



Florida State University

- Founded 1851, Enrollment 44,000
- Ranked 18 of US Public Research Universities (USNWR)

Florida A & M University

- Founded 1887, Enrollment 10,000
- Public HBCU in Florida

FAMU-FSU College of Engineering

- Founded 1982
- Shared by FSU and FAMU

Chemical and Biomedical Engineering

- Enrollment: 500 undergraduates, 50 graduates
- 18 tenure track faculty members



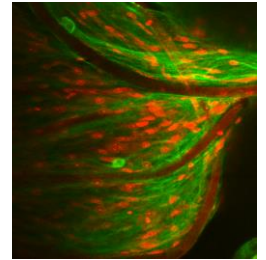
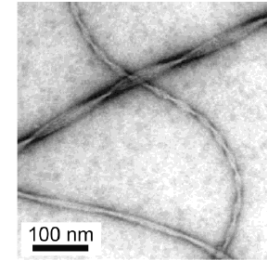
National High Magnetic Field Lab

General Department Research Areas

- Department of Chemical and Biomedical Engineering -

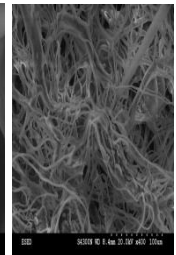
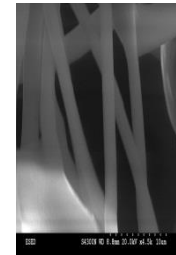
- Biomedical Engineering

- Imaging (NMR,MRI) - Grant, Li, Holmes, Mohammadigoushki
- Cellular and Tissue Engineering – Grant, Li, Holmes
- Biomaterials - Ali, Guan, Holmes, Ramakrishnan



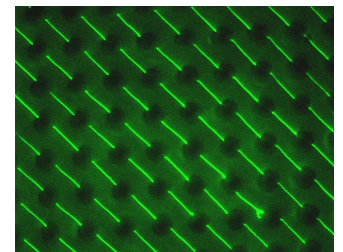
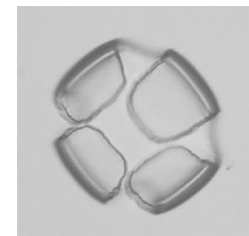
- Materials

- Polymers - Alamo, Arnett, Chung, Hallinan, Ricarte
- Complex Fluids - Mohammadigoushki, Ramakrishnan
- Electronic Materials - Siegrist
- Nano - Materials – Ali, Grant, Guan, Hallinan, Kalu, Ramakrishnan, Siegrist



- Chemical Engineering

- Catalysis – Chung
- Chemical Reaction Engineering – Locke
- Energy storage – batteries – Hallinan, Kalu





FAMU-FSU
Engineering

Chemical and Biomedical Engineering

Hydroxyl Radicals in Gas-Liquid Water Plasma Reactors

Professor Bruce R. Locke

Florida State University

*Department of Chemical and Biomedical Engineering
Tallahassee, FL*

Funding

National Science Foundation CBET – 1236225, 1702166
Czech Fulbright Commission, Florida State University



Contacting Plasma with Liquid Water

Underwater

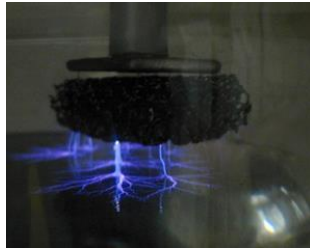


- Electrical discharge underwater (pulsed, RF, microwave)
- 10^{-3} to 1 J/pulse (also ns to μ s pulses possible)
 - up to kJ/pulse - electrohydraulic discharge, arc formation, exploding wire
 - breakdown underwater: 1 MV/cm

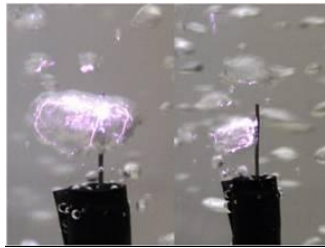
Gas-liquid Interface (AC, DC, or pulsed)



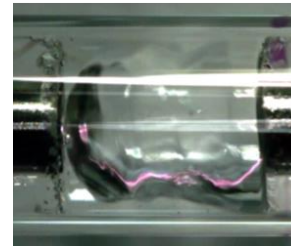
Gliding arc



Planar



Bubbles

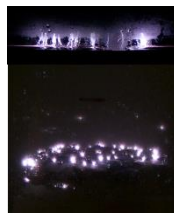


Films

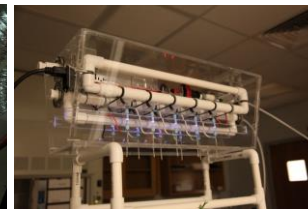
- Discharge in gas
- plasma in gas
 - gas phase breakdown
 - plasma touches water surface
 - liquid properties can be important (conductivity)



Combined gas/liquid



Scaled prototypes



Water spray

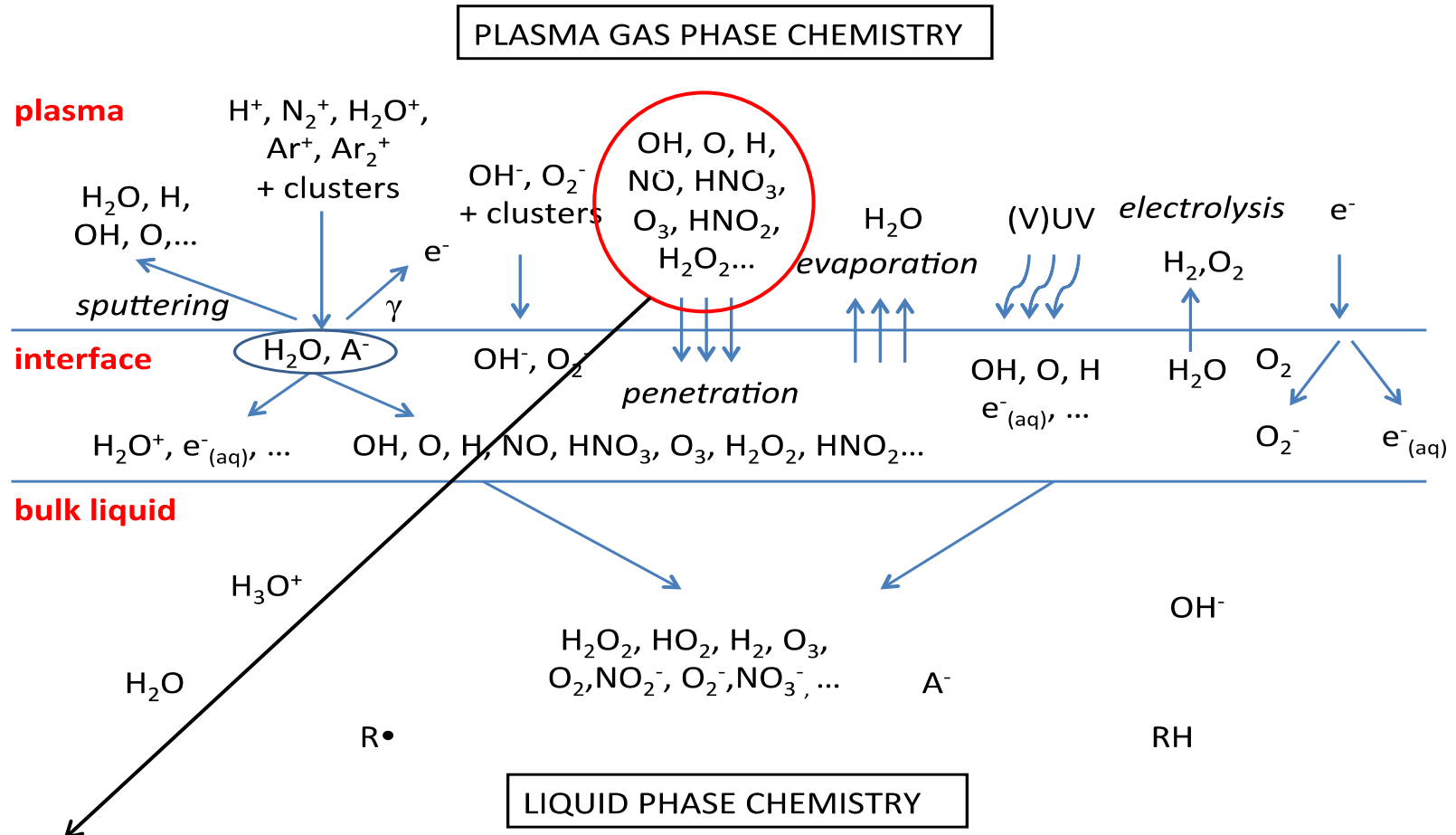
Applications of Plasma with Liquid Water

- Water pollution treatment
 - Wide range of organic and some inorganic compounds – emerging contaminants – perfluorinated species, antibiotics, personal care products
- Air pollution treatment (wet plasma – water sprays and films)
 - Nitrogen and sulfur oxides, volatile organic compounds (VOCs)
- Disinfection and biomedical
 - Bacteria, yeast, viruses
 - Biomedical – wound healing, cancer treatment
- Chemical synthesis
 - Partial oxidation – alcohols, aldehydes...
 - Nanoparticle synthesis
 - Polymer coatings
 - Plasma activated water for agriculture uses – nitrates/nitrites, seed germination...

Many reviews on this subject published in last 10 years: Akiyama, Malik, Locke, Sunka, Sato, Bruggeman, Lukes, Thagard, Weltmann, Brandenburg,.....

