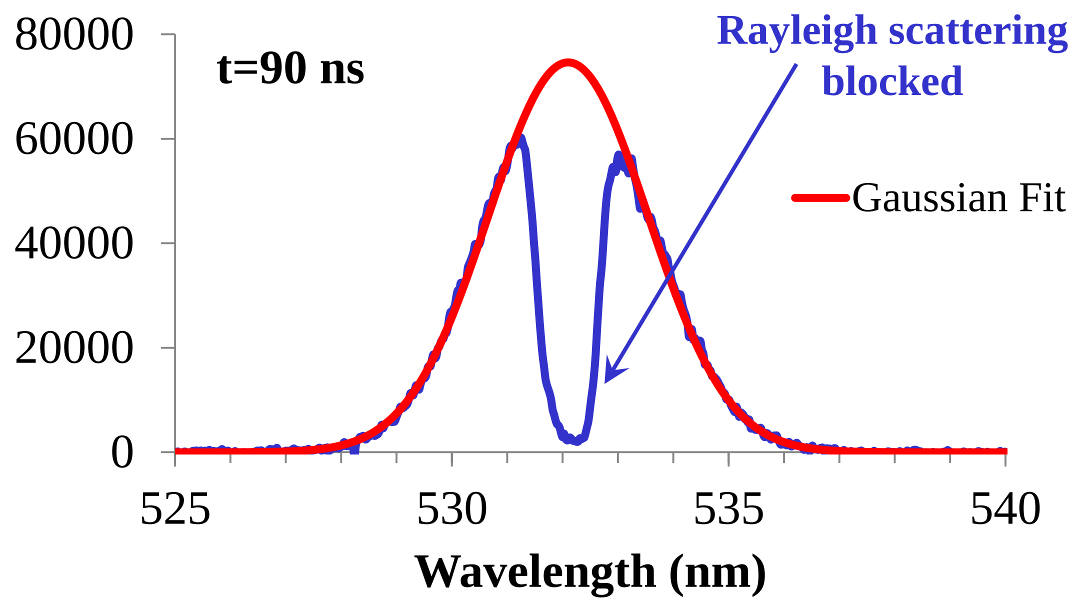
Laser energy 500 mJ/pulse

6 minutes accumulation time

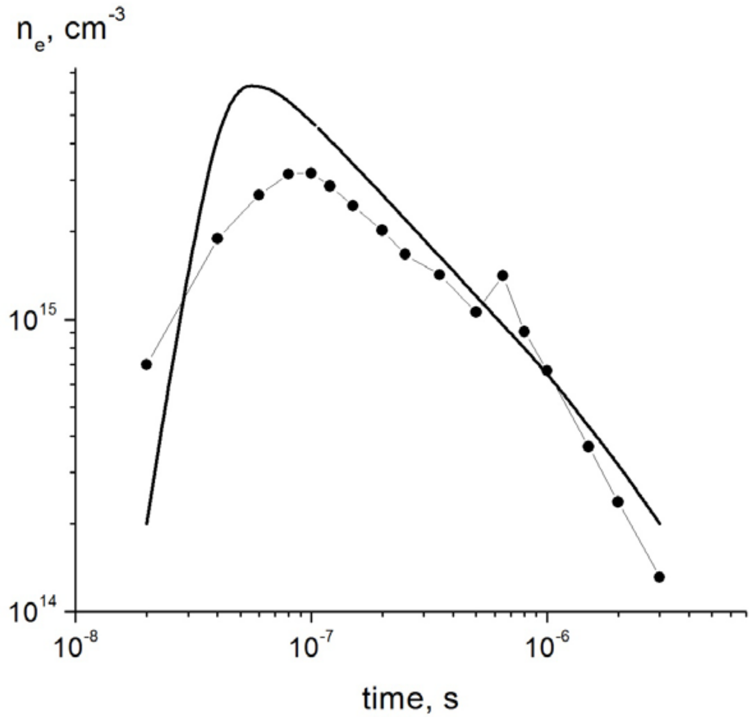
Sample Thomson scattering spectra during and after discharge pulse (t=0-250 nsec)

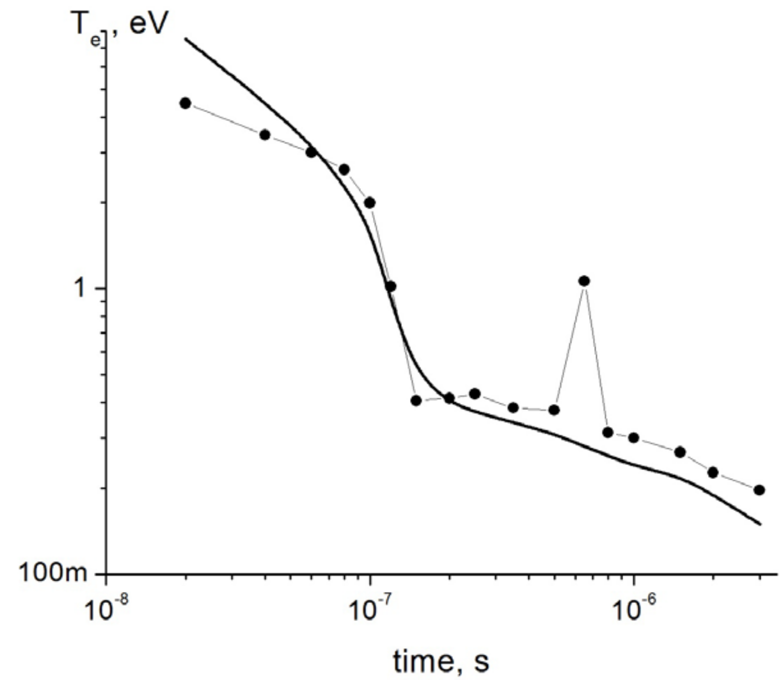
- Helium, 200 torr
- Peak voltage 7 kV
- Peak current 60 A
- Coupled energy ~18 mJ/pulse
- Pulse repetition rate 90 Hz
- t=0 beginning of pulse current rise
- Laser energy 500 mJ/pulse
- 6 minutes accumulation (~3200 shots)





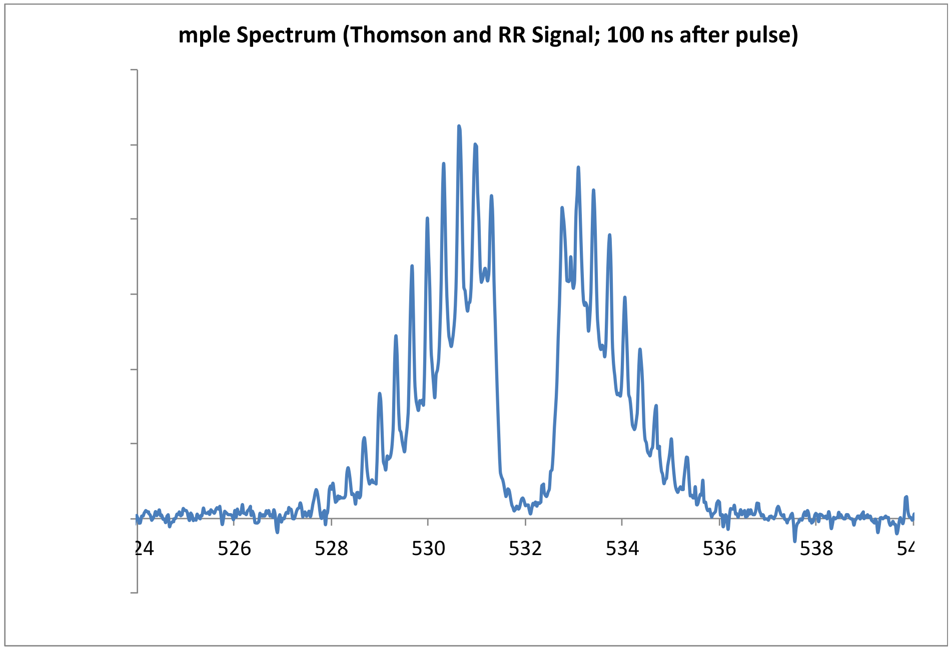
Experimental and predicted (2-D model) electron density and electron temperature in helium

