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Laser diagnostics for low temperature plasma applications

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Combustion Research Facility Seminar, 12/06/17

Outline

- Plasma assisted combustion- measurements of radical species produced during nanosecond pulsed discharges (completed at OSU)
  - Background
  - Atomic species measurements in “0D” plasma flow reactor for radical production and reaction kinetics (Winters, et al. 2017)
  - Spatially resolved measurements of radical species generated by a plasma at a liquid/vapor interface (Winters, et al. 2015)

- Plasma-surface interactions (SNL)
  - Background and motivation
  - Sum frequency generation overview

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Plasma assisted combustion

- **Ignition and combustion become unstable at the conditions of:**
  - Lean equivalence ratios $\varphi = (F/A) / (F/A)_{stoichiometric}$
  - High flow velocities in combustor
  - Low pressures in combustor
- **Capabilities provided by non-equilibrium plasmas:**
  - Efficient generation of a pool of highly reactive radical species→ Not just a temperature rise (Uddi et al. 2009, Stancu et al. 2010, & Schmidt et al. 2015)
  - Radicals react rapidly with fuel, even at low temperatures (Yin, et al. 2013, Tsolas, et al. 2016)
- **Effect of plasma-generated radicals on fuel-air flows (over last ~10-20 years):**
  - Ignition time varies inversely with numbers of ns-pulses (Yin, et al. 2013)
  - Reduction of ignition threshold at $T_0 < T_{thermal}$ (up to 100-200 K, plasma flow reactors) (Yin, et al. 2013)
  - Reduction of lean flammability limit (up to $\Delta\varphi/\varphi \sim 10\%$, premixed turbulent flames) (Pilla, et al. 2006)

Nonequilibrium plasmas

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Reduced Electric Field $\sim \frac{E}{N}\ (V cm^2)$

↓

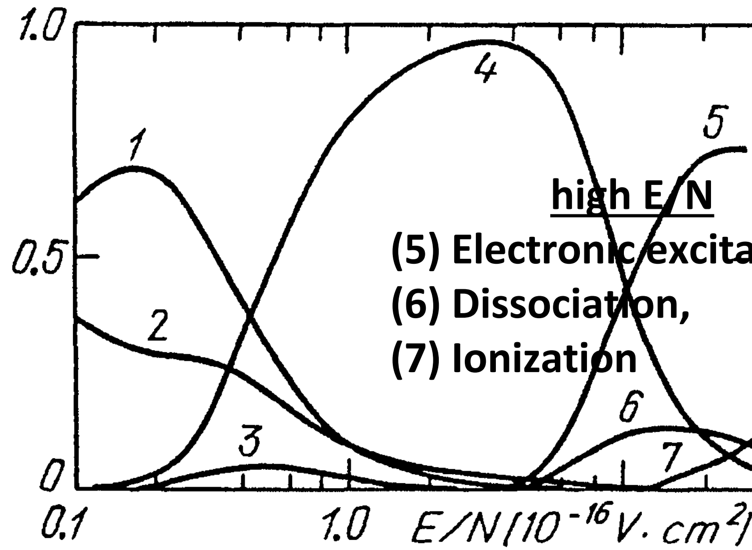
- Electron energy
- Input energy partition
- Rates of electron impact processes

Low to mid E/N

(1) O_2 vibrational excitation
(2) O_2 and N_2 rotational
(3) Elastic losses
(4) N_2 vibrational excitation

Transient plasmas (ns pulse duration):

Input Energy Partition vs. Reduced Electric Field



High E/N

(5) Electronic excitation,
(6) Dissociation,
(7) Ionization

Critical issues / concerns:

1. Plasma stability at high pressures (rapid thermalization = discharge filamentation)
2. Scarcity of experimental data at <u>controlled, well-characterized</u> plasma conditions
3. Validation of kinetic models, developing quantitative predictive capability

In-situ laser diagnostics

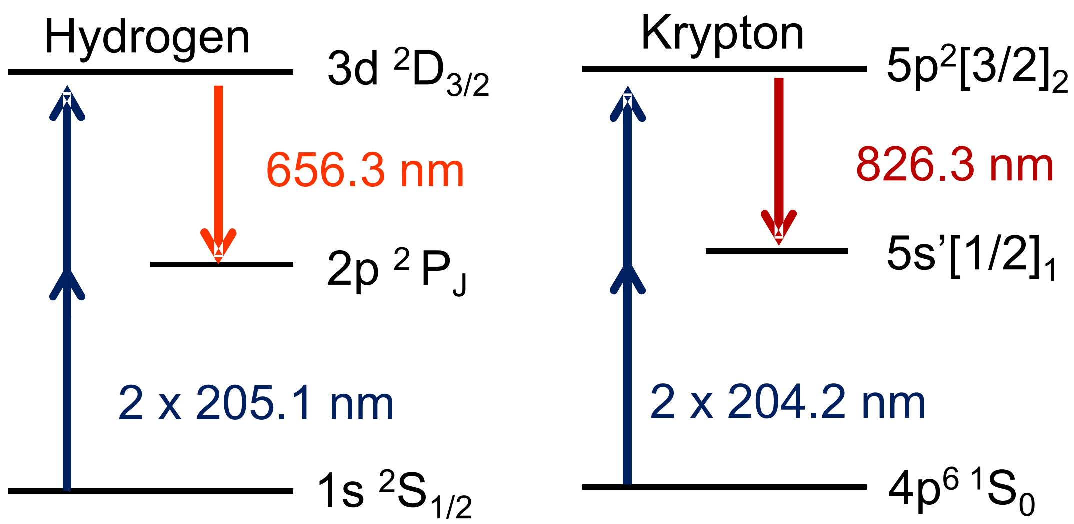
Two-photon Laser Induced Fluorescence (TALIF)

H radical

Calibration via Krypton TALIF

Quenching taken from femtosecond TALIF measurements

(Schmidt, et al. 2015)

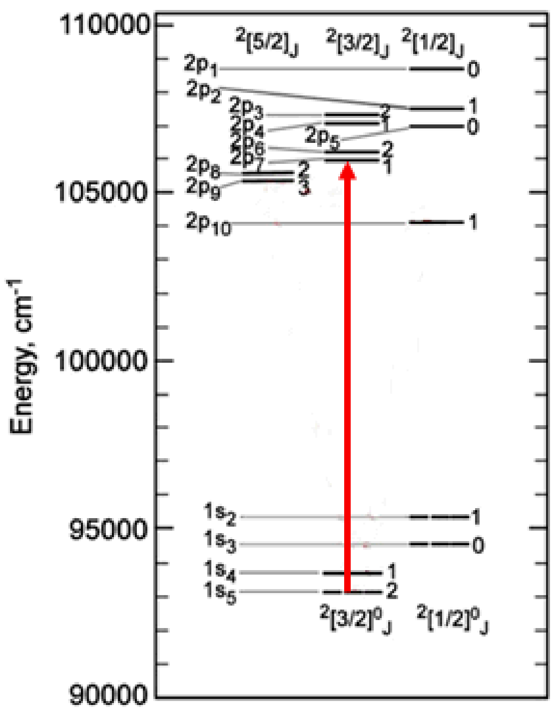


- Similar TALIF scheme used to measure atomic oxygen
  - Calibration via Xenon TALIF
  - Quenching taken from fs-TALIF and ns-TALIF

In-situ laser diagnostics, cont.