P. Bruggeman, M.J. Kushner, B.R. Locke, et al., Plasma-Liquid Interactions: A Review and Roadmap, *Plasma Sources Science and Technology*, 2016

Complexities of Gas-Liquid Water Plasma Chemistry



- Chemistry strongly dependent on gas composition (air, N_2 , O_2 , Ar, He)
- Not all factors equally important or occur in all types of gas-liquid plasma

Key Chemical Species from Electrical Discharge with Water

Electron dissociation



Thermal dissociation



Standard oxidation potentials

$$\cdot\text{OH} = 2.80 \text{ V}$$

$$\text{O} = 2.42 \text{ V}$$

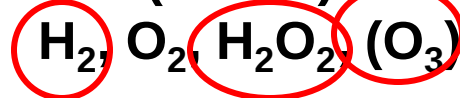
$$\text{O}_3 = 2.07 \text{ V}$$

$$\text{H}_2\text{O}_2 = 1.77 \text{ V}$$

$$\cdot\text{HO}_2 = 1.7 \text{ V}$$

Possible Products and active species

Molecules: (stable)



Disinfection, chemical destruction
Stable molecular carrier for OH radicals

Radicals and atoms: (short life)

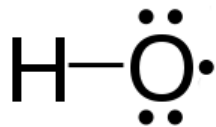


Ions:

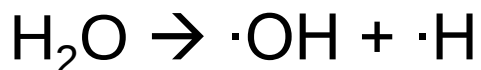


May be important for reduction reactions

Hydroxyl Radical Generation from Water



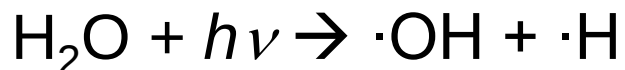
- Thermodynamic limit
(from ΔH_r)



Yields* (molecules/100 eV)

20

- UV light

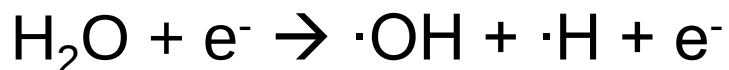


(120 to 190 nm, depends on quantum yields and lamp efficiencies)

2 to 3 (in liquid)

5 to 6 (in gas with vapor)

- Radiation



(electron beams, gamma radiation)

2 to 4 (in liquid)

7 to 9 (in gas with vapor)

- Plasma



Subject of this talk

* -note: yields estimated from literature where data was obtained under wide range of different operating conditions and measurement methods

Note on Importance of Hydroxyl Radical

- Gas Phase -

- Provides insight into oxygen and water chemistry in interstellar space: 10^4 - 10^6 cm^{-3} (low temperature and density)
- Earth atmosphere:
 - Formed in stratosphere by UV: 10^6 cm^{-3}
 - Cleans nitrogen oxides, organics from troposphere, 0.01 to 1 s
- Indoor air – similar chemistry as in atmosphere
 - Clean air: 10^4 to 10^5 cm^{-3}
 - Photolysis of HONO: 10^6 cm^{-3}
 - With air cleaners: 10^7 to 10^8 cm^{-3}
- Combustion – main reactant: 10^{14} to 10^{16} cm^{-3} , high temperature and pressure (1 to 5% of species)
- Gas phase plasma reactors (with water vapor): 10^{13} - 10^{15} cm^{-3} , atmospheric pressure and temperature

Note on Importance of Hydroxyl Radical

- Liquid Phase -

- Close coupling of $\cdot\text{OH}$ with H_2O_2 in the liquid phase
- Natural water:
 - UV photolysis of nitrate, dissolved organic matter
 - H_2O_2 : 50-1000 nM
 - Natural seawater – $\cdot\text{OH}$: 10^{-9} to 10^{-6} nM
 - Acid mine water – $\cdot\text{OH}$: 10^{-5} to 10^{-3} nM
- Found in biology
 - Cells: H_2O_2 1 to 10 nM
- Advanced oxidation technologies ($\cdot\text{OH}$ based processes)
 - O_3 , $\text{O}_3/\text{H}_2\text{O}_2$, $\text{O}_3/\text{H}_2\text{O}_2/\text{UV}$, Fenton($\text{H}_2\text{O}_2/\text{Fe}$)
 - $\cdot\text{OH}$: 10^{-4} to 10^{-1} nM (quasi steady-state due to very high reactivity)
- Plasma contacting liquid water
 - $\cdot\text{OH}$: 10^{-1} nM (quasi steady-state due to very high reactivity)

Reaction Rate Constants

(Second order $\text{M}^{-1}\text{s}^{-1}$, Tarr (2003))

	$\cdot\text{OH}$	O_3	pH	e_{aq}^-	$\cdot\text{H}$
Benzene	7.8×10^9	2	2-3	9.0×10^6	9.1×10^8
Phenol	6.6×10^9	1300	2	2.0×10^7	1.7×10^9
		2×10^6	7		
Chloro-phenol	12×10^9	1600	2		
Formic acid	0.13×10^9	5	2-4		
Trichloro-ethylene	4×10^9	17	2	1.9×10^9	

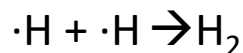
- $\cdot\text{OH}$ reactions near diffusion limits $10^{10} \text{ M}^{-1}\text{s}^{-1}$ in liquids
- Competing (reduction) reactions with $\cdot\text{H}$ and e_{aq}^- (depends upon species)
- O_3 can be important if $[\text{O}_3] \gg [\cdot\text{OH}]$ (ozone solubility range 10^{-5} to 10^{-3} M)
 - $\text{Rate}(\cdot\text{OH})/\text{Rate}(\text{O}_3) = 1$ (chlorophenol); $= 100$ (others) (for max O_3)

Idealized Reaction Pathways

(with H₂O only)



(Primary yield -
radiation chemistry)

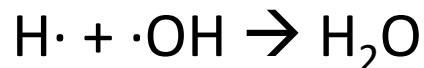


Desired reactions in/near plasma
(very fast reactions)



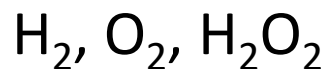
Undesired reactions in/near plasma

$\cdot\text{OH}$ quenching...



(Absolute quenching - Fridman)

Molecular products
(stable)



(Ideal quenching - Fridman)

Used outside of plasma

H₂O₂ – in liquid

H₂ and O₂ – in gas

Underwater Discharge

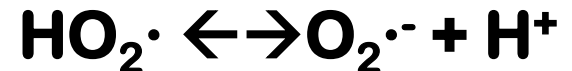
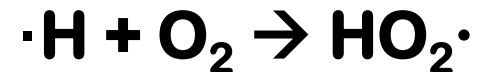
Cooler recombination zone

High T core

Discharge Reactions

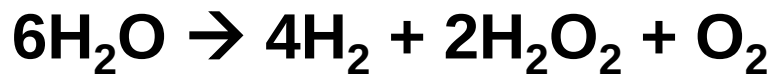


Recombination Reactions



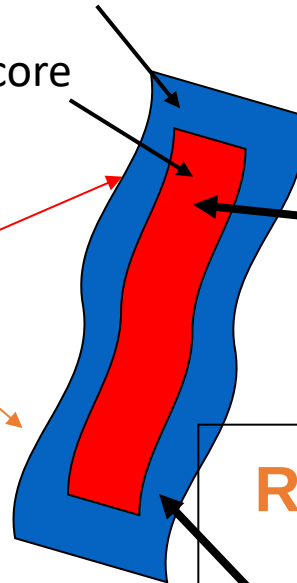
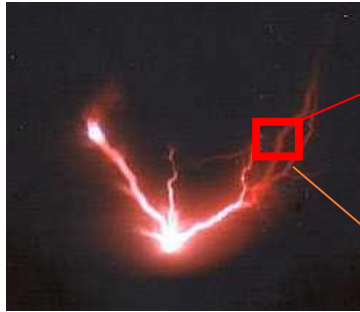
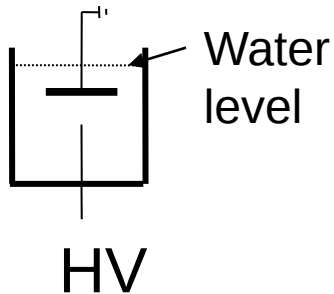
Overall (Bulk) Reaction

(Experimental Observations)



(Joshi et al. 1995; Grymonpre et al. 1998, 1999, 2001; Kirkpatrick and Locke, 2005)

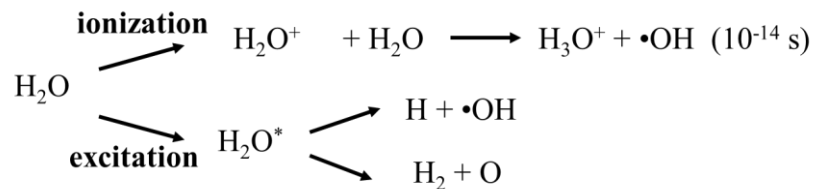
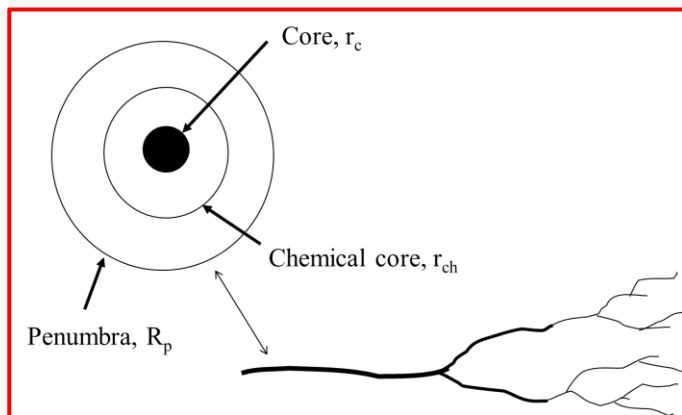
(Mededovic and Locke, 2008, 2009, 2012)



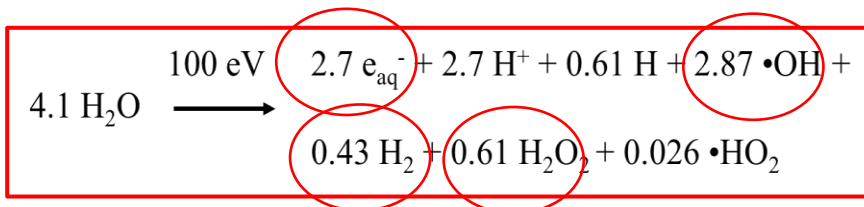
Comments from Radiation Chemistry

(Buxton, 1987; Magee and Chatterjee, 1987)

Radiation track structure



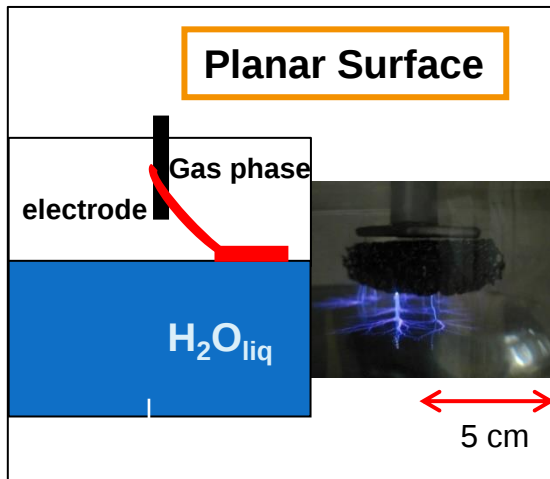
Primary Products



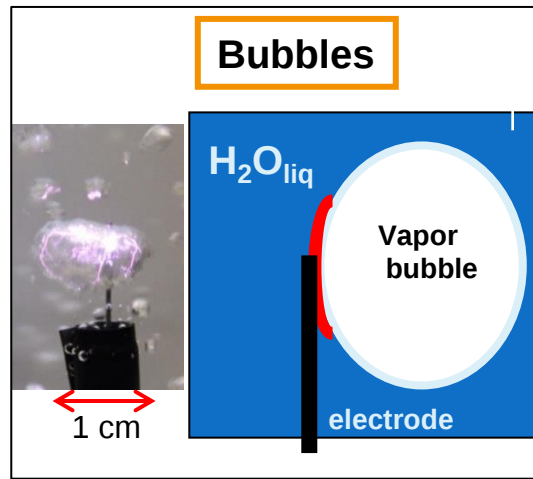
- Geometrical patterns of energy deposition from high energy electrons
- Chemical probes used to determine primary yields – products formed in the chemical core
- Note: O and O₂ not typically found in underwater radiation reactions
- Non-homogeneous energy deposition, fast time scales
- Kinetics in spur leads to homogeneous kinetics at 10⁻⁷ s