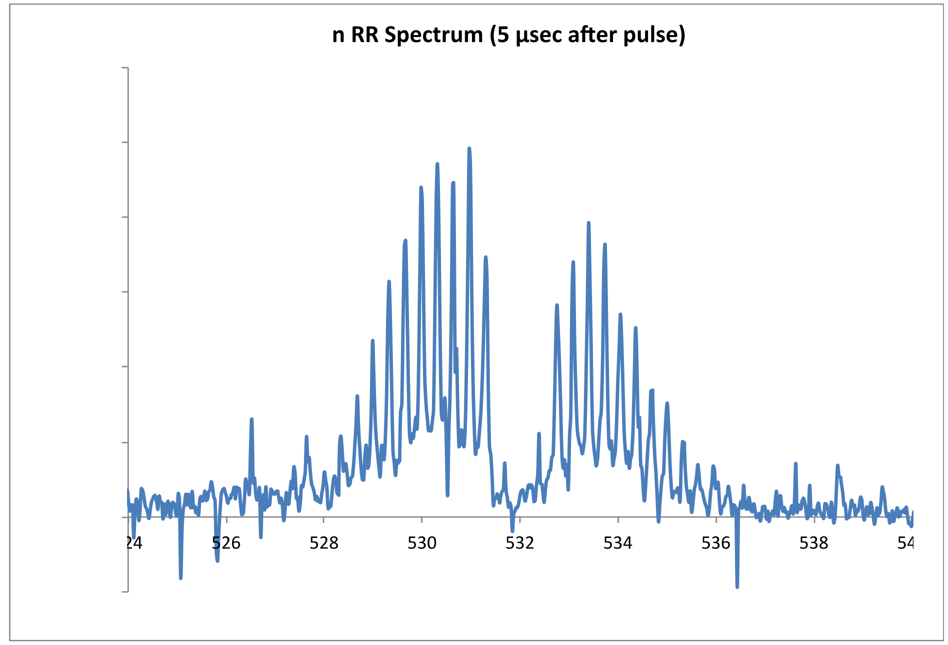


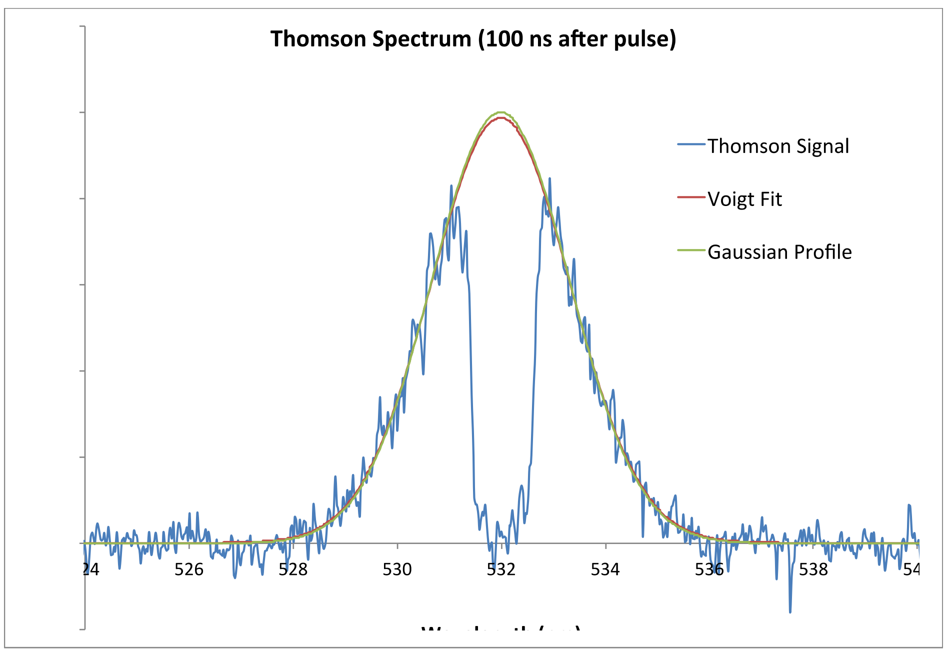


- **Breakdown may be not fully resolved in the experiment (time resolution ±15 nsec)**
- **High electron temperature (up to ~5 eV) during breakdown onset**
- **Peak n_e during the pulse, $n_e \sim 3 \cdot 10^{15}$ cm^{-3}, followed by rapid decay in the afterglow**
- **"Residual" T_e in the afterglow (maintained by superelastic processes) $T_e \sim 0.3$-0.4 eV)**
- **Ongoing work: electron density measurements in molecular gases (H_2, O_2, N_2, air)**
- **Rotational Raman spectra are "in the way" (except for H_2), but**
- **High electron density, $\sim 10^{14} \sim 10^{15}$ cm^{-3} helps inferring n_e , T_e from underlying "envelope"**

Combined Thomson / Raman spectra in nsec pulse discharges in O_2-He mixtures







10% O_2 in He, P=100 torr

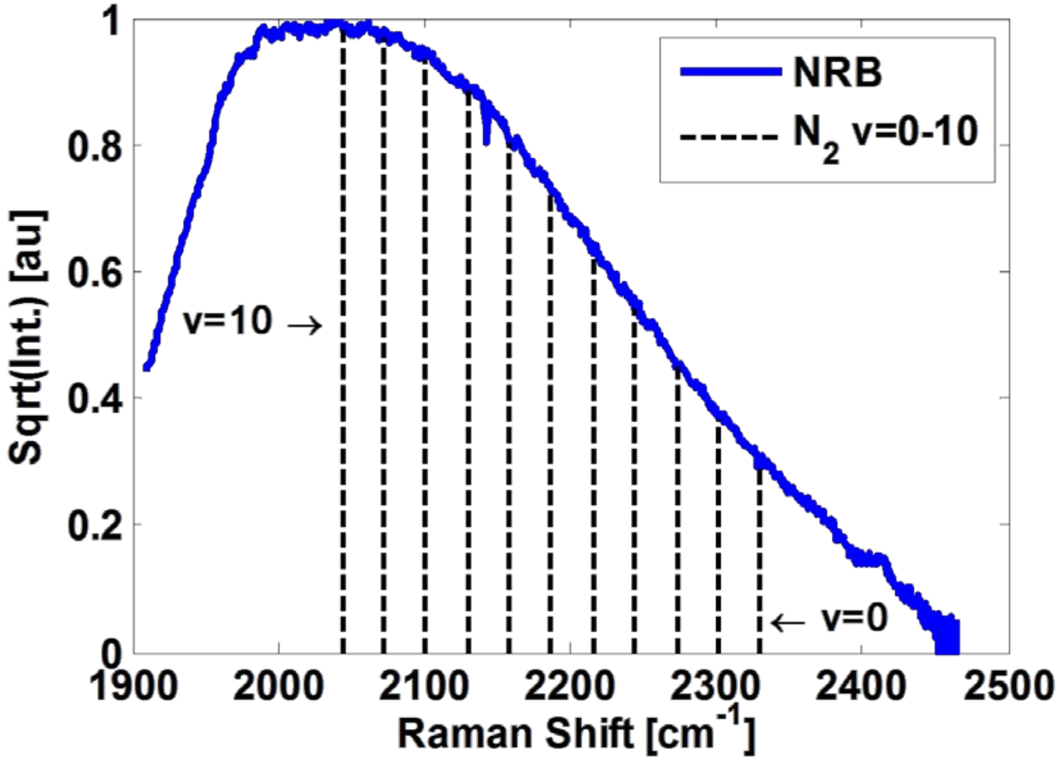
$n_e = 6 \cdot 10^{13}$ cm^{-3}, T_e =1.7 eV

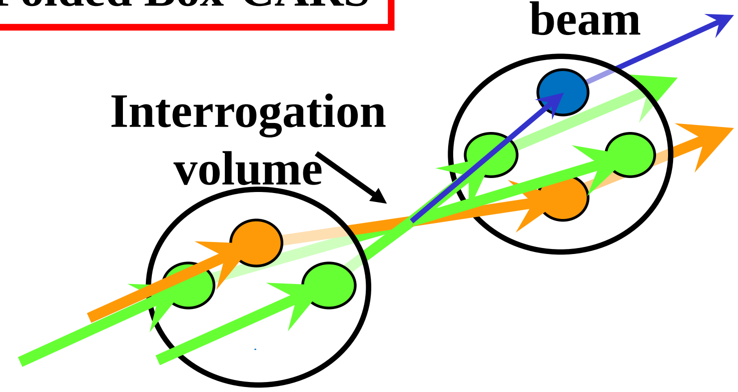
- **Raman spectrum is taken after electron-ion recombination has occurred (5 μs after the pulse) and subtracted**
- **Temperature can be inferred from the Raman spectra**

Temperature, $N_2(X,v)$ populations measurements: psec BoxCARS with broadband dye mixture

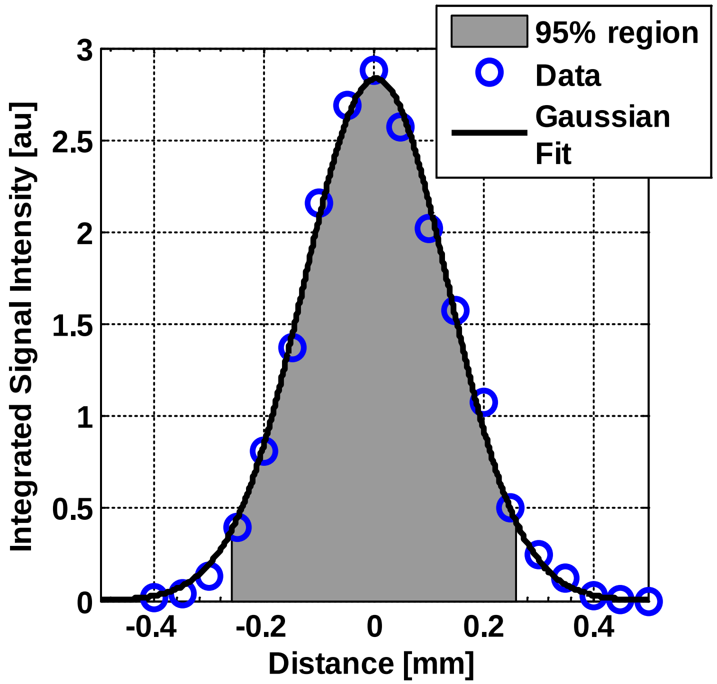
Very broadband pyrromethene dye mixture:

access to high vibrational levels





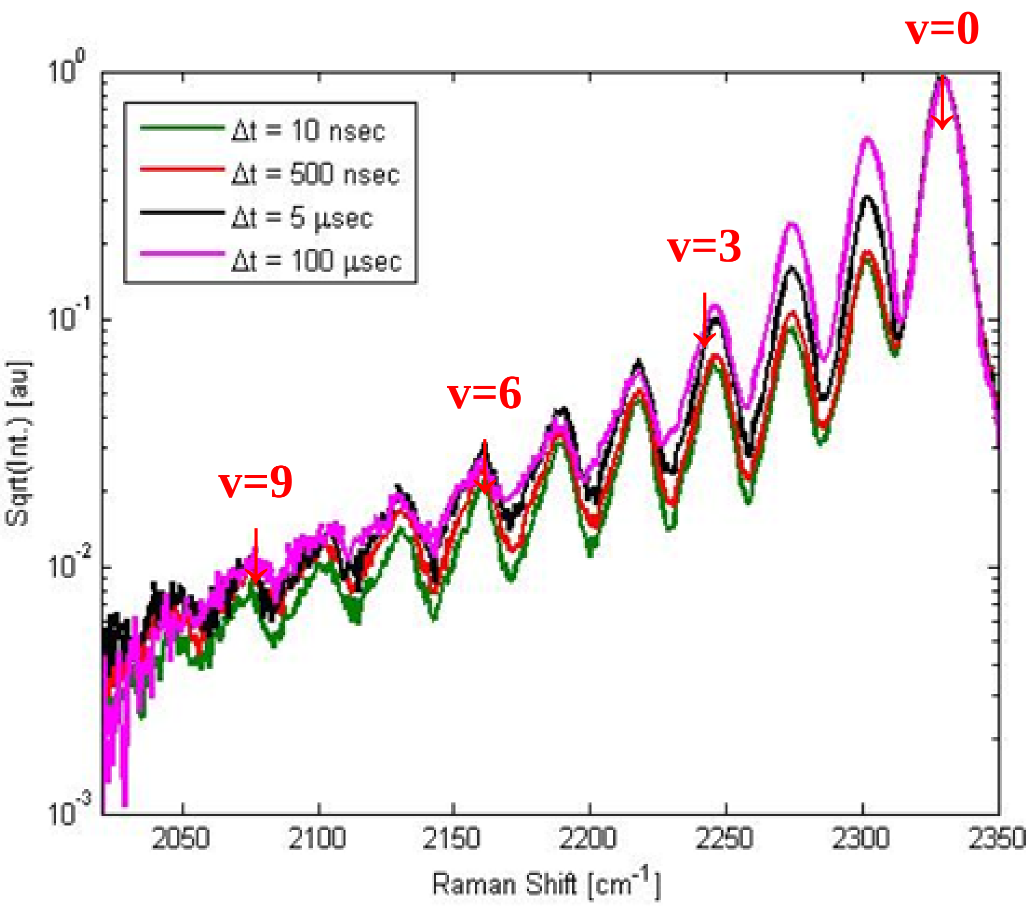
High spatial resolution:
95% of signal generated over ~0.5 mm



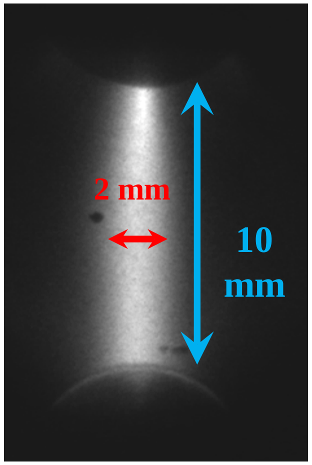
Typical Psec CARS Spectra, 100 Torr N_2

(Normalized to v=0, corrected for dye laser spectral profile)

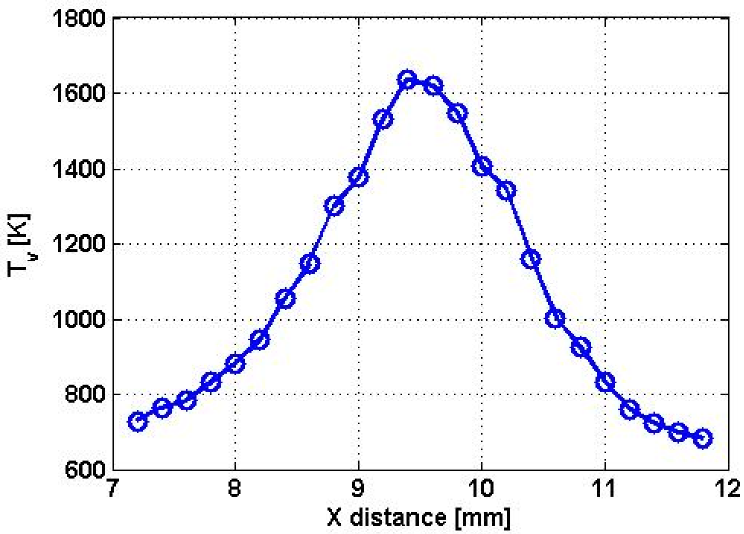
100 laser "shot" averaged spectra
vs. time after rising edge of current pulse



Vibrational level populations inference:
least squares fitting to Voigt line shape



N_2, P=100 torr,
5 mJ/pulse, 100 µs delay

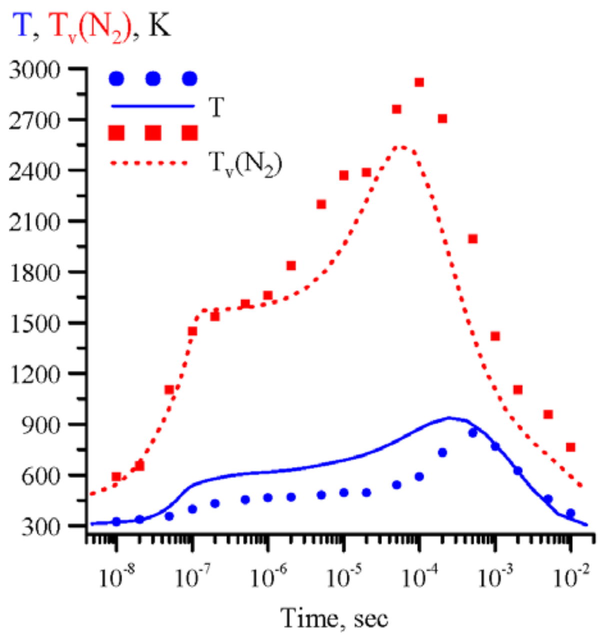


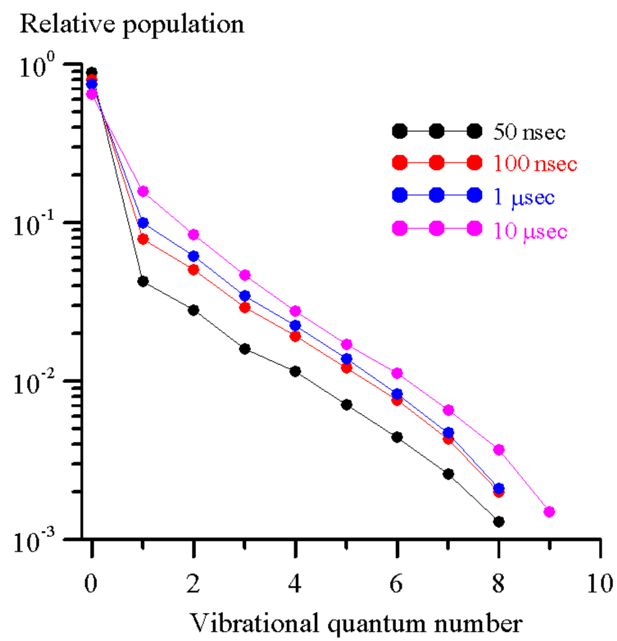
Radial distribution of "first level"
vibrational temperature

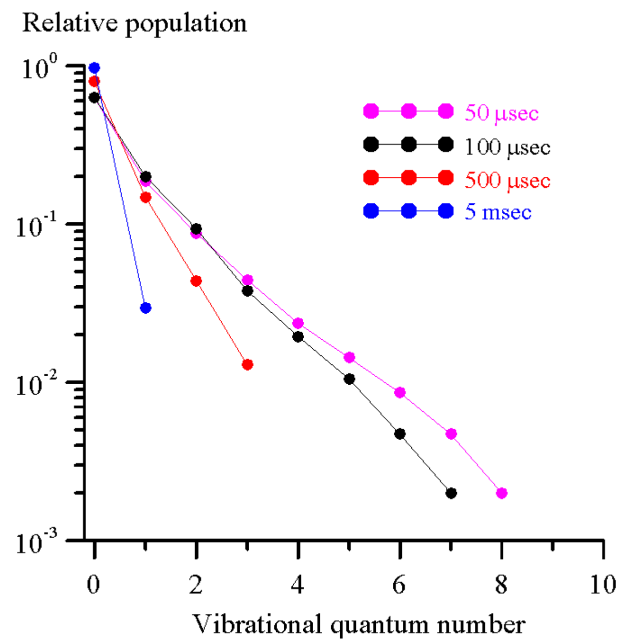
Results: psec CARS measurements in air, during and after nsec discharge pulse