Tunable Diode Laser Absorption Spectroscopy (TDLAS)

Ar(3p^{5}4s): Ar(1s$_5$, 1s$_4$, 1s$_3$, 1s$_2$)

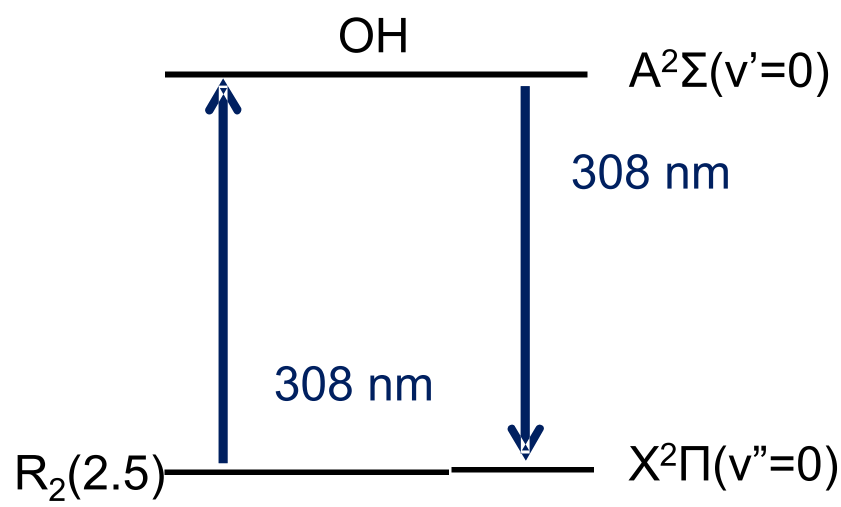


Laser Induced Fluorescence (LIF)

OH radical

Calibration via Rayleigh Scattering

Quenching is measured directly



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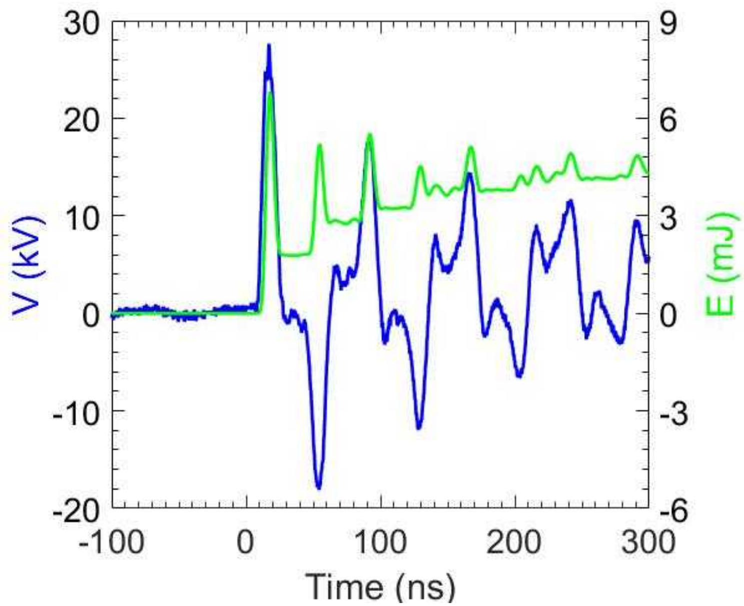
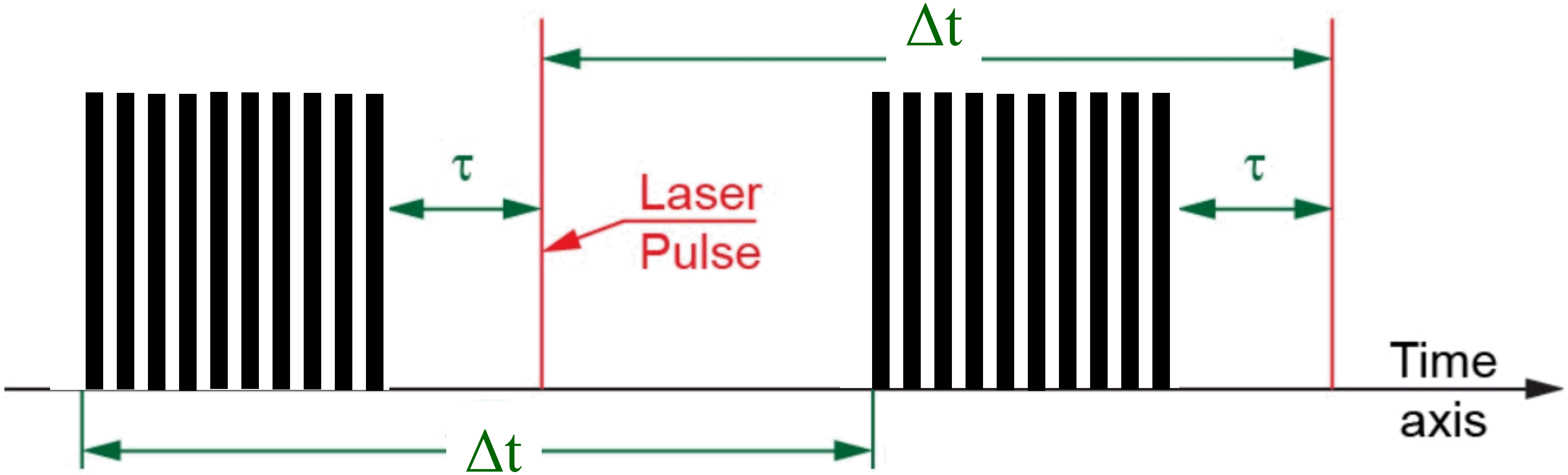
Ns pulsed discharge in "burst" mode

Pulser produces a rapid "burst" of:
25-75 pulses
Repetition rate = 10-20 kHz
FWHM of ~ 5 ns
Peak Voltage of ~ 30kV

Burst is repeated at Δt =10 Hz to match laser repetition rate.

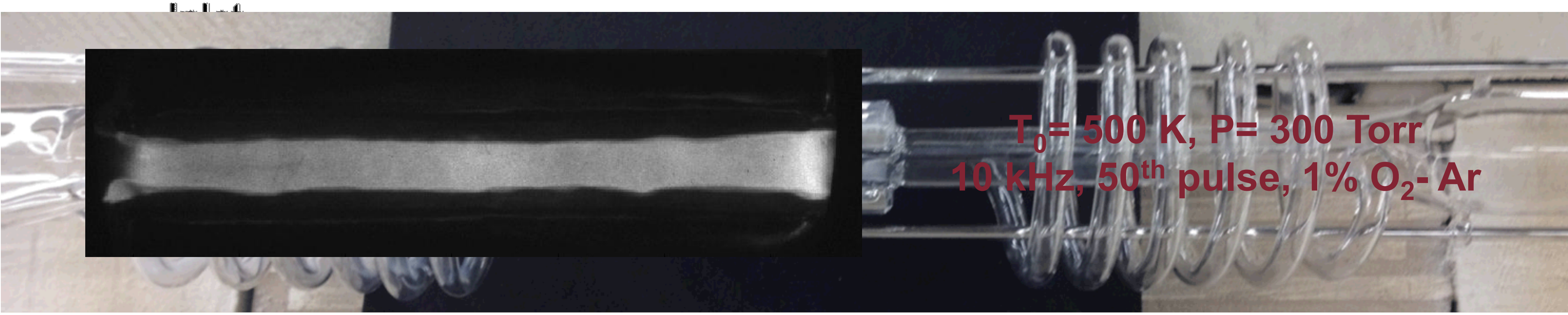
T_0= 500 K, P= 300 Torr
20 kHz, 75th pulse, 1% O_2- Ar