Discharges at Gas-Liquid Interface

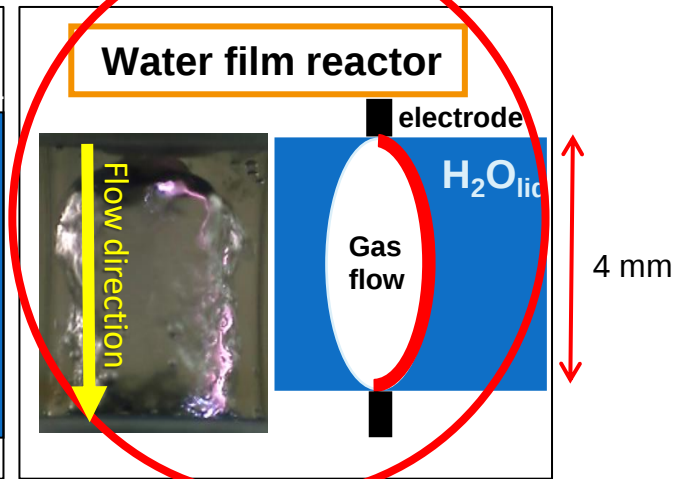
- Plasma propagates in gas phase along the gas/liquid interface
- Requires lower electric field to generate plasma than inside water
- More efficient generation of plasma



(Grymonpre et al., 2004)



(Shih and Locke, 2009)



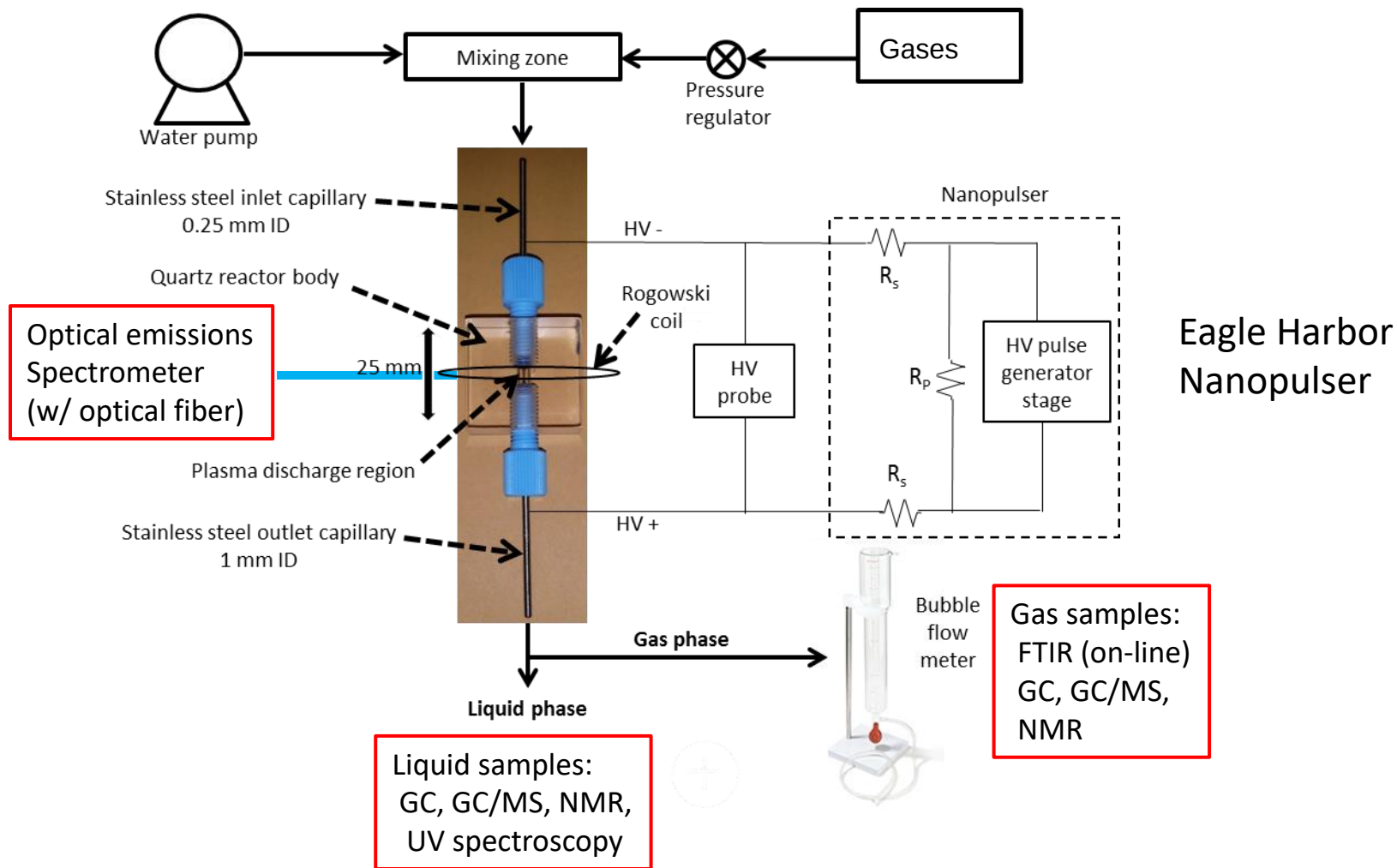
(Wandell and Locke, 2014)

Batch, semi-batch systems

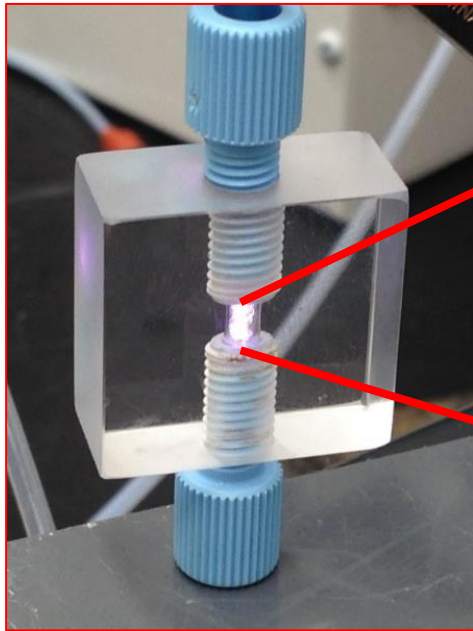
Continuous flow system

Flow system useful to control gas, liquid, and plasma contacting, fluid residence times, and to measure gas and liquid products and reactants.