Air, P=100 torr, 16 mJ/pulse

$$T_{v01} = \frac{\theta_v}{\ln[n_0/n_1]}$$

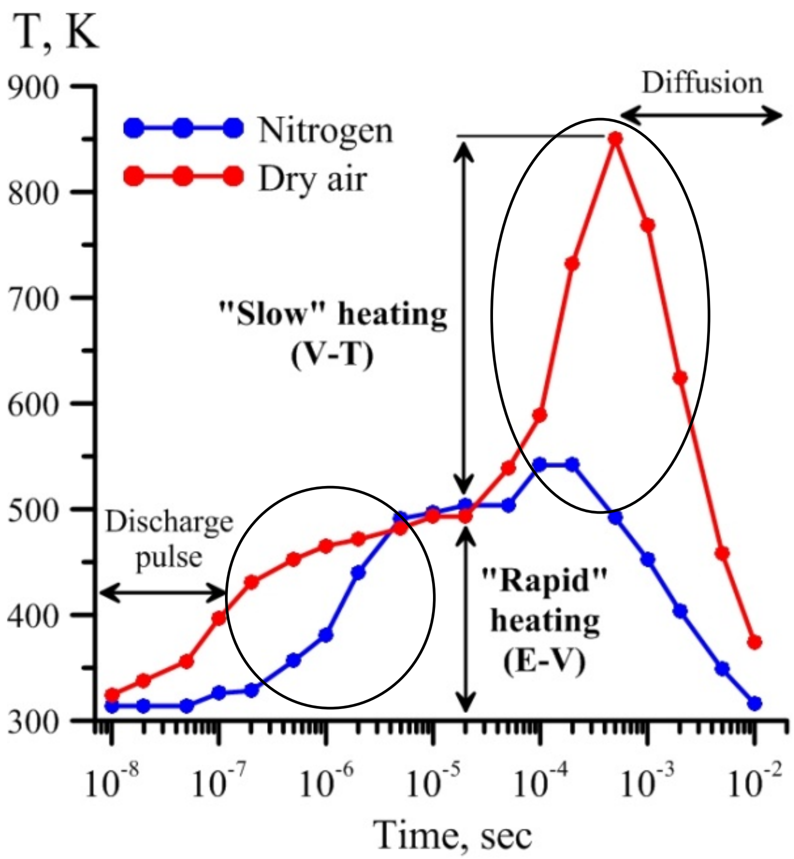


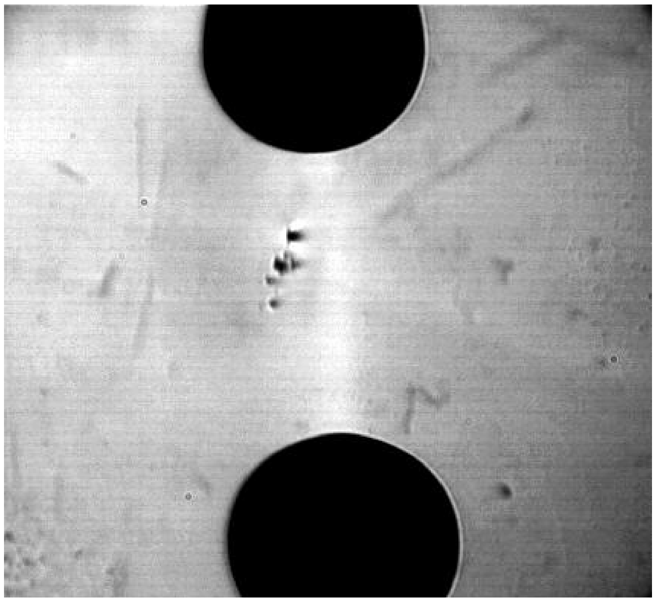




- **Strong vibrational disequilibrium, up to $T_{v01}(N_2)$ = 3000 K (≈ 0.8 vibrational quanta per molecule), moderate translational/rotational mode temperatureT_{rot} = 300-800 K**
- **$N_2(X)$ vibrational levels up to v=9 are detected**
- **First level vibrational temperature keeps rising after the discharge pulse: V-V energy transfer from higher vibrational levels, e.g. $N_2(v=2) + N_2(v=0) \rightarrow N_2(v=1) + N_2(v=1)$**
- **Gradual relaxation on long time scale: V-T relaxation, diffusion out of the filament region**

"Rapid" and "Slow" Heating in Air and Nitrogen





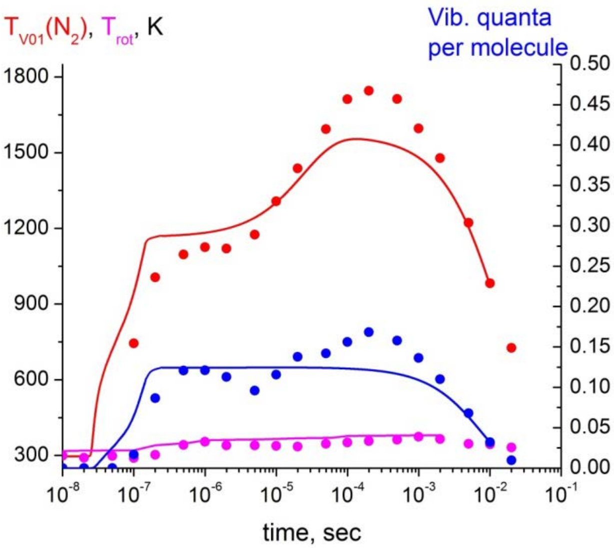
Compression waves generated by the filament at 1-10 μsec (frames are 1 μsec apart)

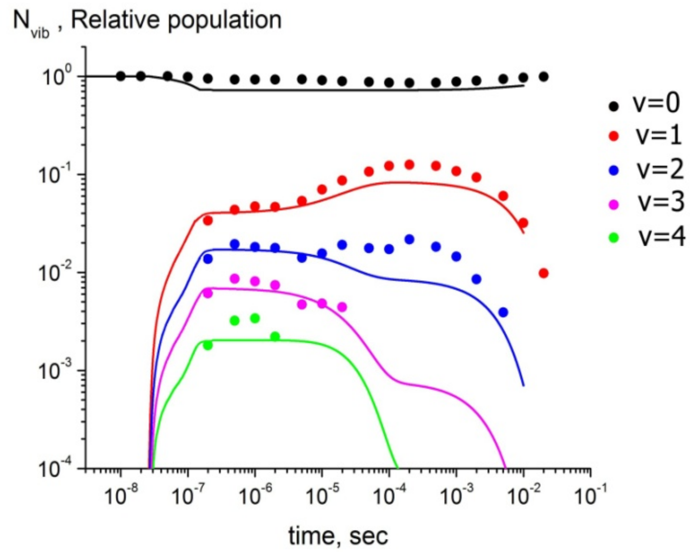
- "Rapid" heating in N_2 and air:
  - $N_2(A) + N_2(A) \rightarrow N_2(B,v) + N_2(X,v)$ (nitrogen)
  - $N_2(A,B,C,a) + O_2 \rightarrow N_2(X,v) + O + O$ (air)
- "Slow" heating in air (nearly absent in N_2),
  - V-T relaxation by O atoms: $N_2(X,v) + O \rightarrow N_2(X,v-1) + O$

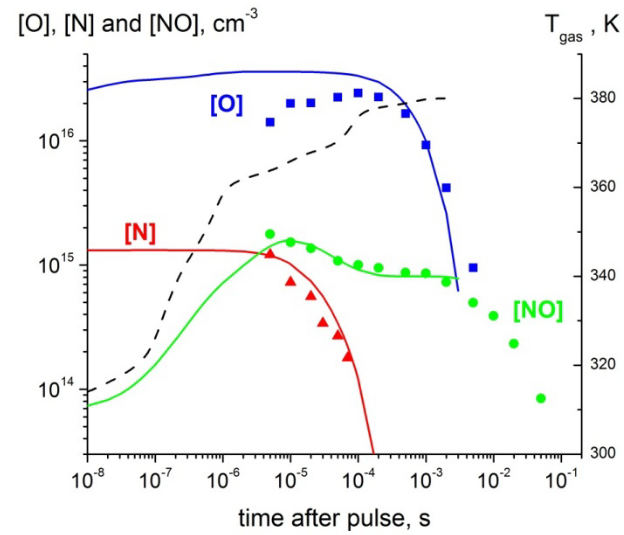
Air, P=100 torr:

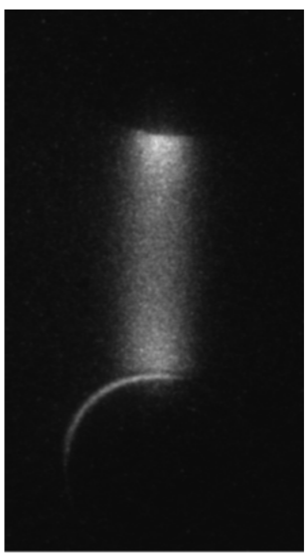
"Full set" of data (T, [N_2(v)], [N], [O], [NO], NO PLIF)