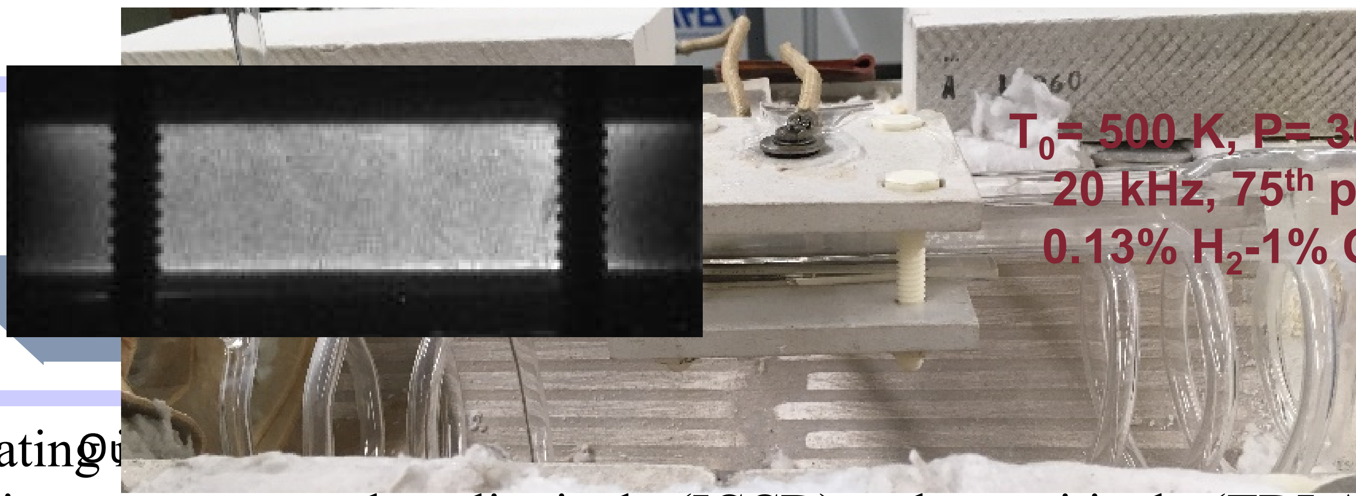


Designs for “0D” plasma flow reactor

Liquid Metal-Quartz Electrodes

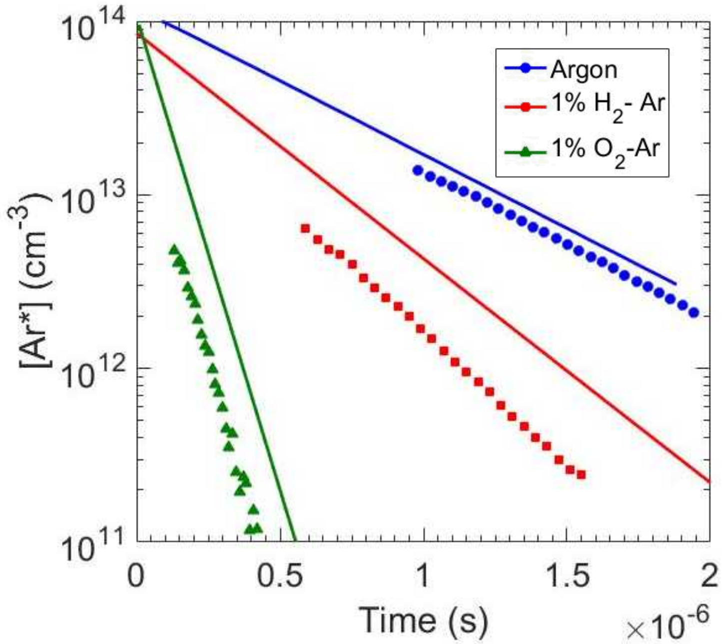


Copper-PDMS Electrodes



- Preheating
- Variation was measured qualitatively (ICCD) and quantitively (TDLAS)

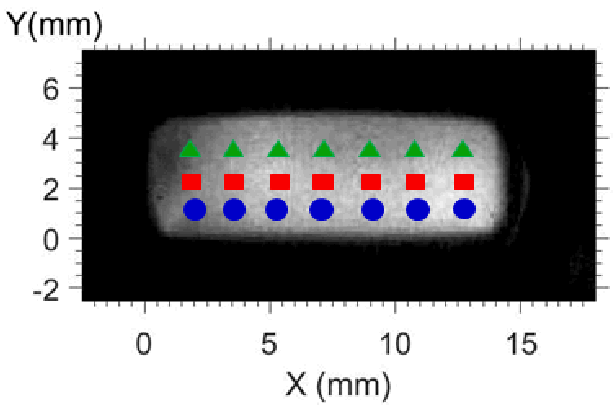
$[Ar(3p^54s)]$ distribution across the reactor channel



T_0 =500 K, P=300 Torr
50^{th} Pulse
pulse rep. rate 10 kHz

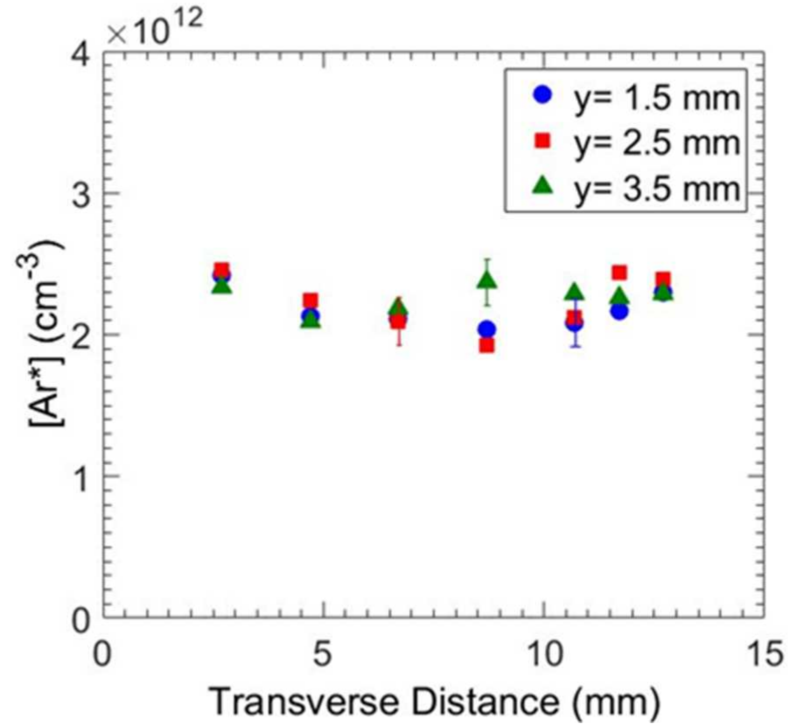
1% O_2-Argon mixture

End view



Symbols indicate laser beam locations

[Ar*] illustrating plasma uniformity



Insight into radical production

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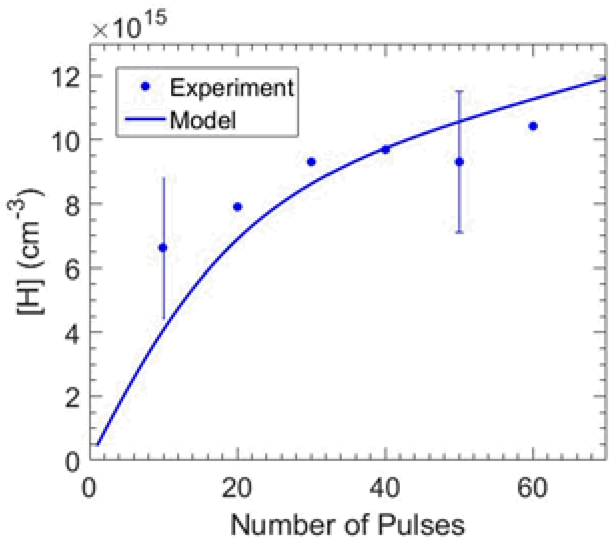
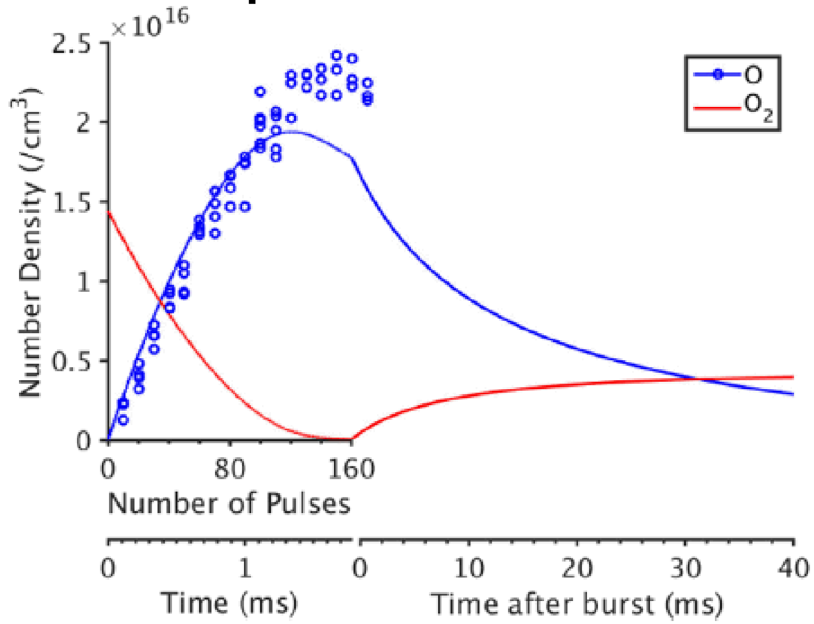
[H] produced with varying pulse burst size



T_0= 500 K, P= 300 Torr, 10 kHz, 1% H_2-Ar

[O] produced with varying pulse burst size



20 kHz, 1% O_2-Ar

- Kinetic modeling predicts **80% of the E_{CDP} → Ar excitation**
- 70% of that ($0.8E_{CDP}$) → dissociation
- In other terms, **56% of the initial E_{CDP} → dissociation**