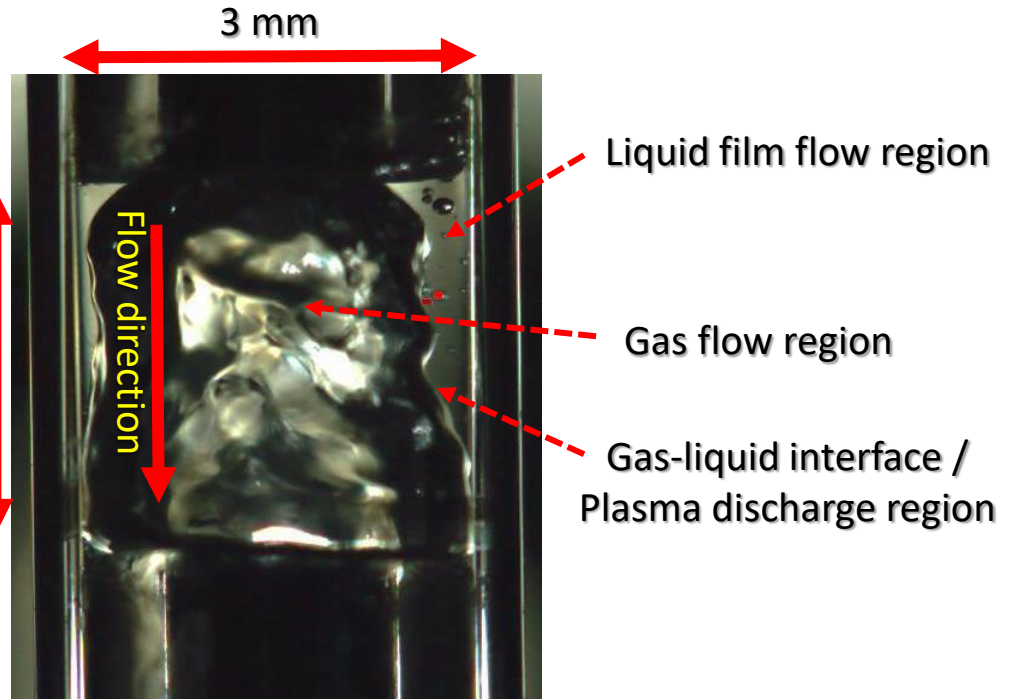
Flowing Film Plasma Reactor System



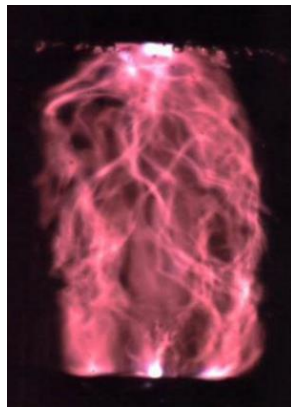
High Speed Imaging



4 mm



*4,000 fps



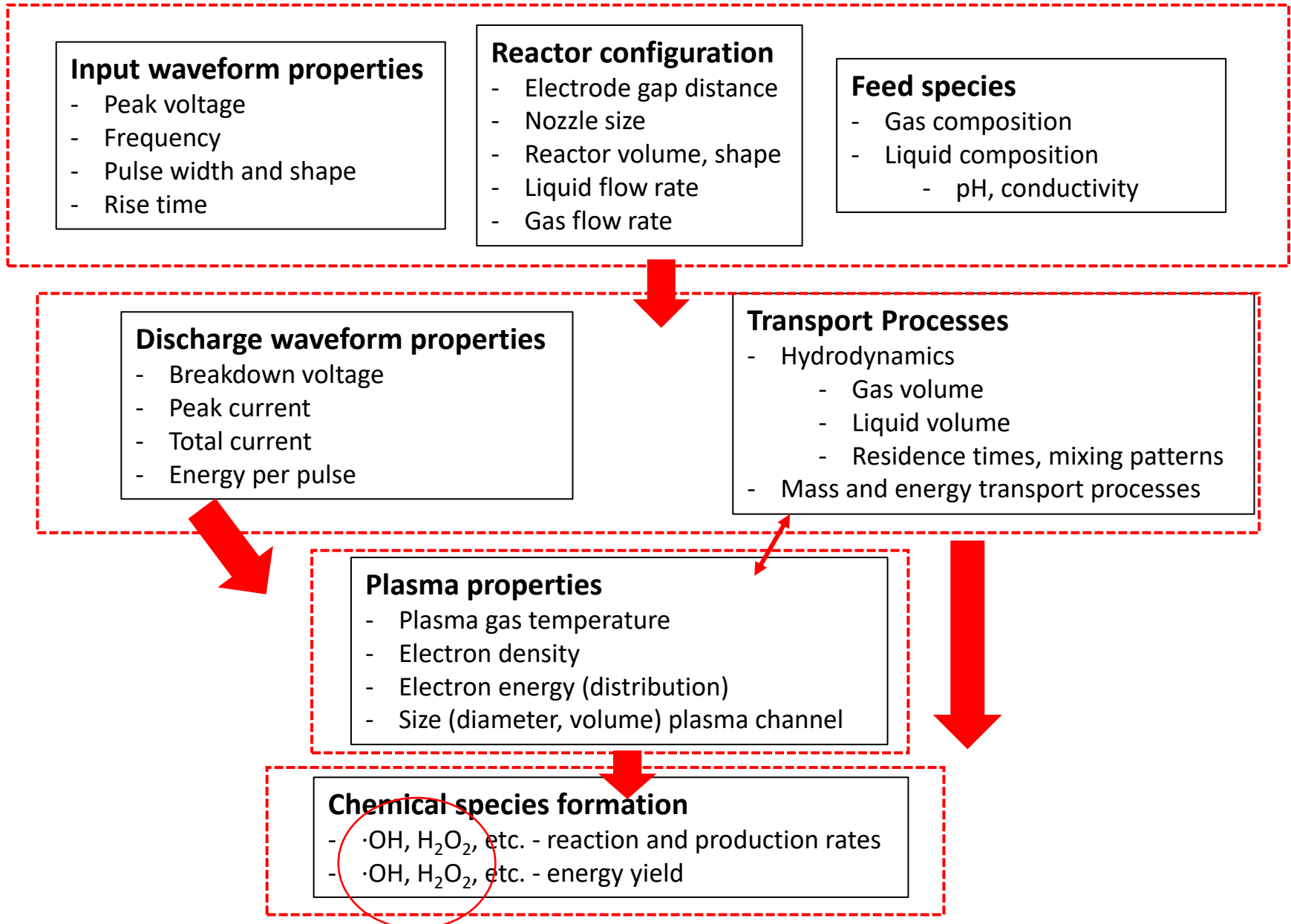
*1/60 sec. shutter speed



*1/12,000 sec.
shutter speed

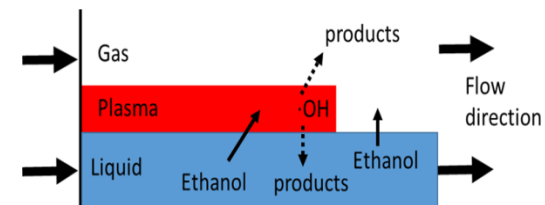
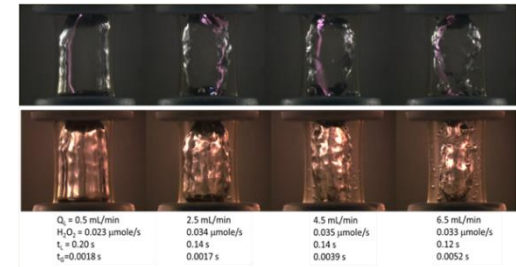
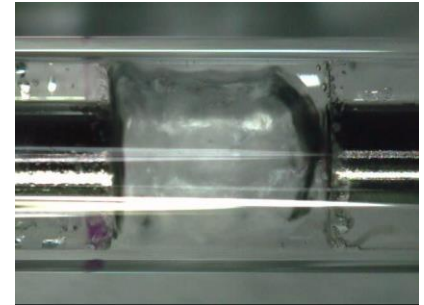
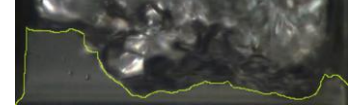
Deionized water
with argon carrier.

Connecting Physical and Chemical Processes



Reactor Characterization

- Geometrical Properties (Wandell et al., 2018)
 - Volumes of liquids and gases
 - Interfacial area (gas-liquid and plasma-liquid)
 - Residence times of liquids and gases
 - 100-250 ms (liquid), 2–5 ms (gas); nozzle size dependent
- Hydrodynamics (Wandell et al., 2018)
 - Roles of nozzle size, gas and liquid flows
 - Flow patterns and regimes (annular flow)
 - Pressure in reactor (choked flow) higher pressure forces liquid to form film on walls
 - No evidence of plasma discharge affecting hydrodynamics
- Mass and energy transfer (Hsieh et al., 2016)
 - Liquid and gas (film theory)
 - Liquid and plasma



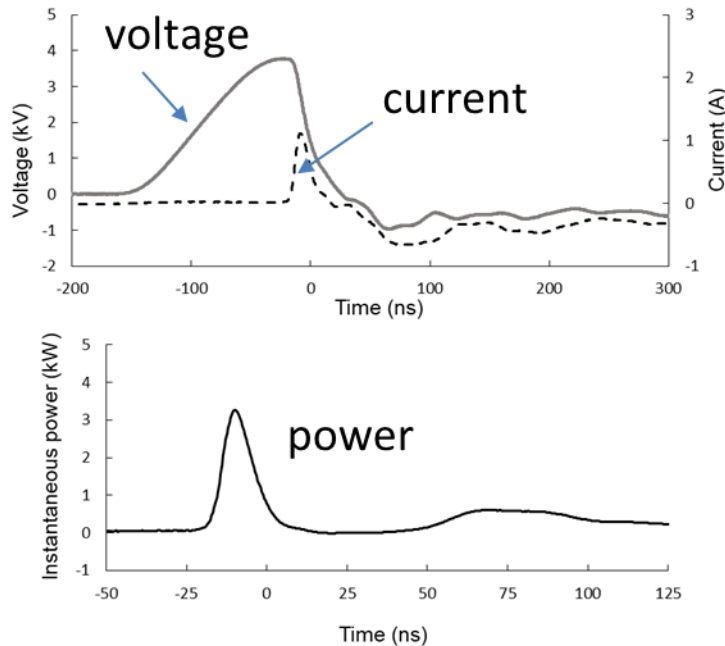
Electrical and Plasma Properties

- Waveforms
 - Ignition coil (microsecond pulser)
 - Nanopulsers
- Plasma properties
 - Plasma gas temperature
 - Electron density
 - Electron energy
 - Plasma volume
- Effects of reactor conditions (Wang et al. 2018, 2019)
 - Effects of carrier gas composition
 - Effects of gas and liquid flows
 - Effect of pulse properties
 - Effects of solution conductivity

Power Supplies - Nanopulsers

1) Airity Technologies (custom)

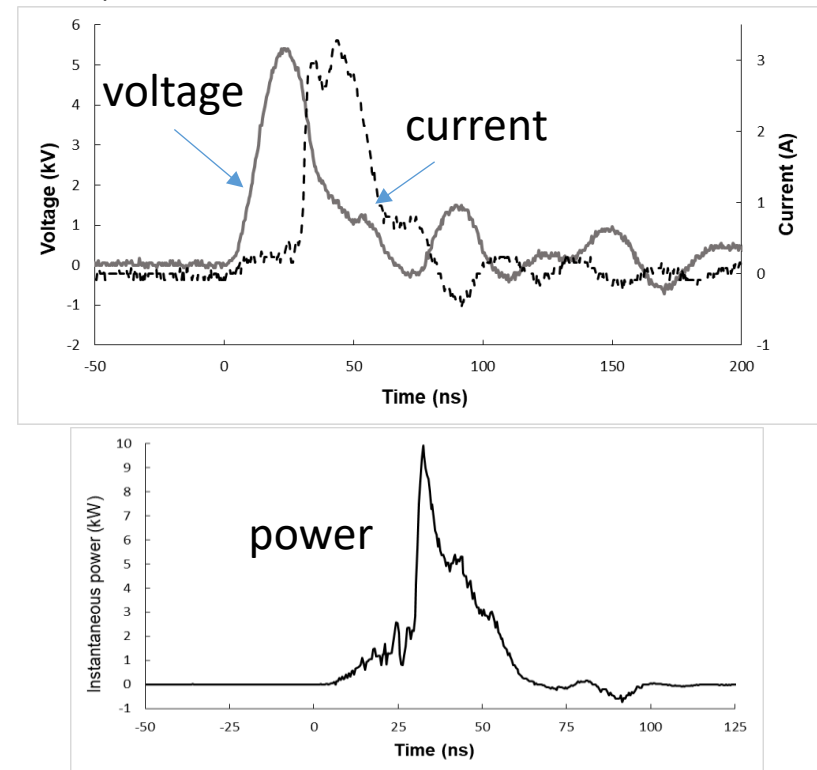
1 kHz, 3.8 kV peak, 140 ns (rise)
130 μ J/pulse, 0.13 W, argon



Energy: 80 to 140 μ J/pulse
Frequency Ranges: to > 60 kHz

2) Eagle Harbor Technologies (commercial)