Air, P=100 torr, 4 mJ/pulse





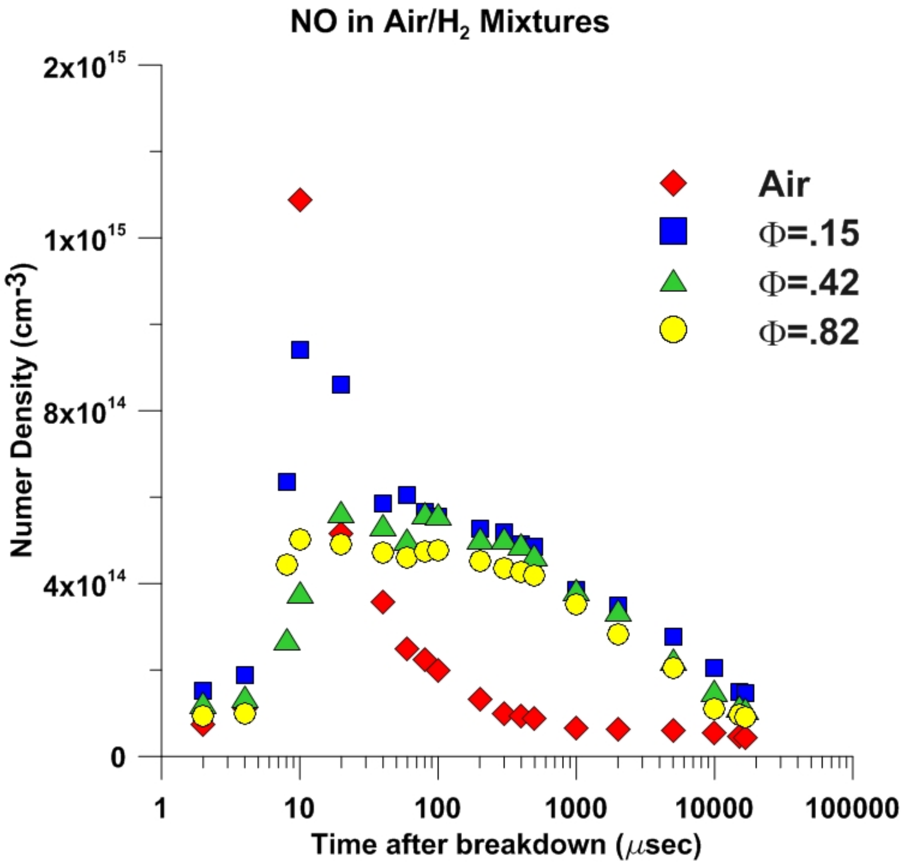


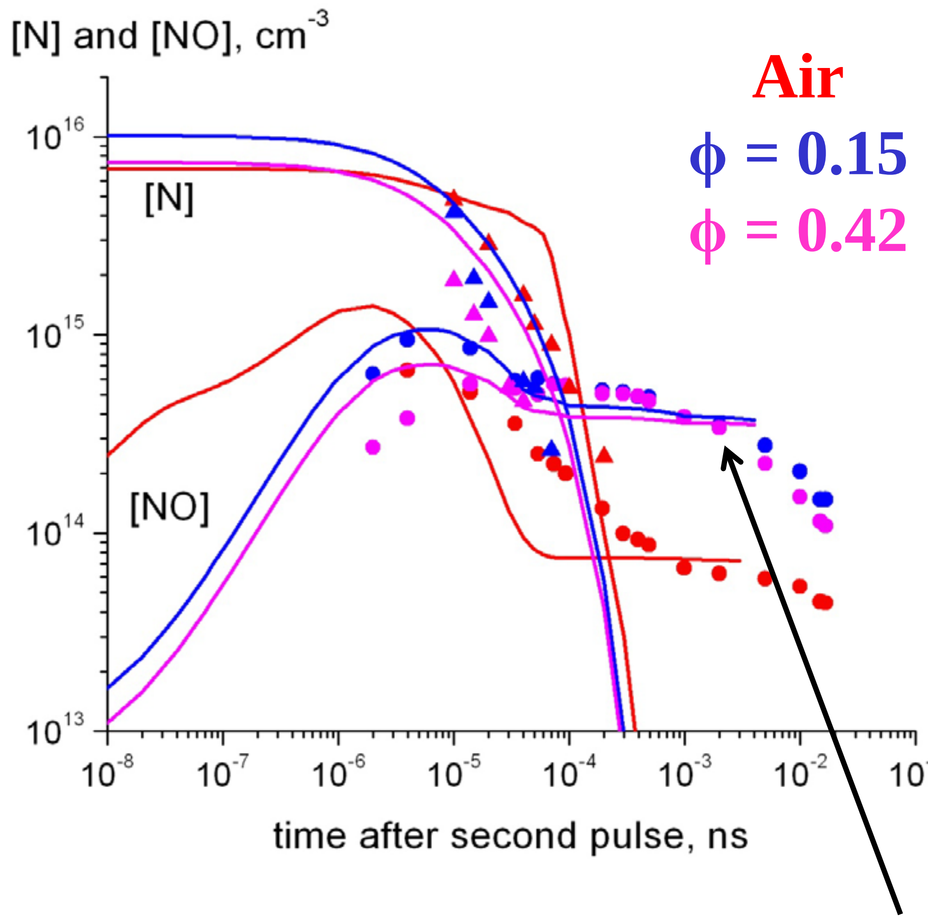


NO PLIF image
10 µs after discharge pulse

- **Psec CARS: T, $T_v(N_2)$, [N_2(X,v)]**
- **TALIF, LIF: absolute N, O, NO number densities**
- **Vibrational excitation and temperature rise predicted accurately**
- **$N_2(X\ ^1\Sigma_g^+, v) + O \rightarrow NO + N$ channel appears unlikely: N_2(X) vibrational excitation (measured by CARS) is fairly weak**
- **[NO] reproduced <u>only</u> when formation processes via multiple N_2 excited electronic states, $N_2^* + O \rightarrow NO + N$, are incorporated**
- **[NO] reduction is nearly the same as initial [N], ~10^{15} cm^{-3}: $NO + N \rightarrow N_2(v) + O$ reaction**

N, NO in air, H_2-air, P=40 Torr
N atoms "scavenge" OH radicals



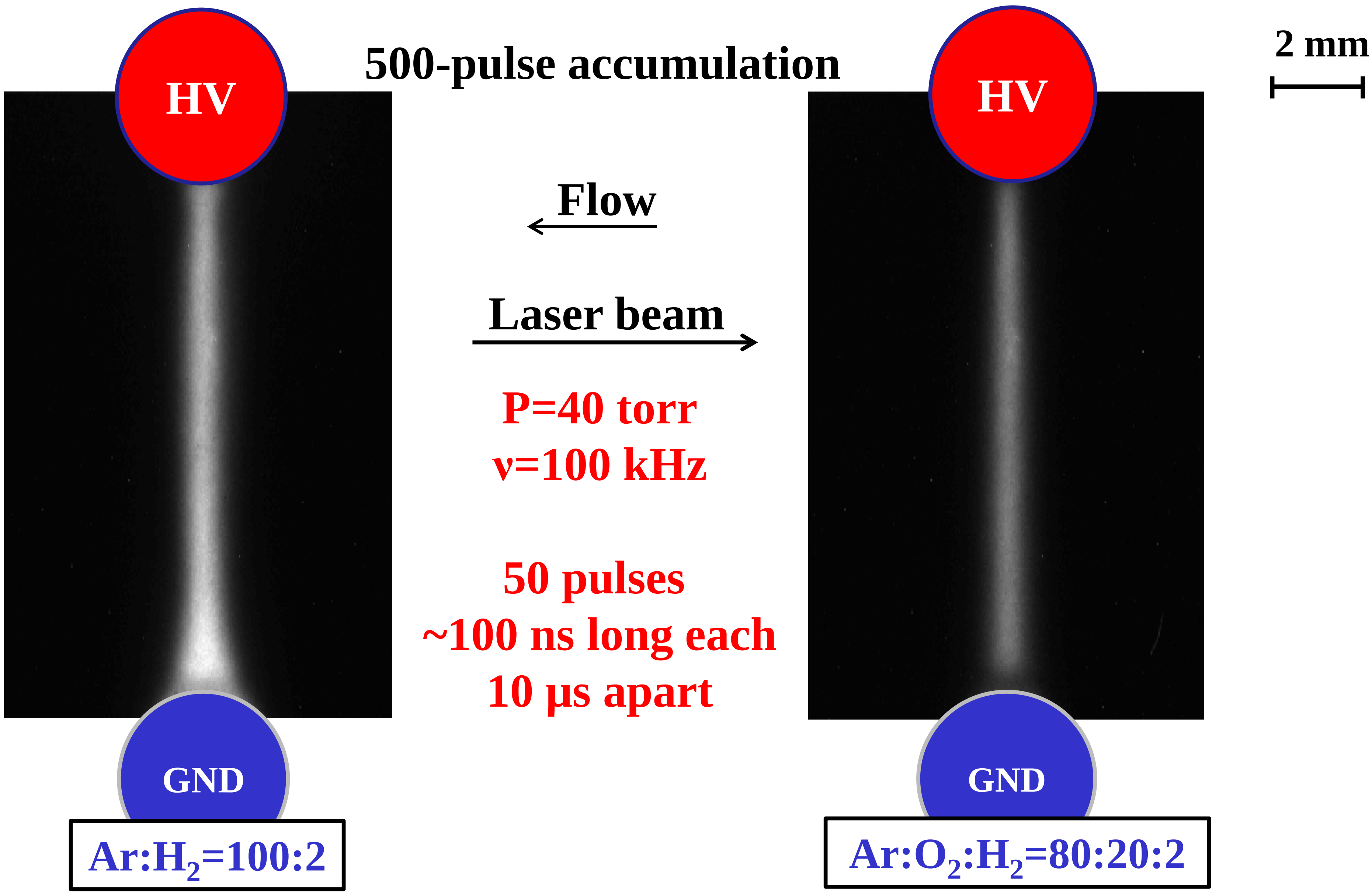


Longer NO decay primarily due to reaction N + OH → NO + H

Adding H_2 increases NO decay time by a factor of ~100, reduces N atoms

Similar effect in C_2H_4 - air

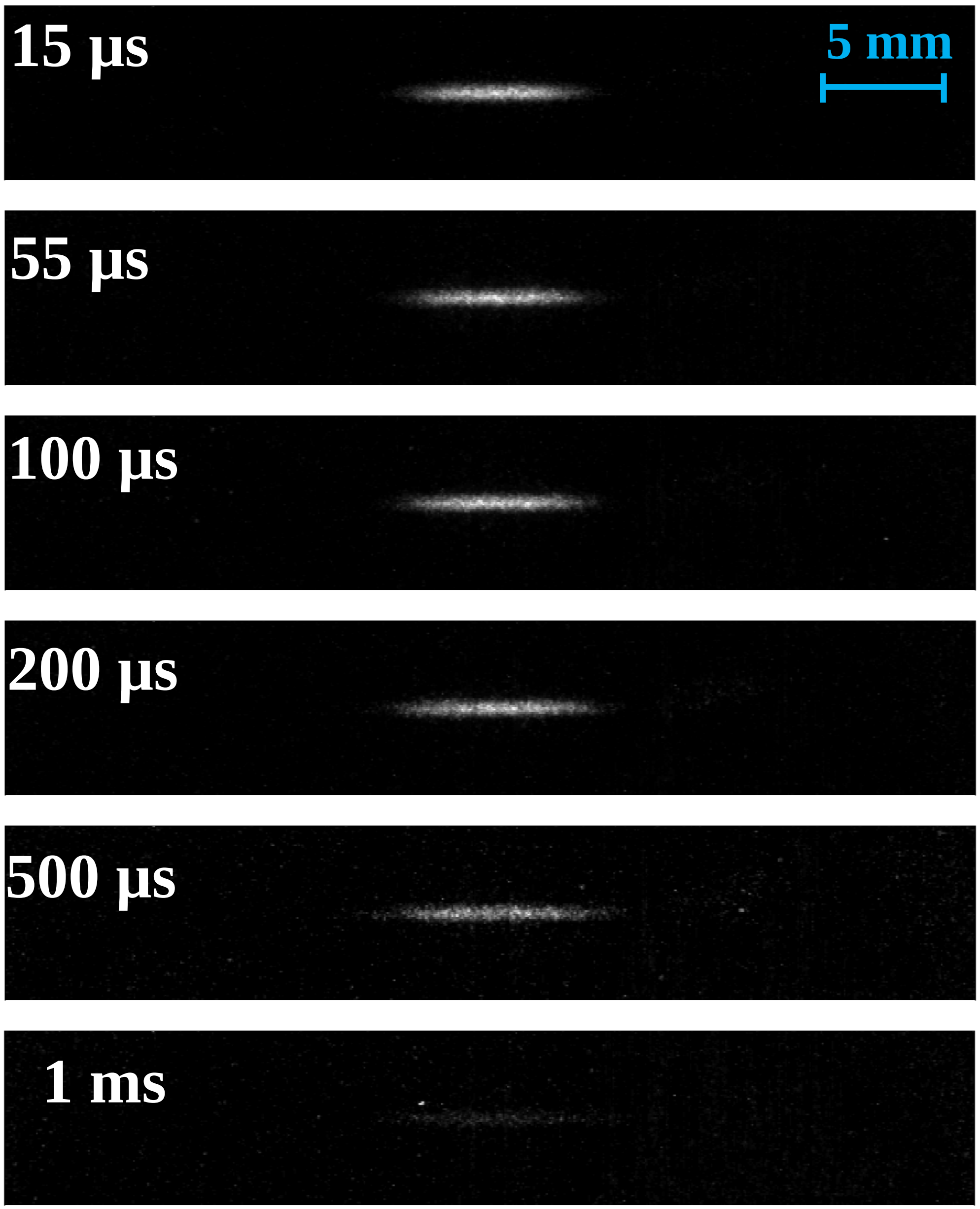
Spatially resolved measurements of H_2-O_2-Ar plasma chemistry, point-to-point discharge