- 100% dissociation of O_2 measured after ~110 pulses
- Measurements after 120 pulses subject to EMI
- Overall good agreement between measurements and predictions

$$Ar + e^- \rightarrow Ar^* + e^-$$

$$Ar^* + H_2 \rightarrow Ar + H + H$$

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

Time-resolved H atom measurements

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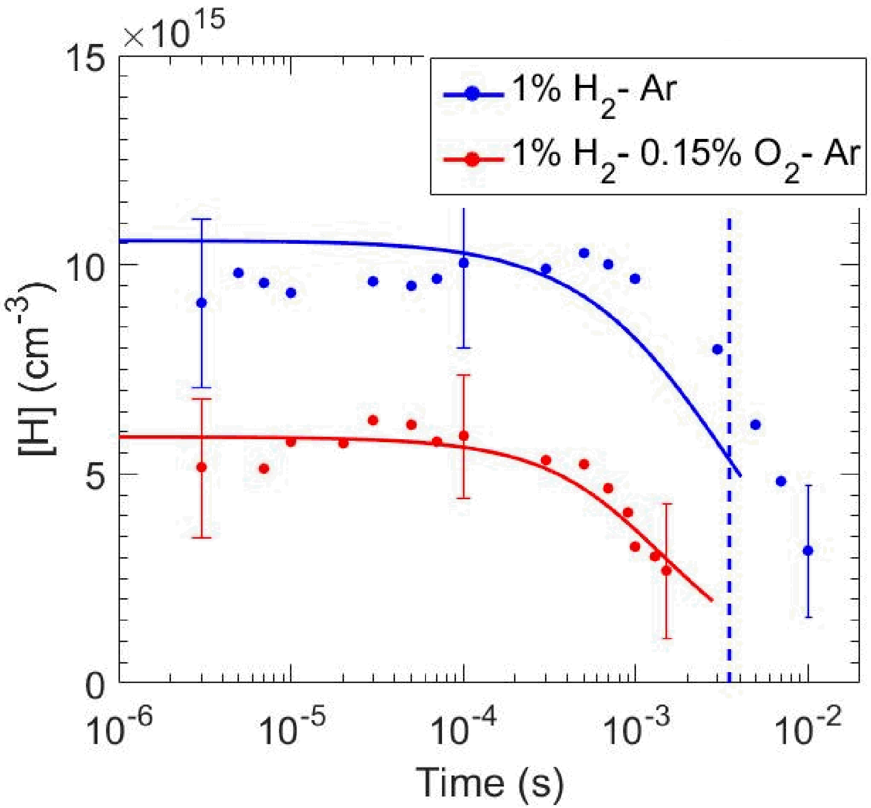
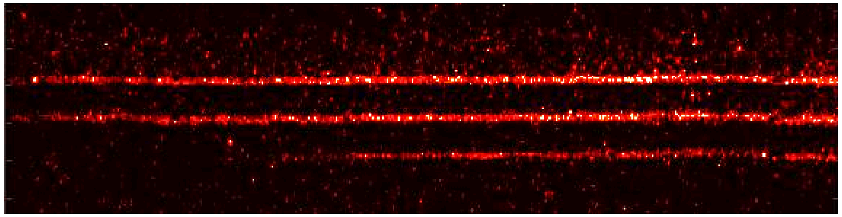
[H] decay after last pulse



T_0= 500 K, P= 300 Torr
20 kHz, 25 pulses

H TALIF Line Images

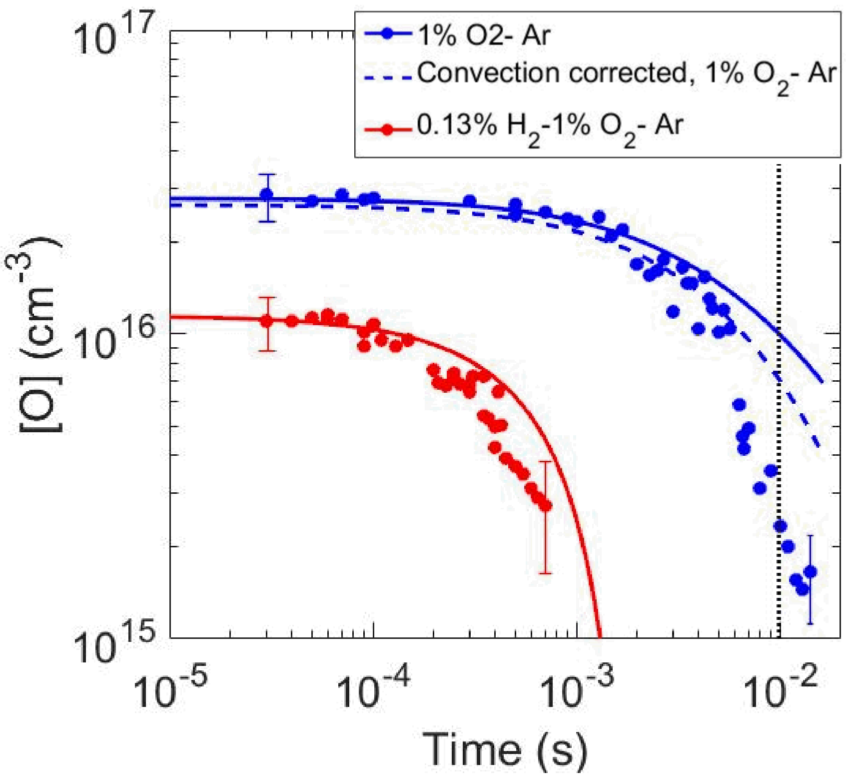


3 μs
300 μs
3 ms

- Good agreement between data and predictions
- H atom decay is overpredicted in H_2-Ar mixture
  - Similar behavior to fs-TALIF experiments (Schimidt, et al. 2015)
- Convection is additional decay mechanism at long enough time scales

Time-resolved O atom measurements

[O] decay after last pulse



T_0= 500 K, P= 300 Torr
20 kHz, 75 pulses

- Good agreement between data and predictions
- O atom decay is underpredicted in O_2-Ar mixture
  - Inclusion of convection improves agreement in O atom decay rate
- Addition of H_2, reduces peak [O] produced during the discharge burst and increases the decay rate
- In a O_2-Ar mixture, ≈40% of initial O_2 is dissociated during the discharge burst

Insight into reaction kinetics

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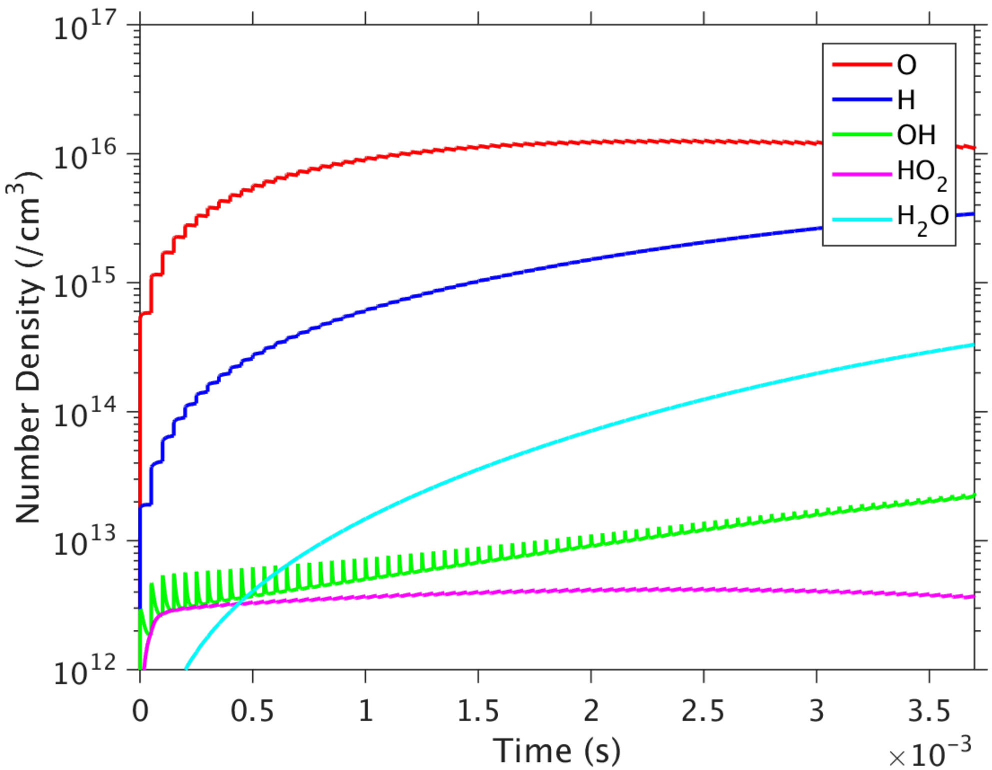
Number density predictions of dominant species, during the burst

dominant species, after the burst



T_0= 500 K, P= 300 Torr
20 kHz, 75 pulses
0.13% H_2-1% O_2-Ar

Kinetic modeling predicts in a

H_2–O_2 -Ar mixture:

Reduced Mechanism for radical decay

H atoms recombine with O_2,

$$H + O_2 + Ar \rightarrow HO_2 + Ar$$

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

Additional H atom reaction with HO_2 forms OH,

$$H + HO_2 \Rightarrow 2OH$$

O atoms react with OH,

$$H + O_2 + Ar \rightarrow HO_2 + Ar$$

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

Estimated chain length is $\frac{H_2O}{[H][O]} \sim 1.1$

$$O + H \rightarrow OH$$

→Chain branching reactions are negligible

Conclusions

- Measurements of [H] and [O] by TALIF provide quantitative insight into reaction kinetics using a “0D” plasma flow reactor
- Atomic radicals are produced by Ar* quenching reactions with H_2 and O_2 (~20% $E_{CDP} \rightarrow$ H atom, ~50% $E_{CDP} \rightarrow$ O atom)
- At long timescales, the near 0D approximation fails and predictions must account for the convection of the flow
- In low temperature plasma oxidation, chain branching reactions are negligible
- A reduced mechanism demonstrates atomic radical species decay is dependent only the amount of primary radicals produced during the discharge burst

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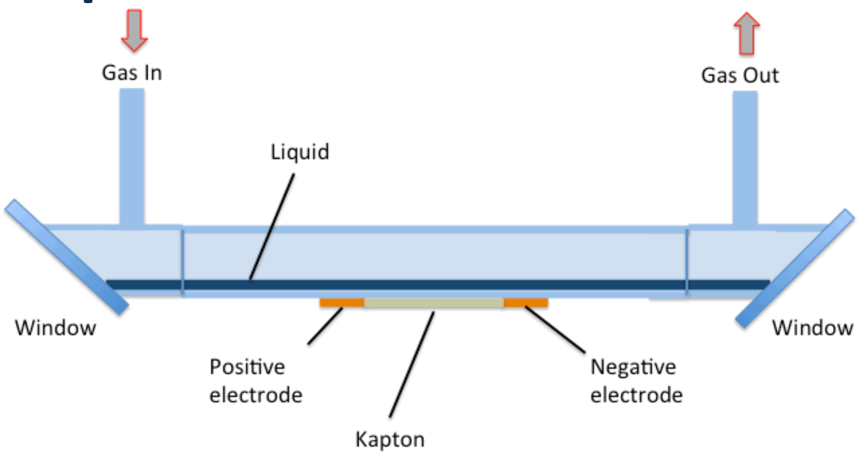
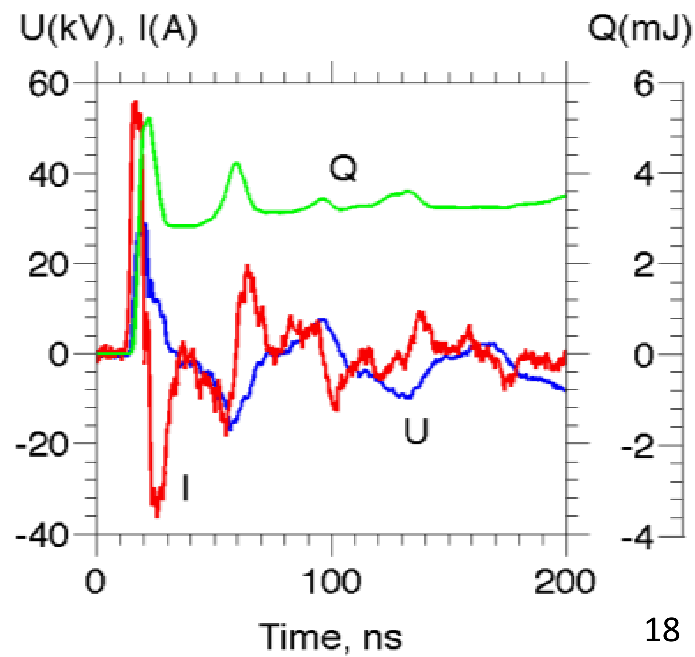
- Plasma-surface interactions
  - Background and motivation
  - Sum frequency generation overview

Radical measurements in a ns pulse discharge at a liquid/vapor interface

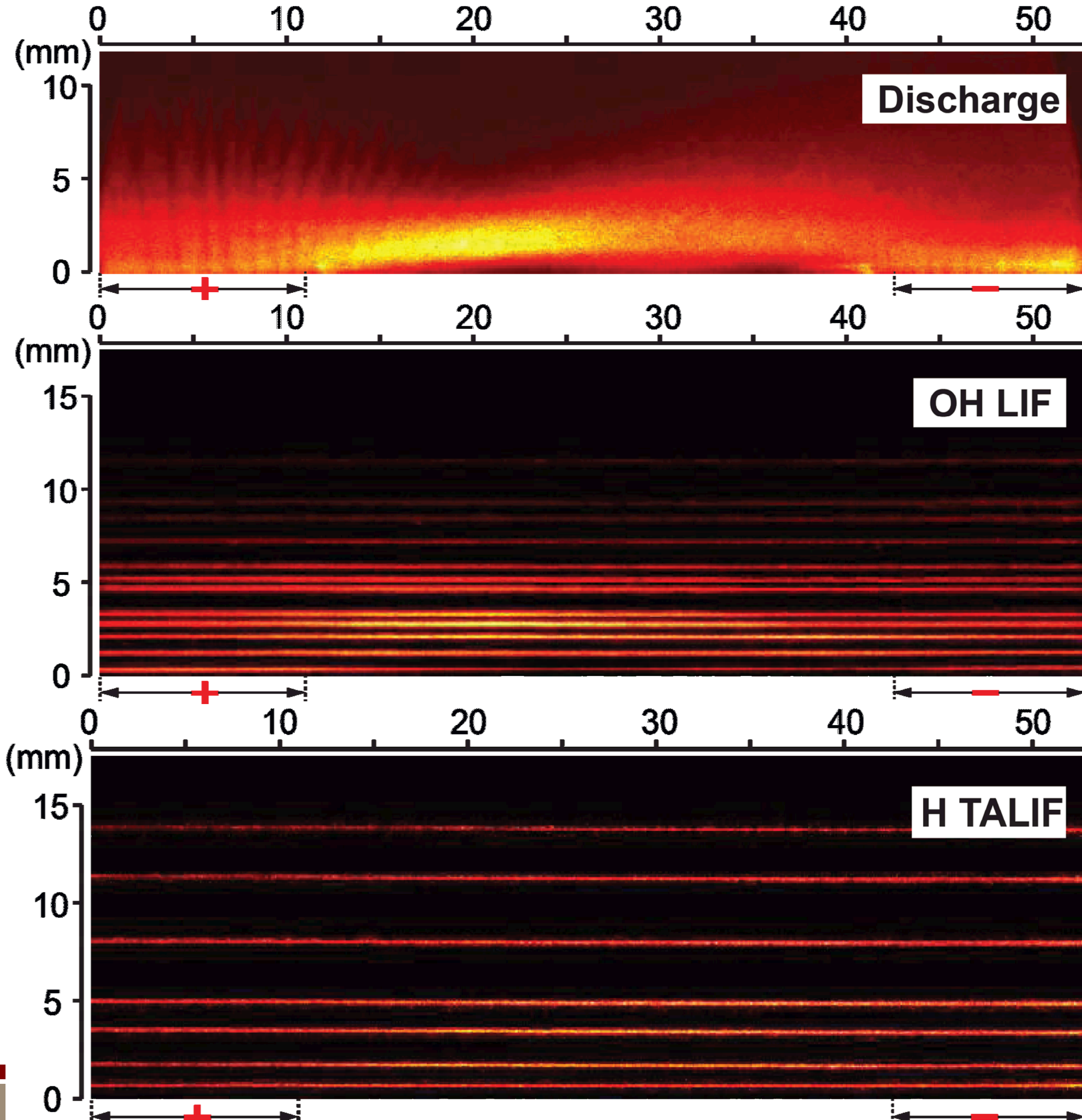
- Nonequilibrium plasma has two interaction areas
  - the plasma/air boundary
  - the plasma/liquid interface
- Dielectric barrier discharge generates a surface ionization wave plasma
- Flow a saturated H_2O vapor / Argon buffer over distilled water
- Use LIF and TALIF techniques to measure radical species generated by the plasma in evaporating water vapor