2 kHz, 5.5 kV peak, 20 ns (rise), 0.3 kV/ns,
150 μ J/pulse, 0.30 W, argon

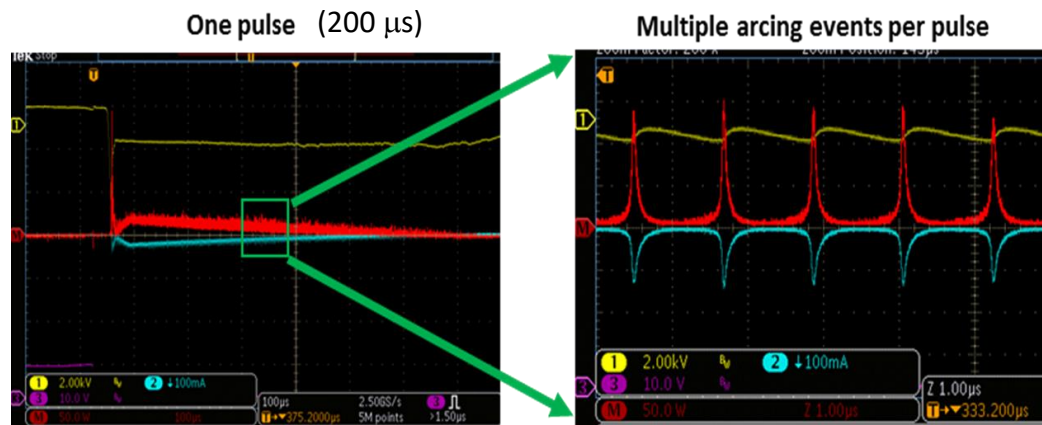


Frequency range: to 10 kHz
Pulse width range: 20 to 260 ns

Power Supplies – Microsecond Pulsers

3) Ignition Coil Based (Professor Radu Burlica – Iasi, Romania)

- High efficiency ignition coil
 - Audi
- DC power supply
 - input voltage (12 V)
 - BK Precision 1740B
- Frequency generator
 - 500 Hz, 40% duty cycle
 - BK Precision 4010A
- Characteristics:
 - Inexpensive, small
 - Microsecond pulses
 - Robust
 - Limited control, Waveforms noisy
 - Restricted range of liquid conductivities (500 $\mu\text{S}/\text{cm}$)



500 Hz pulse, argon with deionized water

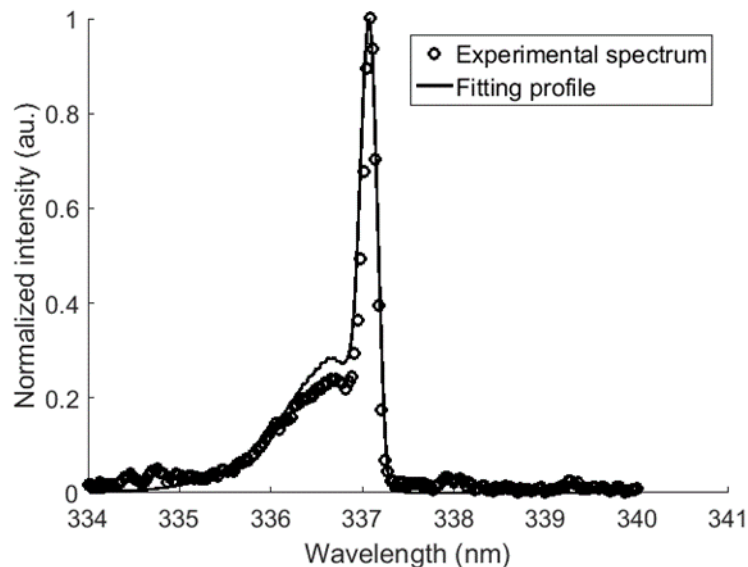
Yellow = voltage

Red = power

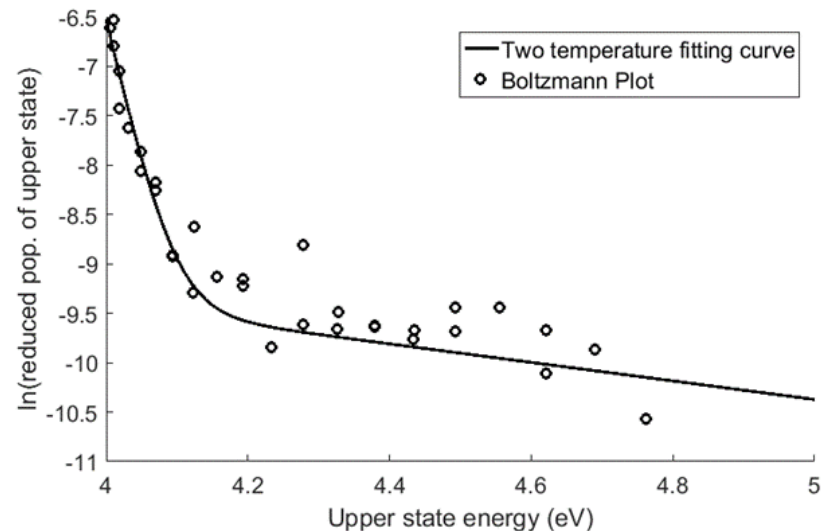
Blue = current ($\sim 200 \mu\text{s}$)

Temperature Measurement Methods

- Example: (Eagle Harbor nanopulser)
 - Power setting: 12kV 20ns 2kHz
 - Water flow rate: 2 ml/min
 - Helium



Trace N₂ added
N₂ (C-B)
Specair fitting

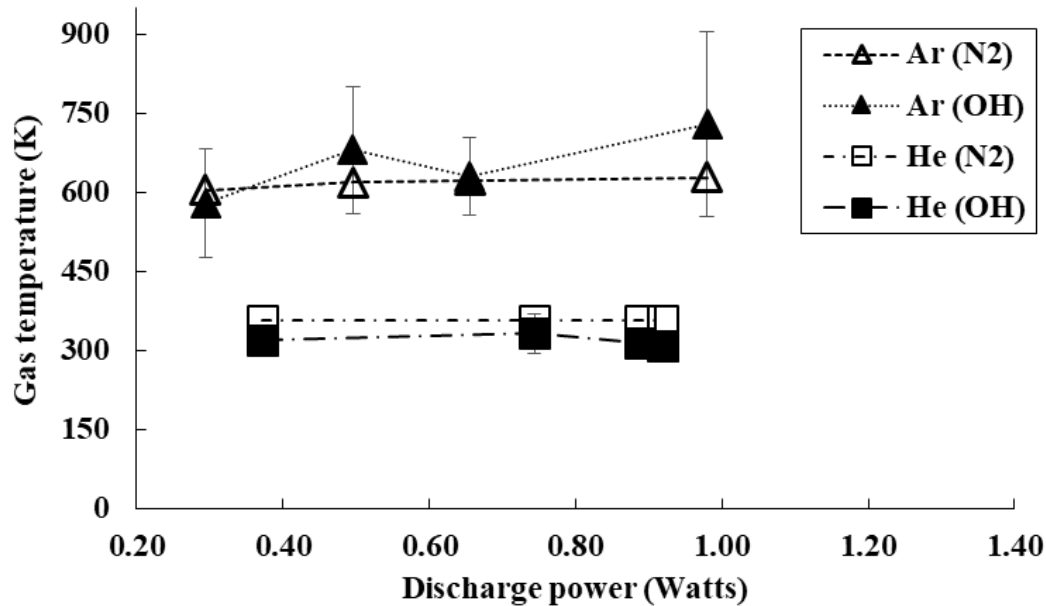


Two temperature fitting
Boltzmann plot of OH (A-X)
Program from Dr. Jan Vorec
(Masaryk University)

(Wang, Wandell, Locke, 2018)

Plasma Gas Temperature Results

(Eagle Harbor nanopulser)



- Method of measurement, N₂ or OH, gives similar results.
- Helium significantly cooler than argon.
- Temperature independent of discharge power.

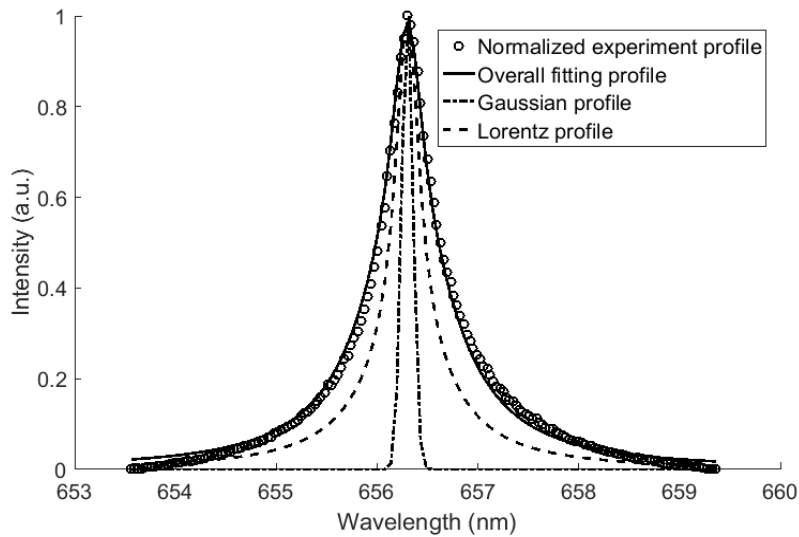
(Wang, Wandell, Locke, 2018)

Electron Density Measurement

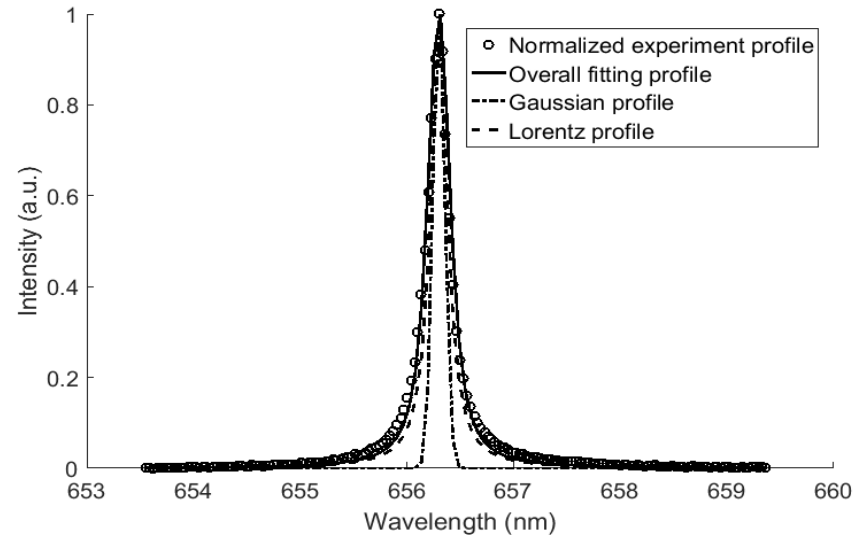
(Eagle Harbor nanopulser)