Electrode gap: 11.7 mm, laser beam 4.7 mm from high voltage electrode

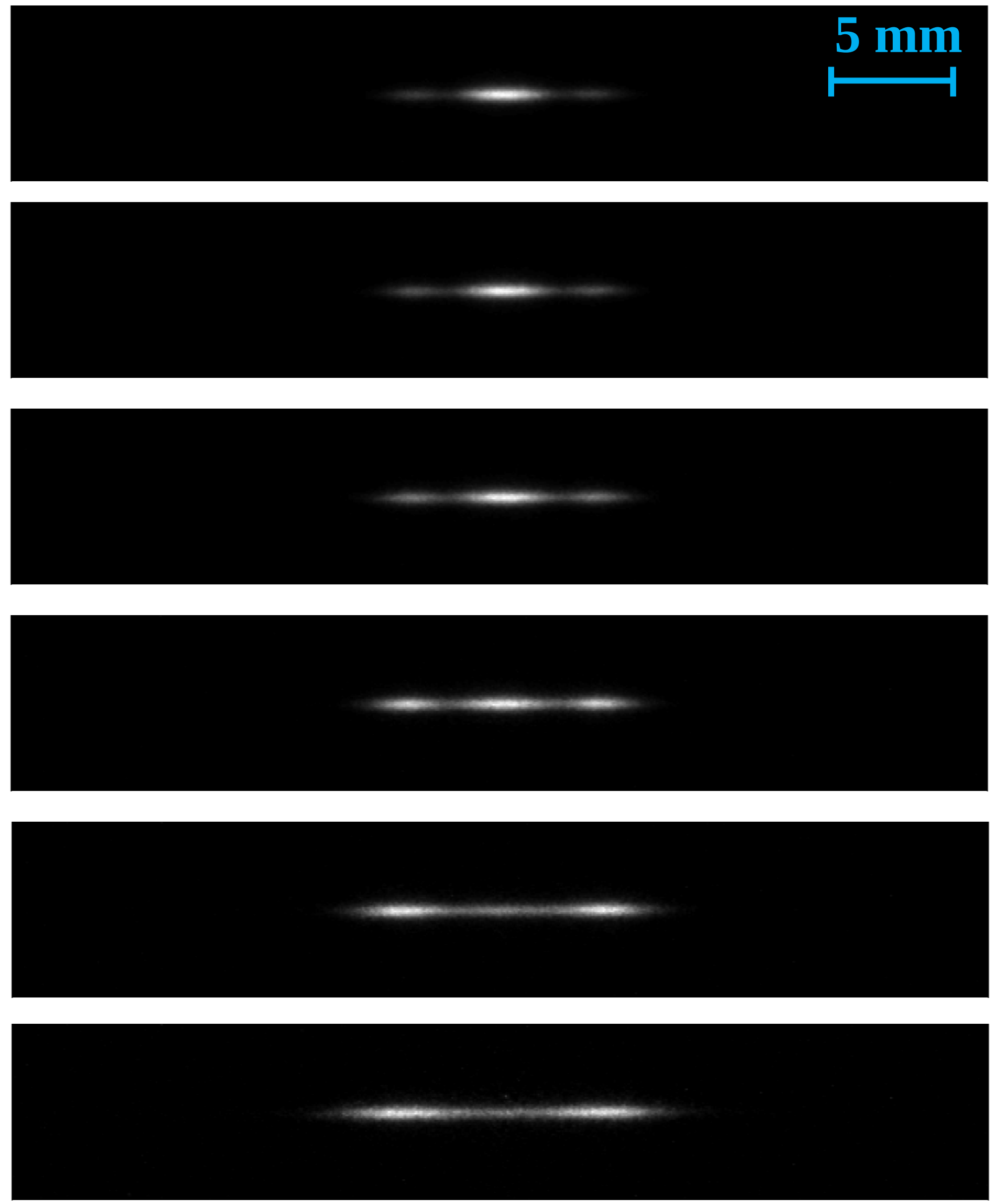
H atom TALIF and OH LIF after 50-pulse burst, 2% H_2 - 20% O_2 – Ar, P=40 torr