T_0= 300 K, P= 30 Torr
1 kHz, 20 pulses

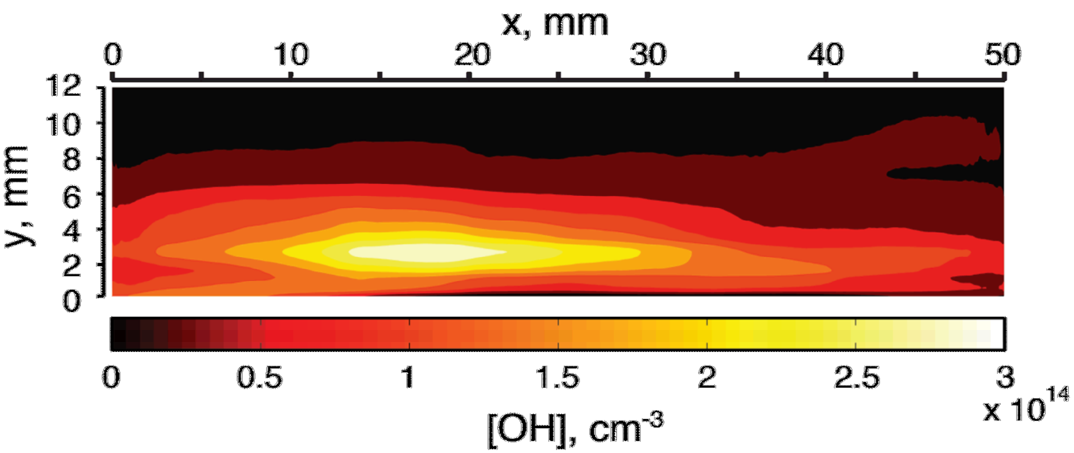
Plasma emission, OH and H line images

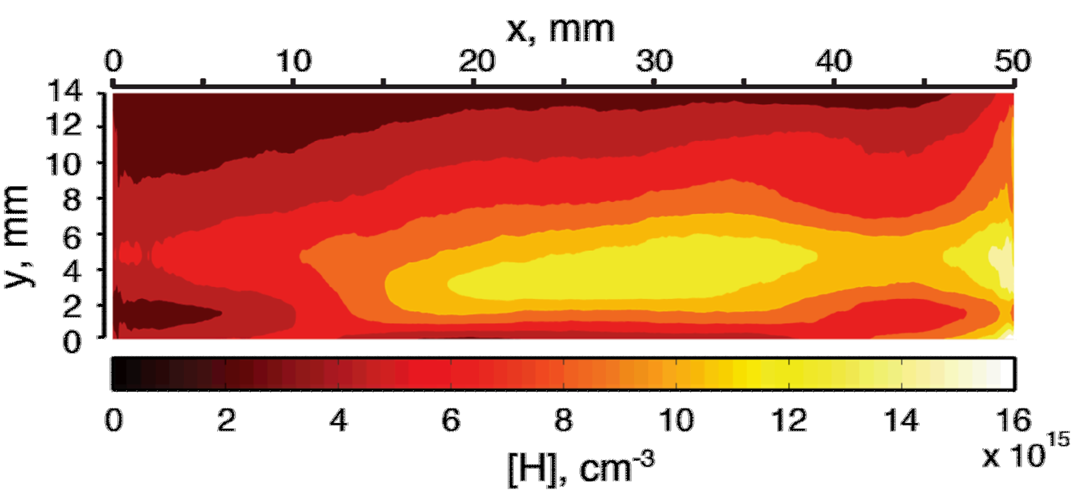


- Plasma is "lifted" from surface
- Liquid water surface at y=0
- *h* = 300 µm to 15 mm above the surface
- Sets of line images used to obtain 2-D contour plots of OH and H Distribution

Ar/H_2O
T_0= 300 K, P= 30 Torr
1 kHz, 20 pulses
Flow rate of 0.1slm

Spatially resolved [OH] and [H] in the plasma afterglow





- OH distribution follows plasma emission intensity
- H atoms diffuse / convect away from liquid surface, generation region

$H_2O + e^- \rightarrow H + OH + e^-$

$[OH]_{peak} = 3\times10^{14}\ cm^{-3}$

$[H]_{peak} = 1.6\times10^{16}\ cm^{-3}$

[H] >> [OH]

$OH + OH \rightarrow H_2O + O$
$\tau \sim 100\ \mu s$

$H + OH + M \rightarrow H_2O + M$
$\tau \sim 1\ ms$

Conclusions

- Measurements of radical species generated at a liquid/vapor interface demonstrate the capabilities of laser diagnostics for plasma-assisted-chemistry
- OH distribution follows plasma emission intensity, while H radicals diffuse/convect away with the gas flow
- H atom number density is greater compared to OH molecule number density because two-body recombination is faster than three-body recombination

What about the plasma/liquid interface?

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- **Plasma-surface interactions**
  - **Background and motivation**
  - Sum frequency generation overview

Background and motivation

- **Plasma enhancement of reaction kinetics at an interface**
  - Atmospheric pressure plasmas at interfaces→ strong electric fields, (V)UV emission, and charge deposition
  - These factors influence species at the interface
    - Radical and reactive species
    - Ions and electrons
  - Key challenge→ Identifying physical and chemical processes occurring at the plasma interface (Bruggeman, et al. 2016)
    - Measurement of chemical species produced during the plasma discharge
    - Measurement of species lifetimes
    - Insight into recombination kinetics

Background and motivation, cont.

- **Characterization of adsorbates and effect on plasma generation**
  - Initial plasma breakdown removes species from electrode surface
  - Exposure to gases allows deposition and absorption of new/other species
  - Do these species contribute to subsequent plasma breakdown behavior?
  - LDRD: Agile Component Design Through Integrated Diagnostics and Computational Optimization
    - What species are absorbed onto the electrode surface?
    - Will these species by chemisorbed or physisorbed?
    - Can breakdown behavior be controlled by preferentially adsorbing certain species?

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Femtosecond Sum Frequency Generation

- Sum Frequency Generation – 2nd order nonlinear process

$$\boldsymbol{P} = \varepsilon_0 \chi^{(2)} \boldsymbol{E}^{\boldsymbol{2}} \qquad \boldsymbol{E} = \boldsymbol{E_1} \cos(\omega_1 t) + \boldsymbol{E_2} \cos(\omega_2 t)$$

$$\boldsymbol{P}^{(\boldsymbol{2})} = \varepsilon_0 \chi^{(2)} \left\{ (\boldsymbol{E}_{\boldsymbol{1}}^2 + \boldsymbol{E}_{\boldsymbol{2}}^2) + (\boldsymbol{E}_{\boldsymbol{1}}^2 \cos 2\omega_1 t + \boldsymbol{E}_{\boldsymbol{2}}^2 \cos 2\omega_2 t) + (\frac{1}{2} \boldsymbol{E_1 E_2} \cos(\omega_1 - \omega_2) t) + (\frac{1}{2} \boldsymbol{E_1 E_2} \cos(\omega_1 + \omega_2) t) \right\}$$

DC Field

Second Harmonic Generation

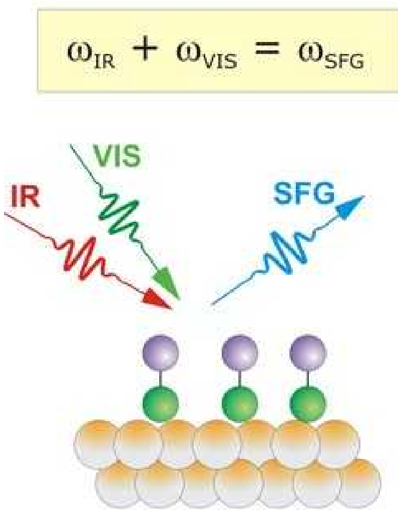
Difference Frequency Generation

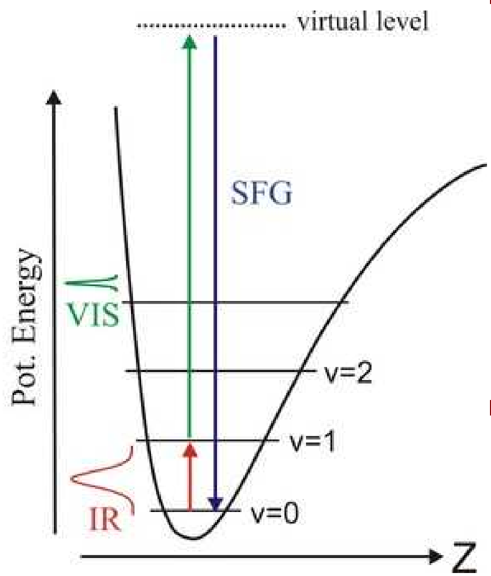
Sum Frequency Generation

$$\boldsymbol{P}^{(\boldsymbol{2})} = \varepsilon_0 \chi^{(2)} \left\{ (\frac{1}{2} \boldsymbol{E_1 E_2} \cos(\omega_1 + \omega_2) t) \right\}$$