H $_{\alpha}$ fitting: example, 18 kV, 20 ns, 2 kHz

Argon



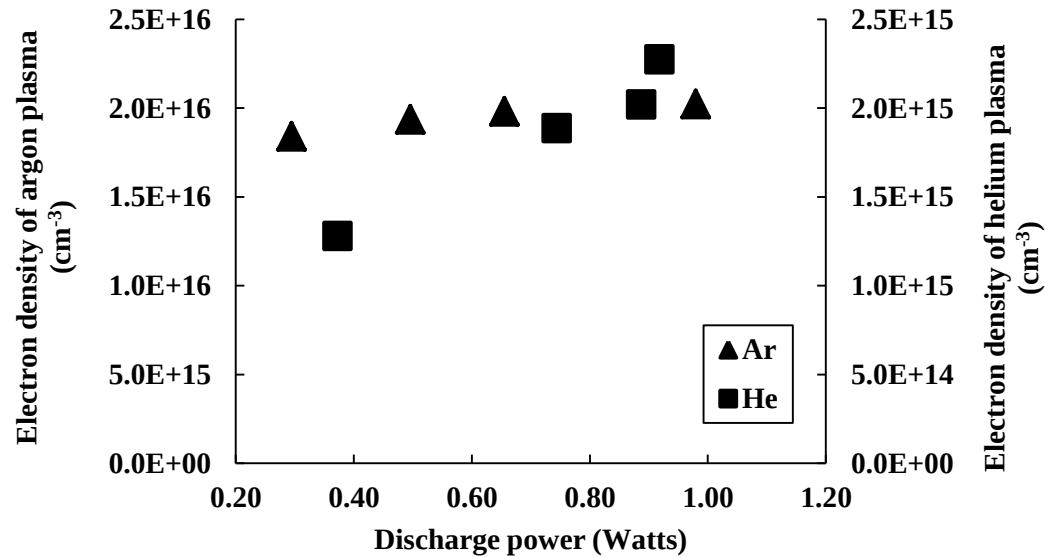
Helium



(Wang, Wandell, Locke, 2018)

Electron Density Results

(Eagle Harbor nanopulser)

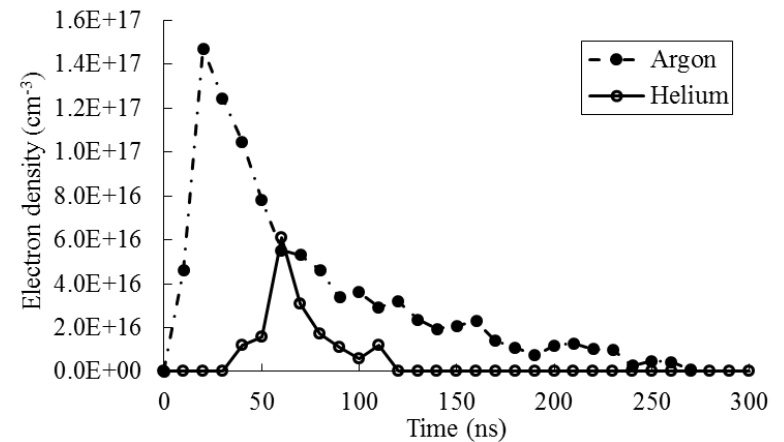
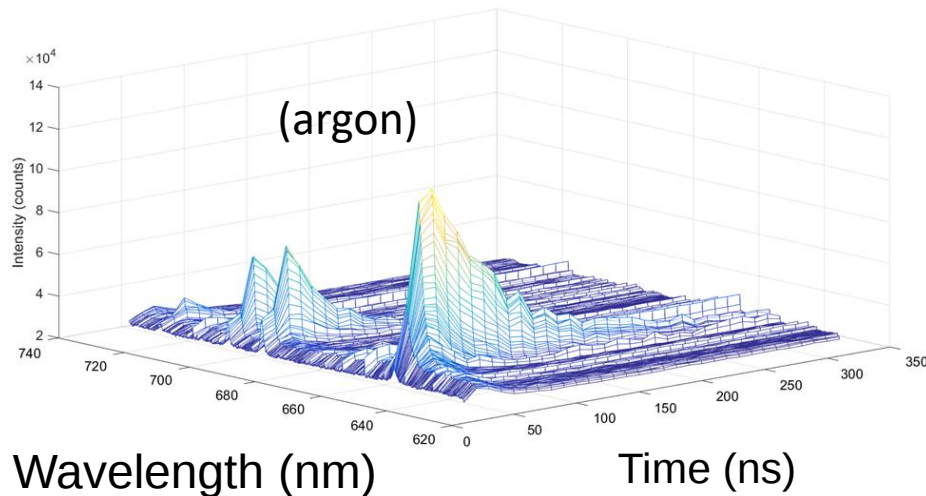


- Electron density in helium 1 order of magnitude lower than in argon.
- Electron density in helium relatively more sensitive to discharge power.
- Discharge power varied by changing voltage.

(Wang, Wandell, Locke, 2018)

Time Resolved Electron Density

(Eagle Harbor nanopulser)



(20 kV, 1 kHz, and 20ns, DI water liquid flow rate 2 mL/min)

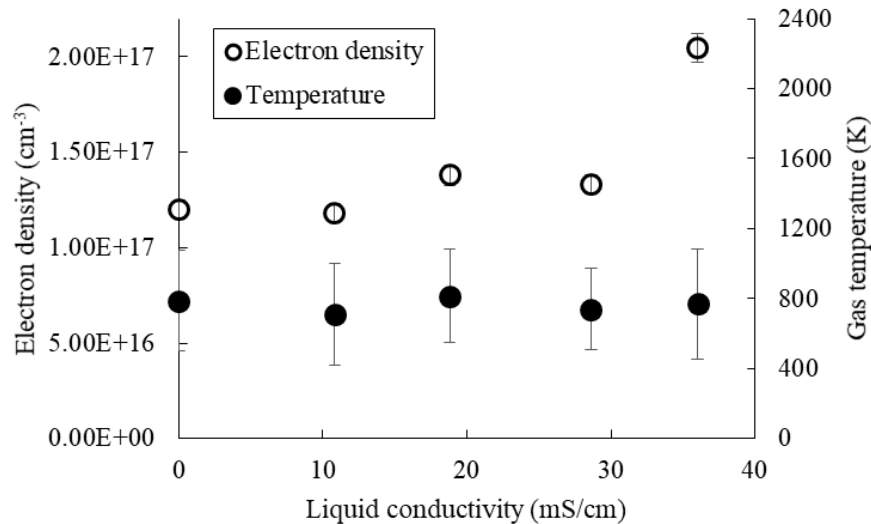
- Note time decay of electron density longer than current/voltage pulse in argon.

(Wang, PhD dissertation, 2018)

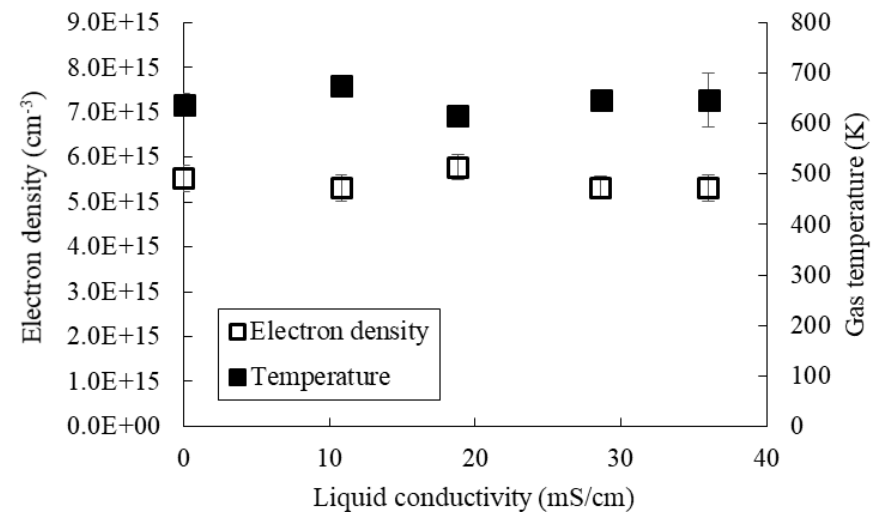
Influence of Liquid Conductivity

(Eagle Harbor nanopulser)

Argon



Helium



- Plasma properties relatively unaffected by large changes in liquid conductivity. (Discharges effectively in near seawater, (seawater = 50 mS/cm), conductivity.)
- Unique for EH nano-pulser (not found with microsecond pulser), fast rise time.
- Some effects of conductivity above 36 mS/cm seen for argon, but not helium.

(Wang et al., 2019)

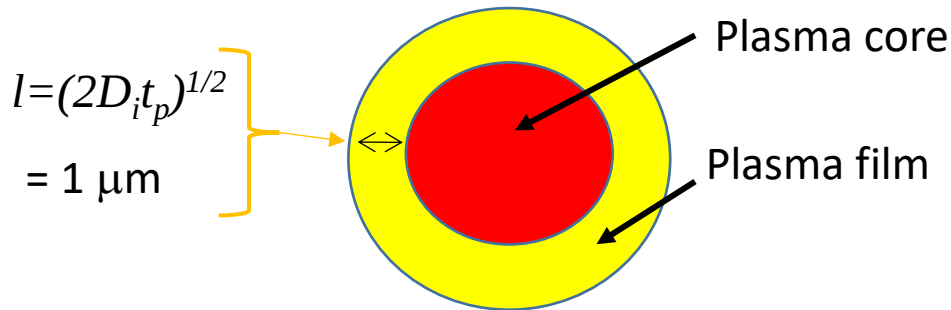
Chemical Processes Analyzed

- role of hydroxyl radicals -

- A simple model of hydroxyl radical formation (Wang et al., 2018)
- Hydroxyl radical formation from probes (ignition coil, nanopulser)
 - Methylene Blue (non-volatile, liquid phase) (Hsieh et al., 2016)
 - Ethanol probe (volatile, liquid phase) (Hsieh et al., 2017)
 - Carbon dioxide probe (gas phase) (Hsieh et al., 2017)
 - Effect of frequency (EH and Airity nanopulsers)
- Hydrogen peroxide formation (EH nanopulser)
 - Effects of flow and carrier gas (Wang et al., 2018a)
 - Effects of solution conductivity (Wang et al., 2018b)
 - Effect of pulse properties (Wandell et al., 2018)
- Hydrocarbon partial oxidation (Bresch et al., 2015, PCPP)
- Dioxane oxidation with plasma + bioreactor (Yiong et al., 2019)
- Nitrogen oxide formation (Wandell et al., 2019; Bulusu et al. 2019)
 - Hydroxyl radicals with gas phase probes (NO and CO)
 - Gas phase NO/NO₂ measurements, liquid phase NO₂⁻, NO₃⁻