H TALIF signal



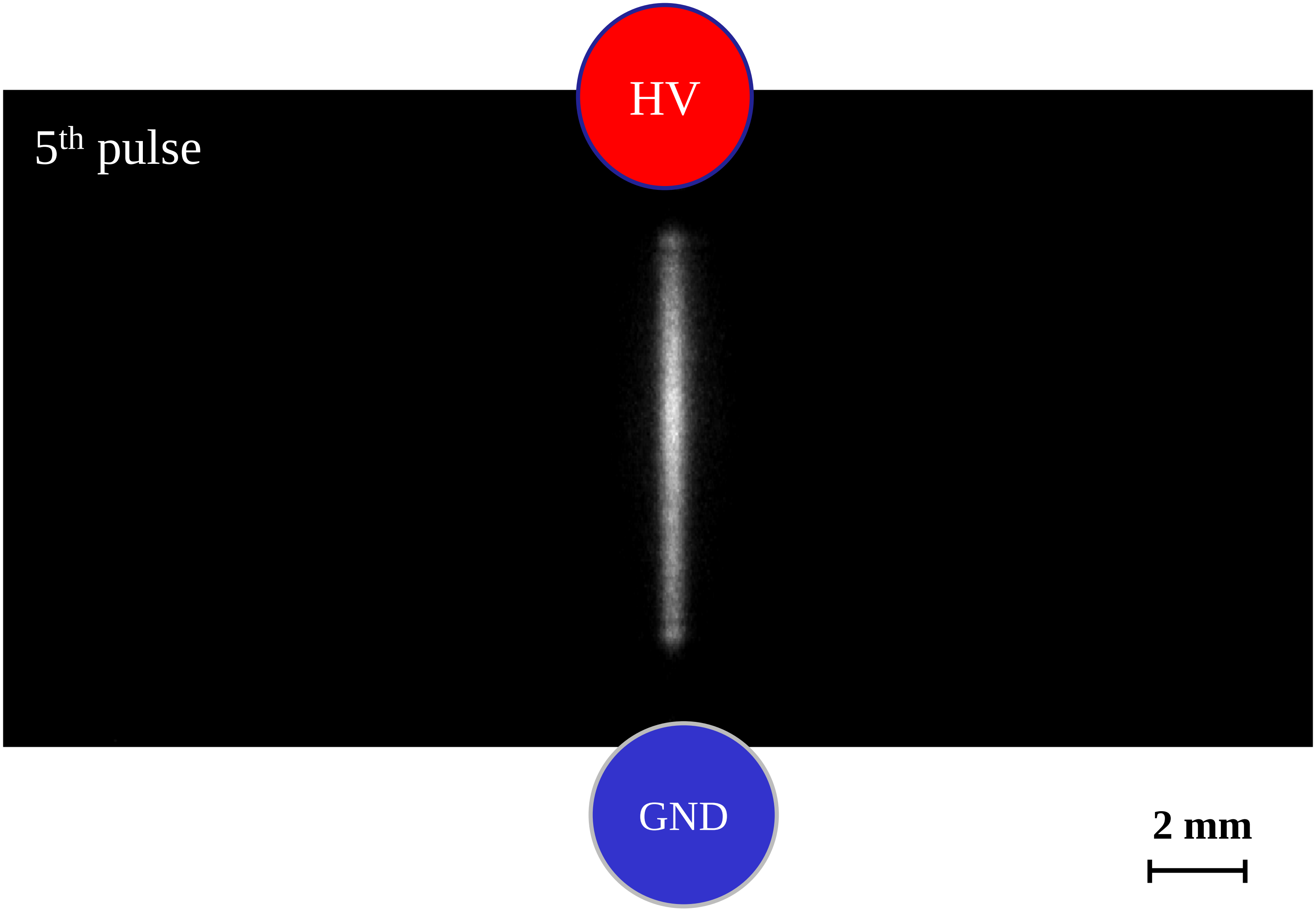
OH LIF signal

← Flow



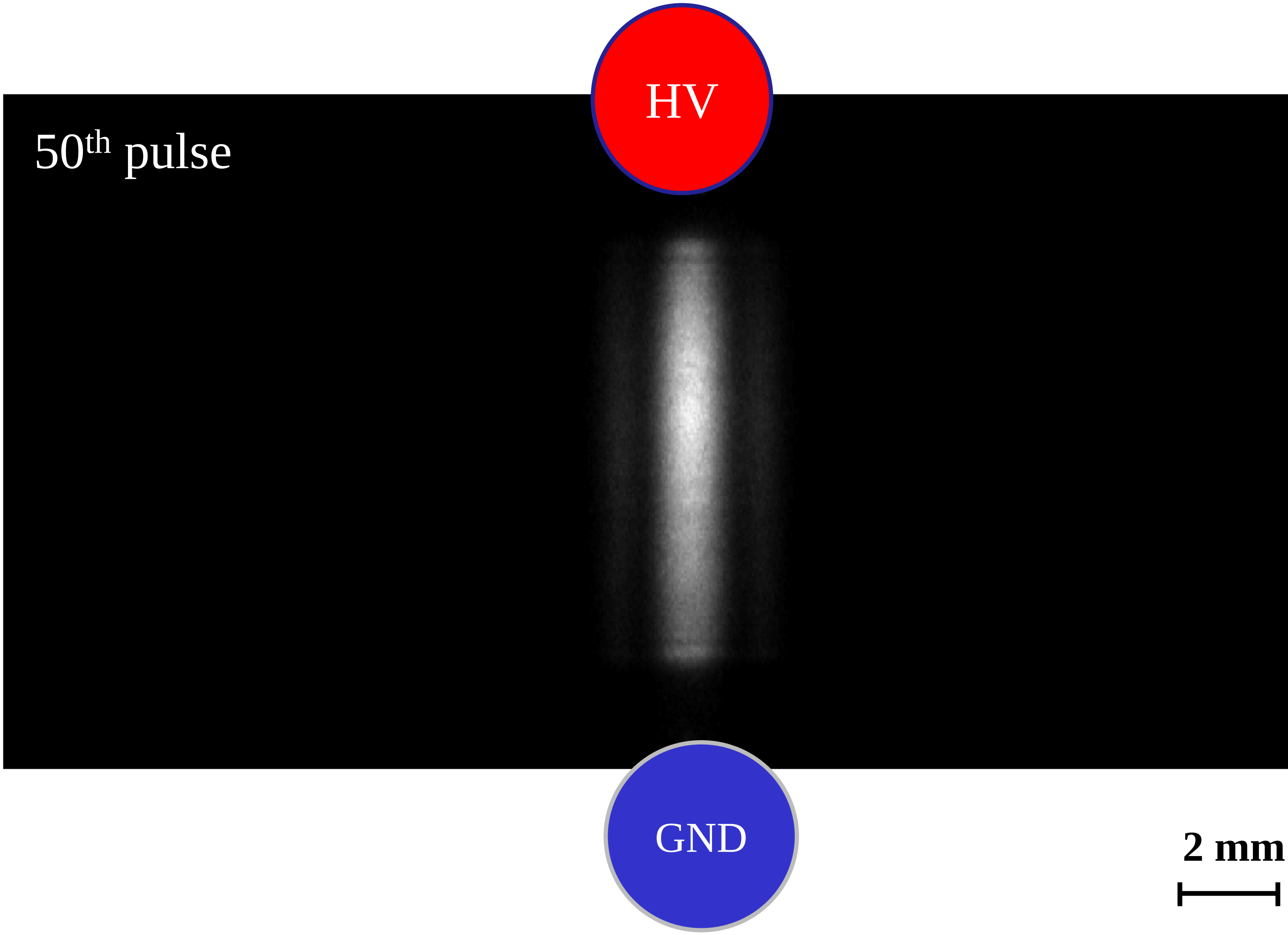
OH PLIF image

2% H_2 - 20% O_2 - Ar



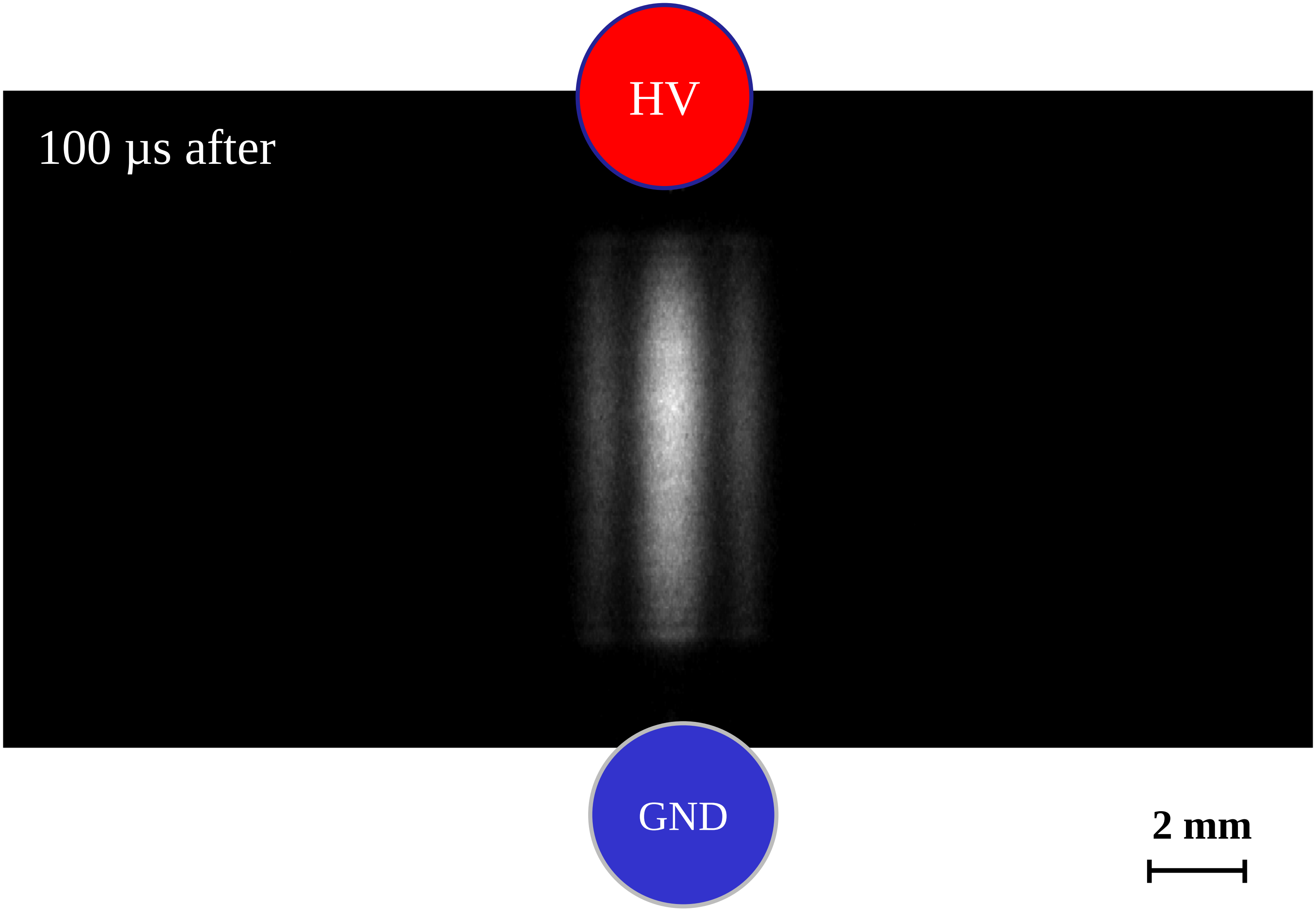
OH PLIF image

2% H_2 - 20% O_2 - Ar

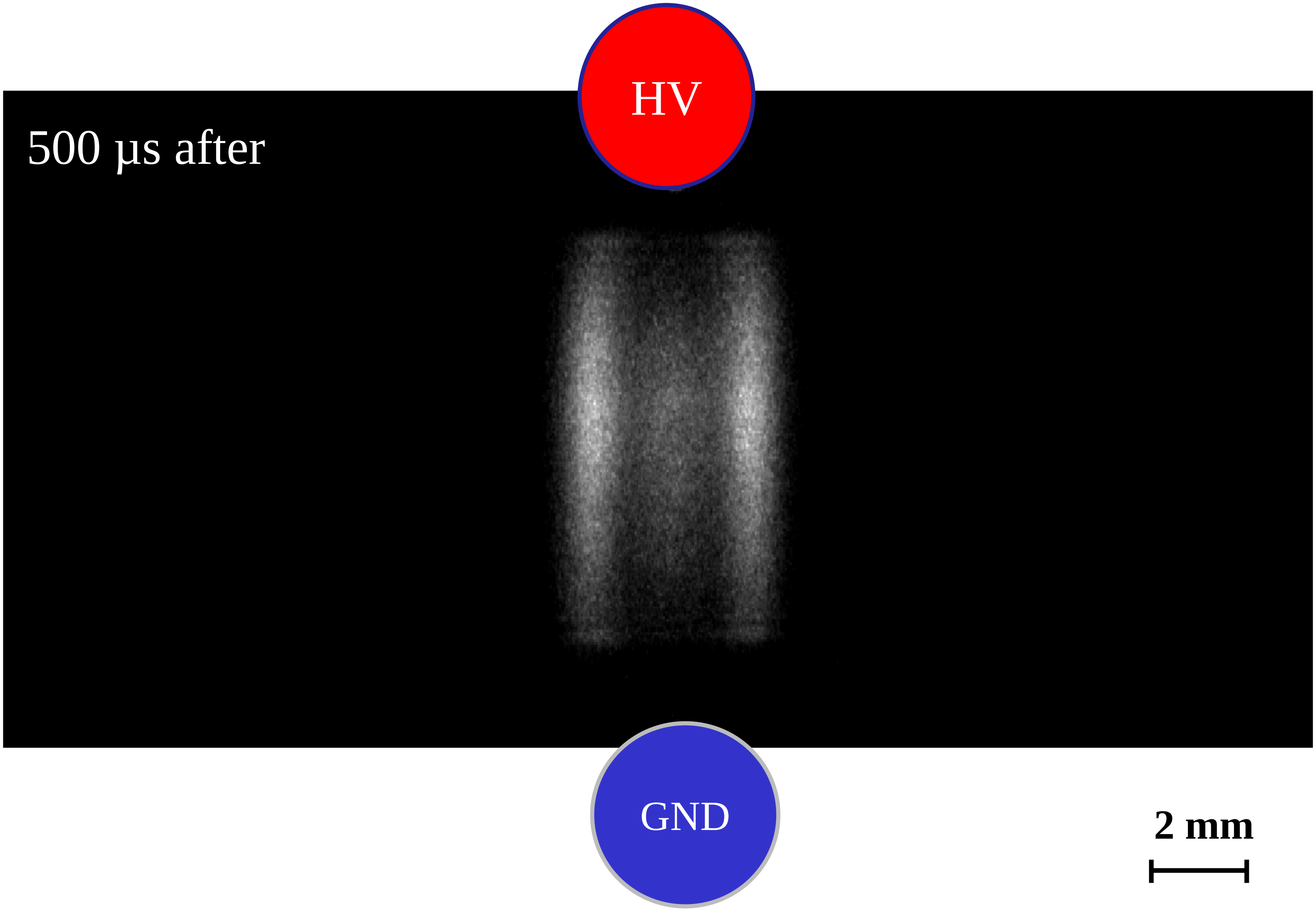


OH PLIF image

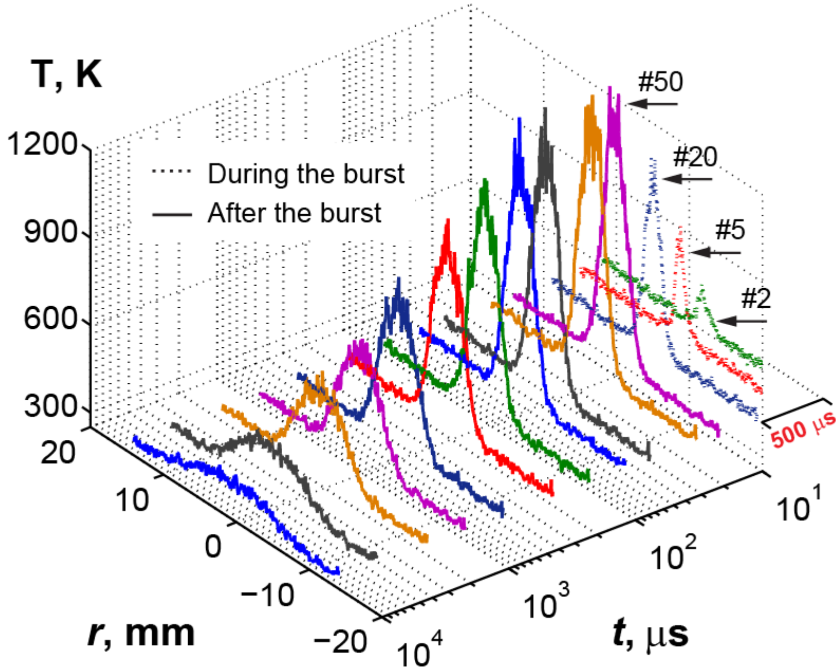
2% H_2 - 20% O_2 - Ar

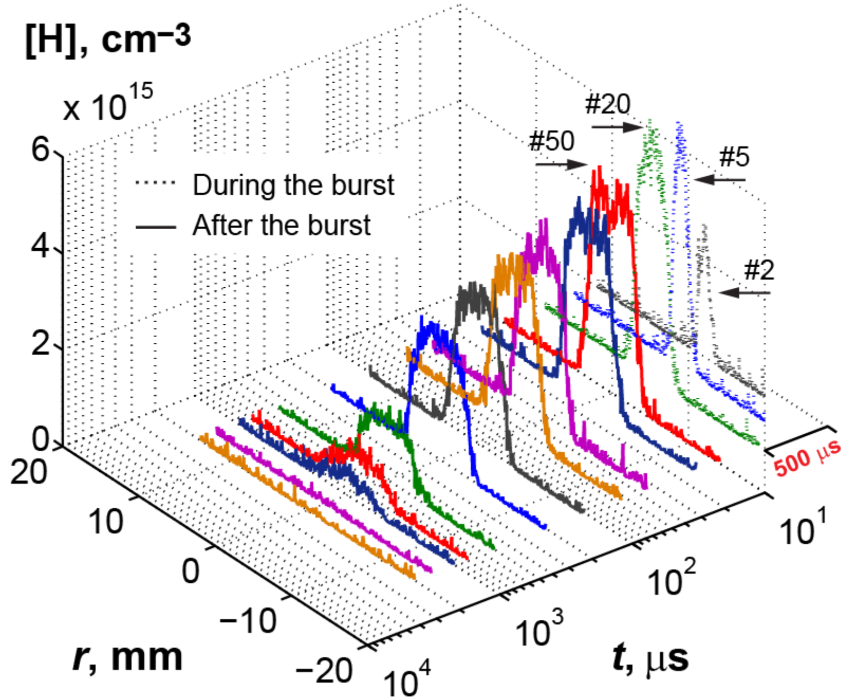


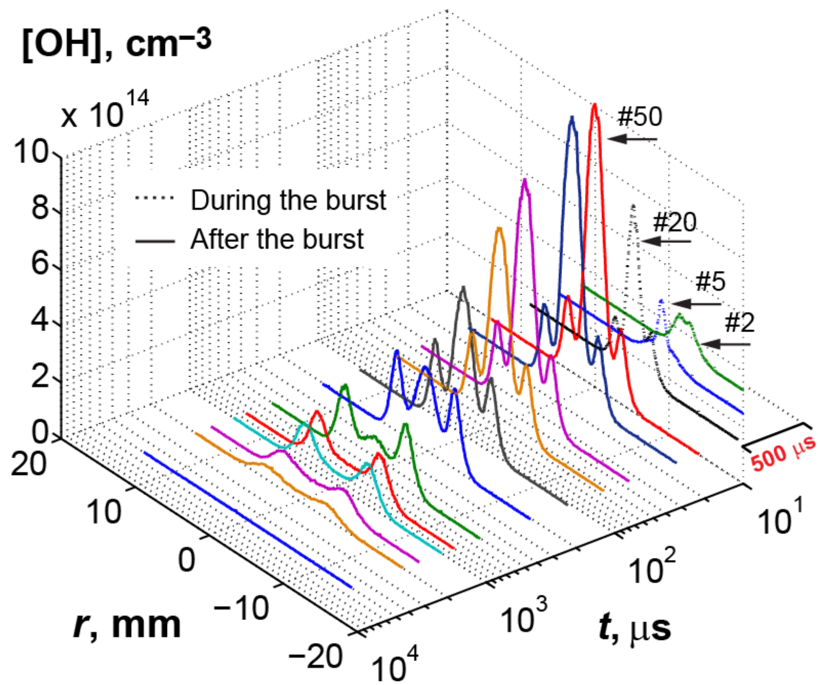
OH PLIF image
2% H_2 - 20% O_2 - Ar



T (Rayleigh scattering), absolute [H] (TALIF), and [OH] (PLIF) after 50-pulse burst, 2% H_2 - 20% O_2 - Ar, P=40 torr







Hot central region: chain branching reactions dominate OH production

$H + O_2 \rightarrow OH + O$; $O + H_2 \rightarrow OH + H$

Lower temperature peripheral region: predominant OH accumulation

H radial diffusion ; $H + O_2 + M \rightarrow HO_2$; $H + HO_2 \rightarrow OH + OH$

Summary / Future Work

- Growing body of time-resolved, spatially-resolved data characterizing pulsed, high-pressure fuel-air plasmas
- Measurements and predictions of electric field, electron density, temperature, and $N_2(X,v)$ populations are necessary for insight into discharge energy partition
- Measurements and predictions of excited electronic states of N_2^* and key radicals (O, H, OH, and NO) are critical for quantifying their effect on fuel-air plasma chemistry
- “Minimum” data set for validation of low-temperature plasma assisted combustion chemistry mechanism: time-resolved temperature, N_2 vibrational temperature, and key radical concentrations during a repetitively pulsed plasma-enhanced ignition process
- Parameters used for conventional combustion mechanism validation (such as ignition delay time, laminar flame speed) are insufficient by far
- Kinetic sensitivity analysis: identify reduced reaction mechanism for coupled discharge dynamics / molecular energy transfer / plasma chemistry kinetic model, incorporating a wide range of time scales and realistic geometry