Femtosecond Sum Frequency Generation

- Sum Frequency Generation: 2 beams in → 3 beams out



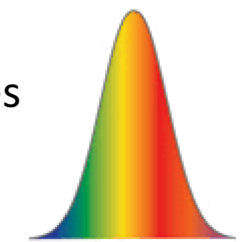


$$I_{SFG}(\omega_{SFG}) \propto \left|P^{(2)}(\omega_{SFG})\right|^2$$

$$I_{SFG}(\omega_{SFG}) \propto \left|X^{(2)}{}_R + X^{(2)}{}_{NR}\right|^2$$

- Femtosecond pump beam
  - Fourier transform limited pulses

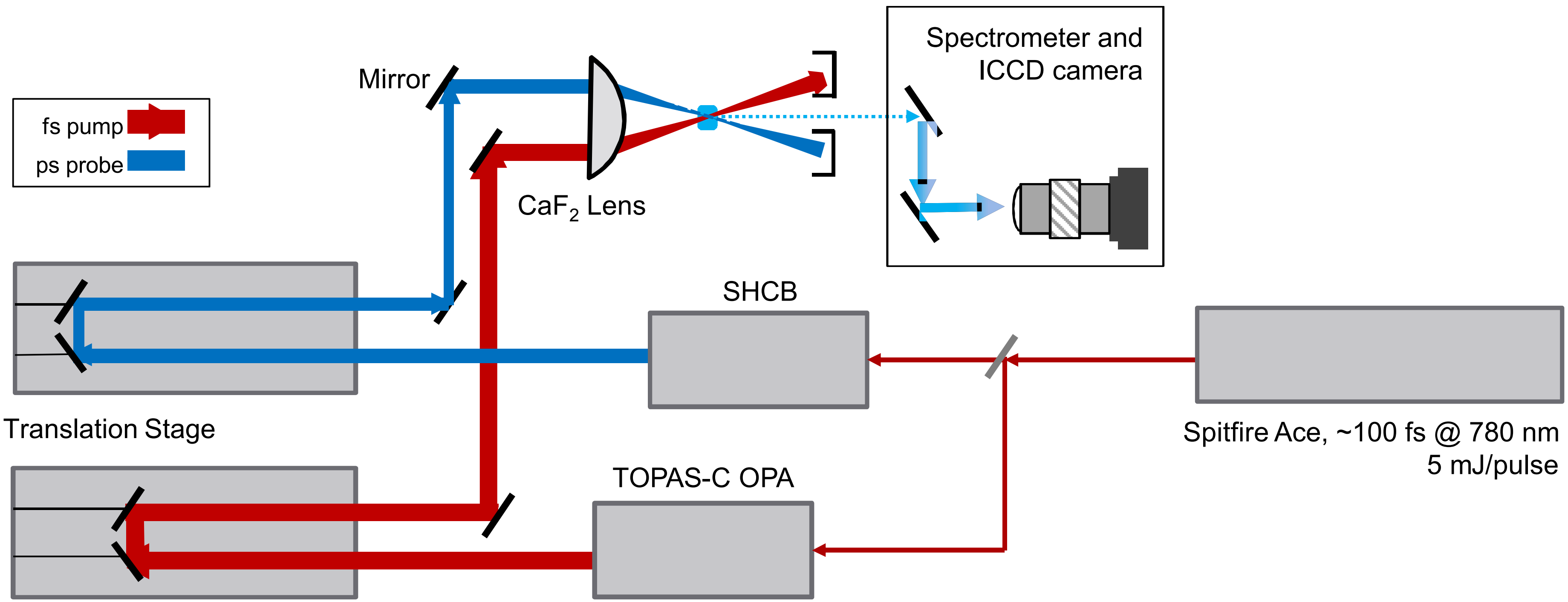
$$\Delta\omega * \Delta t \geq \frac{1}{2} \; for\ Gaussian$$



  - Single pulse can reach a broad range of absorbance features: C-H, $C\text{-}H_3$, and O-H
- Picosecond probe beam
  - Narrowband
  - Scatters off polarized molecules
  - Produces blue-shifted signal beam
- Spectra has resonant and non-resonant contribution
- Fit with Voight profile

Proposed diagnostic

- ~3000 nm fs beam; 390 nm ps beam
- Metal Substrate: use p-p-p polarization configuration
  - Simple, enhanced signal, no phase information
- Calibration targets
  - Distilled water on a ceramic?
  - Self Assembled Monolayers on Au or Ag, to provide known density of C-H, O-H stretch



Acknowledgements

- The Ohio State University
  - Igor Adamovich, Bill Rich, and the Non-equilibrium Thermodynamics Laboratory
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- Sandia National Laboratories
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Acknowledgements, cont.

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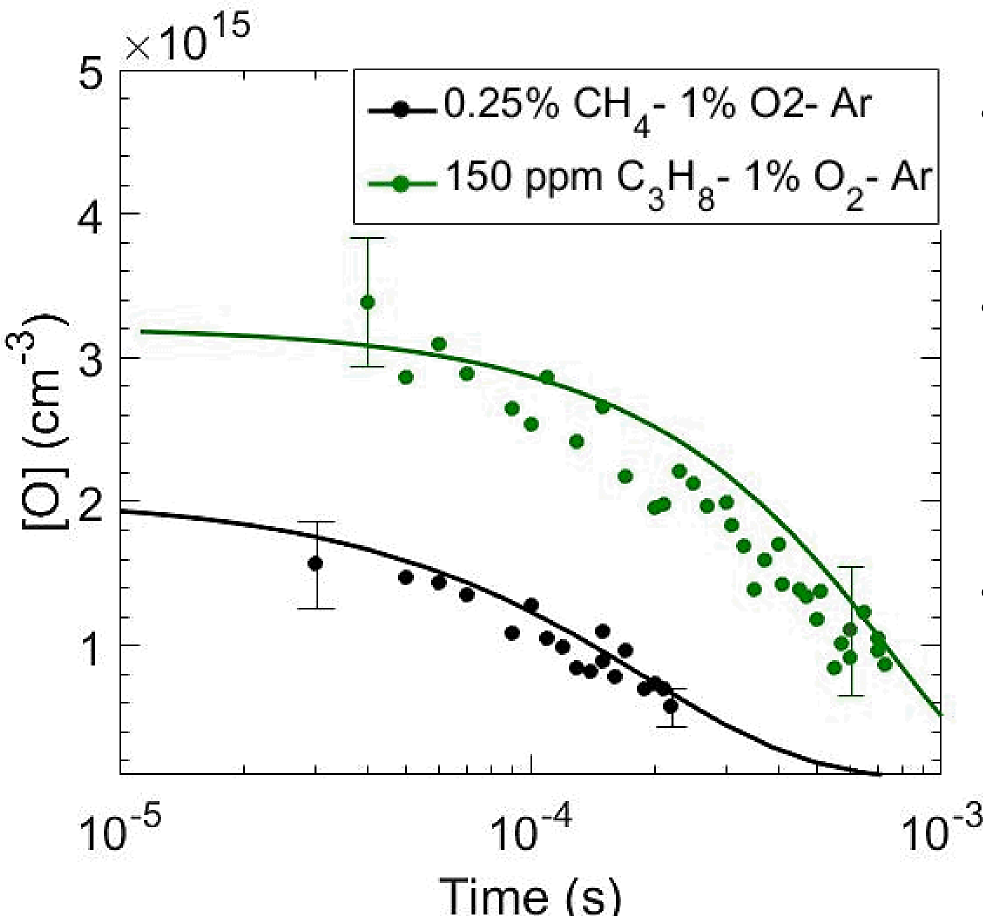
- DOE PSAAP-2 Center “Exascale Simulation of Plasma-Coupled Combustion” (under U. Illinois at Urbana-Champaign prime)
- US DOE Plasma Science Center “Predictive Control of Plasma Kinetics: Multi-Phase and Bounded Systems”
- NSF “Fundamental Studies of Accelerated Low Temperature Combustion Kinetics by Nonequilibrium Plasmas”
- Agile Component Design Through Integrated Diagnostics and Computational Optimization LDRD

Thanks for your attention!

Questions?