Reaction Model Based upon Fast Quenching in Film

Cross section of plasma channel



$$V_{film} = L\pi \left(R_p^2 - (R_p - l)^2 \right)$$

Hydrogen peroxide mass balance in film: neglect diffusion and spatial variation in film

$$\frac{dC_{H_2O_2}}{dt} = k_f C_{OH}^2 - k_d C_{H_2O_2}$$

$$C_{OH} = C_{OH}^0 e^{-bt}$$

$$k_d = k'_d e^{-bt}$$

Decreasing
with pulse

$C_{OH}^0 = \text{concentration of } \cdot OH \text{ in core}$

Production Rate

$$P_{H_2O_2} = C_{H_2O_2}(t_p) V_{film} f$$

Reaction Model Based upon Fast Quenching

Reactions: (k_f and k_d')

H_2O_2 formation from $\cdot OH$ in film

H_2O_2 degradation by $\cdot OH$, $\cdot H$, O , e^-

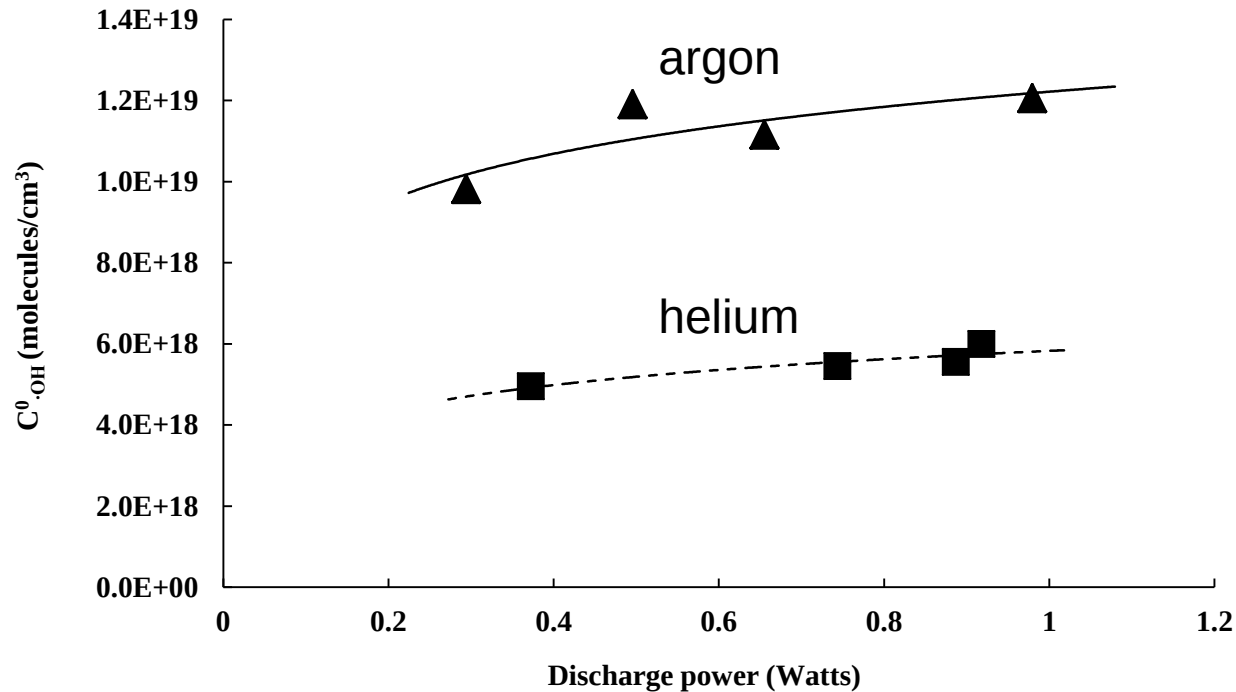
rapid quenching of $\cdot OH$ in film

formation
degradation



No.	Reaction	Rate coefficient k	k in helium at 358 K	k in argon at 600 K
1	$OH + OH + Ar \rightarrow H_2O_2 + Ar$	$6.9 \times 10^{-43} (T_g/300)^{-0.8}$		3.96×10^{-43}
2	$OH + OH + He \rightarrow H_2O_2 + He$	$3.7 \times 10^{-43} (T_g/300)^{-0.8}$	3.21×10^{-43}	
3	$H + H_2O_2 \rightarrow HO_2 + H_2$	$2.81 \times 10^{-18} \exp(-1890/T_g)$	1.17×10^{-19}	8.70×10^{-19}
4	$H + H_2O_2 \rightarrow H_2O + OH$	$1.69 \times 10^{-17} \exp(-1780/T_g)$	1.43×10^{-20}	1.20×10^{-19}
5	$O + H_2O_2 \rightarrow HO_2 + OH$	$1.4 \times 10^{-18} \exp(-2000/T_g)$	5.25×10^{-21}	4.99×10^{-20}
6	$OH + H_2O_2 \rightarrow H_2O + HO_2$	$2.91 \times 10^{-18} \exp(-160/T_g)$	1.86×10^{-18}	2.23×10^{-18}
7	$e + H_2O_2 \rightarrow H_2O + O^-$	$1.57 \times 10^{-16} T_e^{-0.55}$		
8	$e + H_2O_2 \rightarrow OH + OH^-$	$2.7 \times 10^{-16} T_e^{-0.5}$		
9	$e + H_2O_2 \rightarrow 2OH + e$	1×10^{-9}		
10	$e + H_2O_2 \rightarrow H + HO_2 + e$	1×10^{-9}		

Model ·OH Predictions

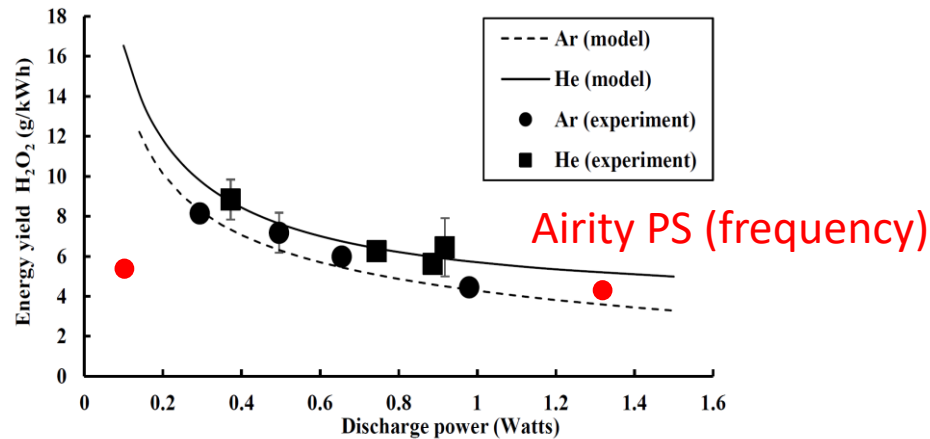


- Smaller size argon plasma has higher $\cdot\text{OH}$ concentration in core during pulse.
- Slight increase in $\cdot\text{OH}$ with discharge power for both gases.
- Data on H_2O_2 used to determine $\cdot\text{OH}$ in plasma using model.
- $\langle\text{OH}\rangle = 4 \times 10^{14} \text{ cm}^{-3}$ in argon and $2 \times 10^{14} \text{ cm}^{-3}$ in helium (time averaged in pulse)
- For comparison in combustion – 10^{14} to 10^{16} cm^{-3}

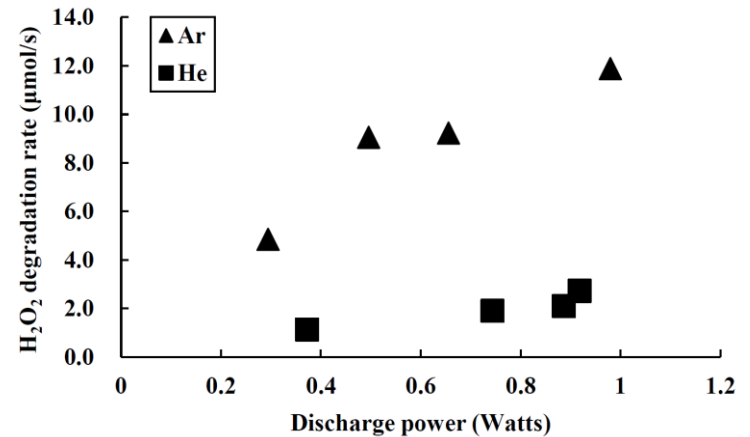
(Wang, Wandell, Locke, 2018)

Other Model Results

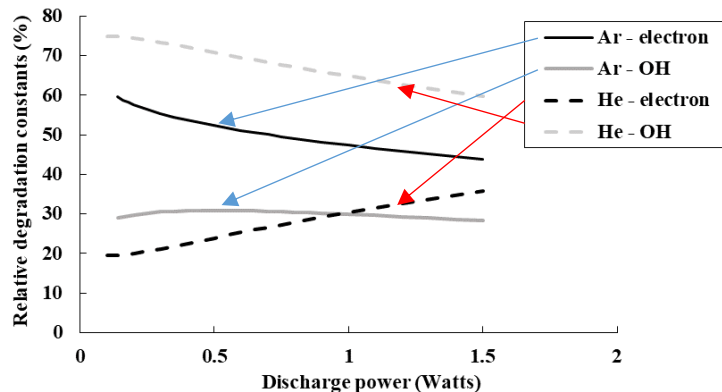
H₂O₂ model data comparison



Calculated H₂O₂ degradation rates



Relative H₂O₂ degradation rates by electrons and ·OH



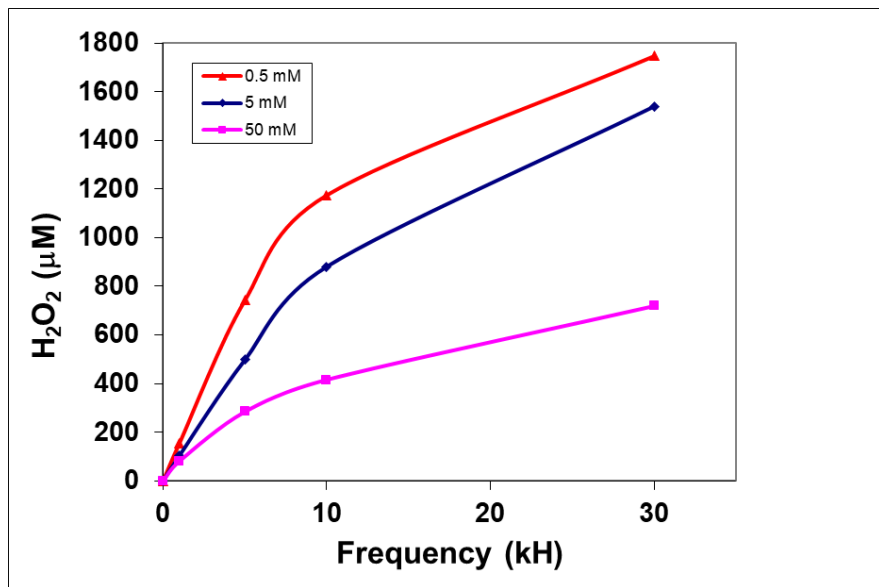
(Wang et al., 2018)