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Unresolved Issues

- **Effect of "rapid" heating compared to reactions of plasma-generated radicals: at what conditions (pressure and temperature) does "rapid" heating become dominant effect in transient fuel-air plasmas, compared to low-temperature radical species chemistry?**

- **Effect of reactions of vibrationally excited molecules, compared to reactions of plasma-generated radicals? Do reactions such as $N_2(X^1\Sigma,v) + O \rightarrow NO + N$ and $N_2(X^1\Sigma,v=1) + HO_2 \rightarrow N_2(X^1\Sigma,v=0) + HO_2(v_2+v_3) \rightarrow N_2 + H + O_2$ really matter and if so, at what conditions?**

- **Effect of fuel molecular structure on plasma-generated radicals chemistry. Is there a difference between plasma assisted combustion of <u>low octane number fuels</u> (exhibiting low-temperature cool flame chemistry) vs. <u>high octane number fuels</u> (cool flames are not observed)?**

- **Dynamic effect of plasma on non-premixed turbulent flames: preventing local extinction by producing radicals where F/A ratio, temperature, or pressure becomes too low to sustain combustion. Need high frame rate (~10 kHz) imaging of temperature and radical species concentrations fields.**

- **Plasma assisted combustion in non-premixed compressible flows: understand coupling between electric discharge dynamics, fuel-air mixing, and combustion instability development.**

Acknowledgments

AFOSR MURI *“Fundamental Mechanisms, Predictive Modeling, and Novel Aerospace Applications of Plasma Assisted Combustion”*

US DOE Plasma Science Center *“Predictive Control of Plasma Kinetics: Multi-Phase and Bounded Systems”*

NSF *"Kinetics of Non-Equilibrium Fast Ionization Wave Plasmas in Gas Phase and Gas-Liquid Interface“*