O TALIF in C_xH_y – O_2 mixtures

[O] decay after last pulse



T_0= 500 K, P= 300 Torr
20 kHz, 75 pulses

- O atom number density after the burst and decay rate are reproduced well
- Addition of hydrocarbon fuels reduces O atom number density and decay time
- H atoms are generated in the plasma by Ar* quenching by C_xH_y,

$$Ar^* + C_xH_y \rightarrow Ar + C_xH_{y-1} + H$$

- H atom number density increases throughout discharge burst
- Dominant mechanisms the same as H_2-O_2-Ar mixtures

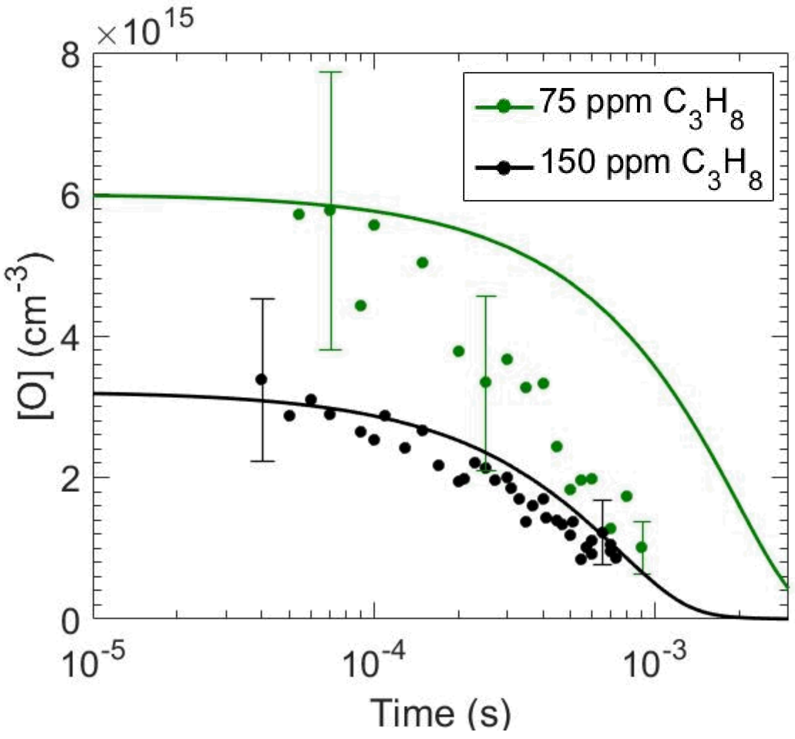
Reduced Mechanism

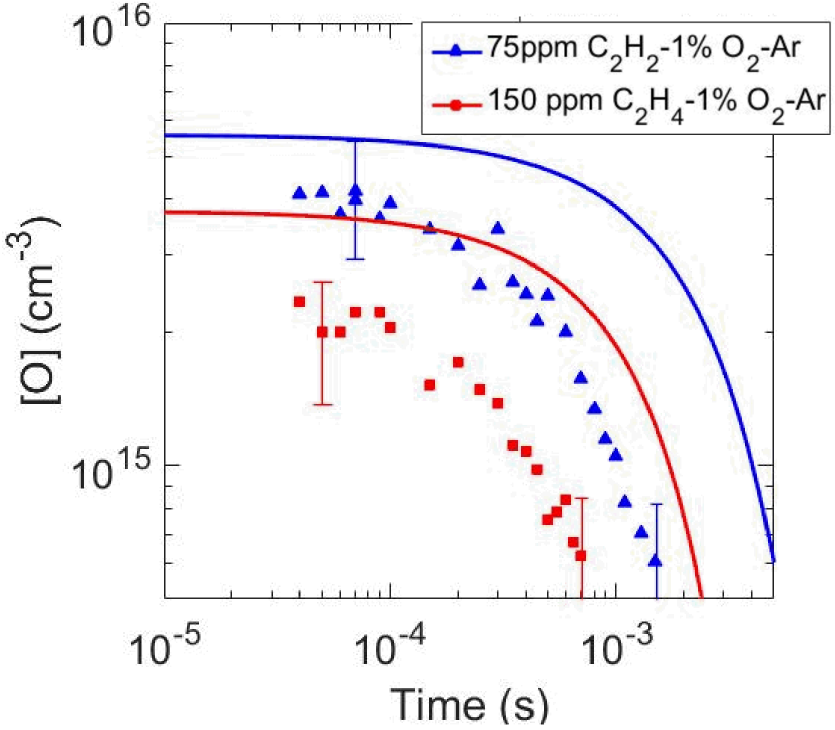
$$O + H \rightarrow OH$$

O TALIF fuel-limited mixtures

T_0= 500 K, P= 300 Torr
20 kHz, 75 pulses

[O] decay after last pulse



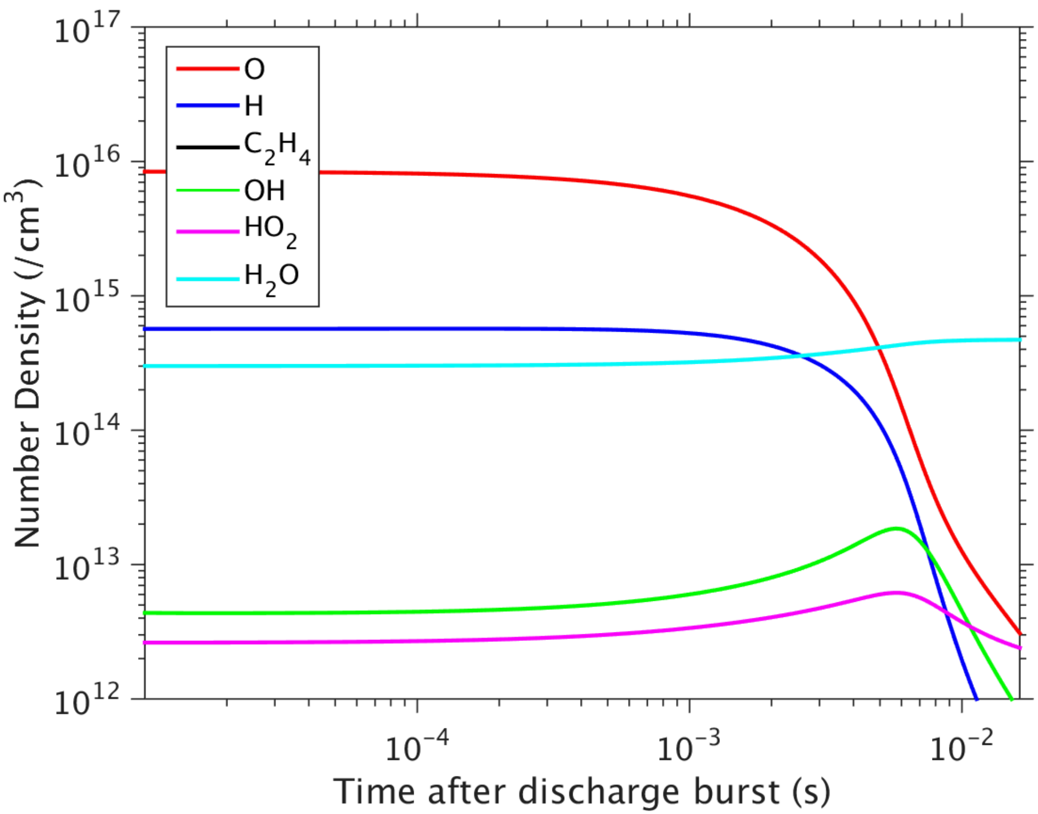


- 75 ppm of C_3H_8 is completely oxidized by ~50 pulses during the discharge burst
- Both 75 ppm and 150 ppm of C_2H_4 is completely oxidized by ~30 pulses during the discharge burst

Fuel-limited reaction kinetics

Predicted number densities of dominant species after the burst

150 ppm C_2H_4- 1% O_2- Ar



T_0= 500 K, P= 300 Torr
20 kHz, 75 pulses

Mismatch between measured and predicted decay rate due to H atom generation

H atom number density "levels off" despite inclusion of Ar* by stable and intermediary species

Resulting in significant decrease in OH produced during the burst

Reduced mechanism is O atom recombination → very slow

Additional H atoms are being mixed in, removing the near "0D" assumption

Reduced mechanism:

$$\boldsymbol{O + OH \rightarrow H + O_2}$$

$$\boldsymbol{O + HO_2 \rightarrow OH + O_2}$$

$$\boldsymbol{H + O_2 + Ar \rightarrow HO_2 + Ar}$$

Kinetic modeling predicts in a C_xH_y –1% O_2 -Ar mixtures:

$$\boldsymbol{O + O \rightarrow O_2}$$

Dominant reaction of O atoms with OH

$$\boldsymbol{O + OH \rightarrow H + O_2}$$

Dominant OH production by O atom reaction with HO_2,

$$\boldsymbol{O + HO_2 \rightarrow OH + O_2}$$

Dominant HO_2 production by,

$$\boldsymbol{H + O_2 + Ar \rightarrow HO_2 + Ar}$$