- More H₂O₂ degradation in argon
- Argon – higher rates with electrons
- Helium – higher rates with ·OH
- Degradation strongly affects net formation of H₂O₂
- Role of liquid water is to sequester H₂O₂ and suppress degradation in plasma

Effects of Frequency on Hydroxyl Radical

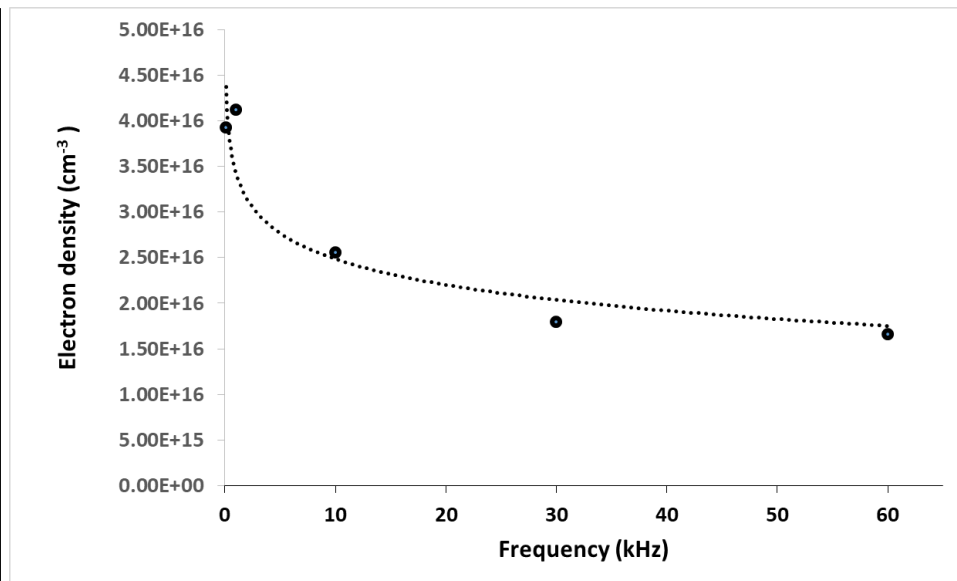
(data for input to model, Airity Nanopulser)

H_2O_2



(with varying input phenol concentration)

Electron density

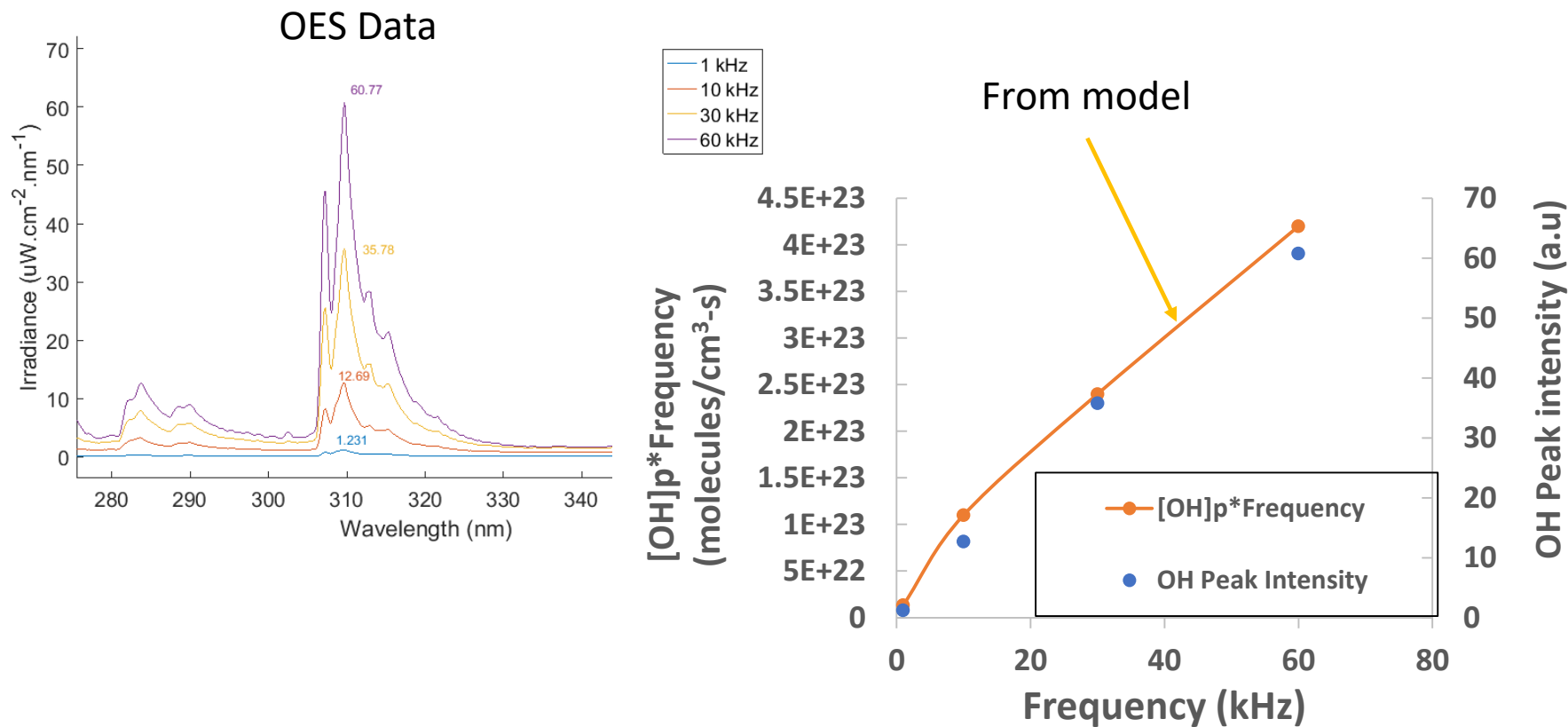


(time and space averaged electron density)

- Airity power supply, 2 mL/min, 0.25 mm inlet nozzle, 70 V delivered
- Energy per pulse ranges from 80 to 140 mJ/pulse
- H_2O_2 data: V. Babicky, M. Clupek, V. Jirasek, P. Lukes

Effects of Frequency on Hydroxyl Radical

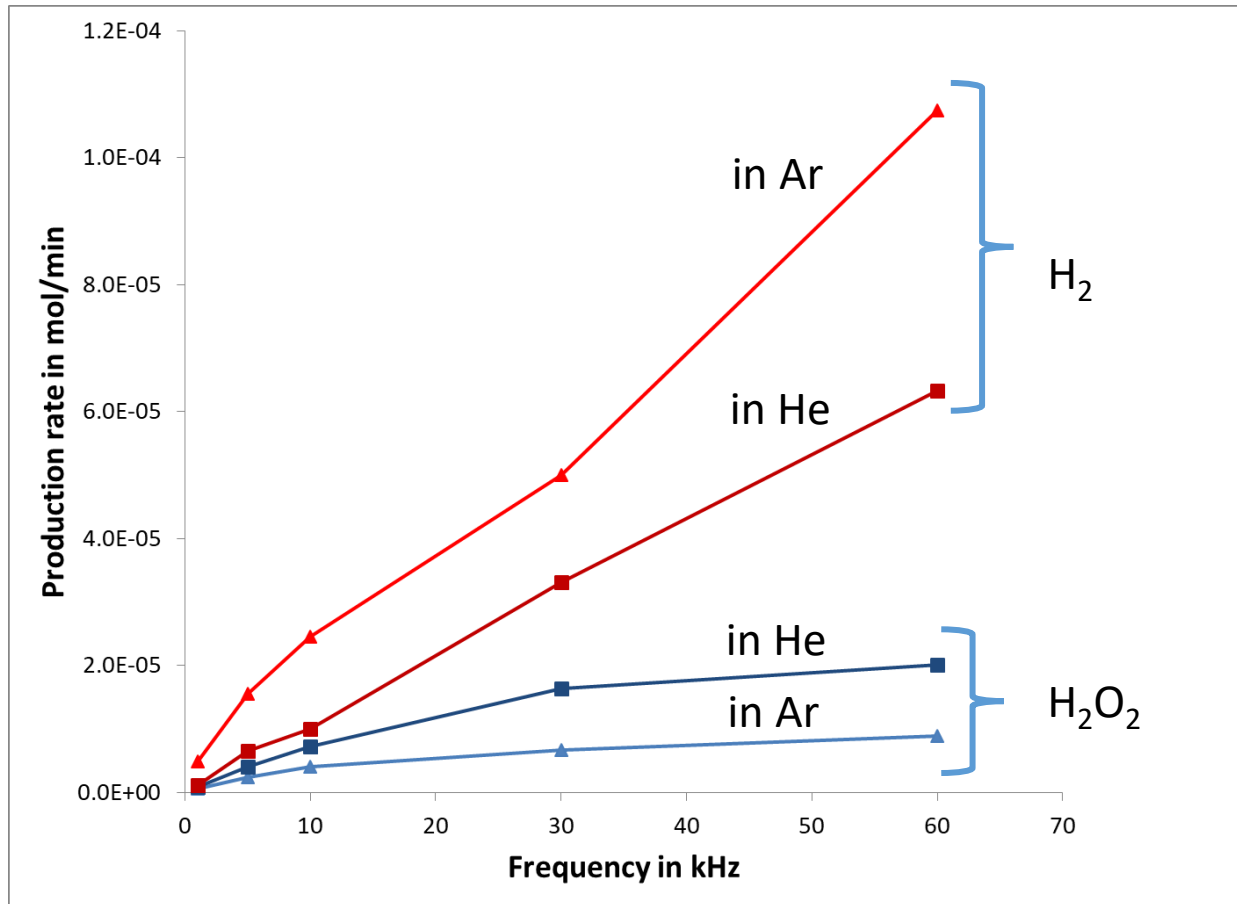
(model results compared with $\cdot\text{OH}$ from OES)



- Variation in $\cdot\text{OH}$ with frequency correlated with electron density variation.
- $\cdot\text{OH}$ measurements with time and space in progress (Vorac & Dvorak – Masaryk U.).

Airity power supply, 2 mL/min, 0.25 mm inlet nozzle, 70V delivered

Molecular Hydrogen Production



- In Helium
 $\text{H}_2:\text{O}_2 = 3.4$

- under water
 $\text{H}_2:\text{O}_2 = 4$

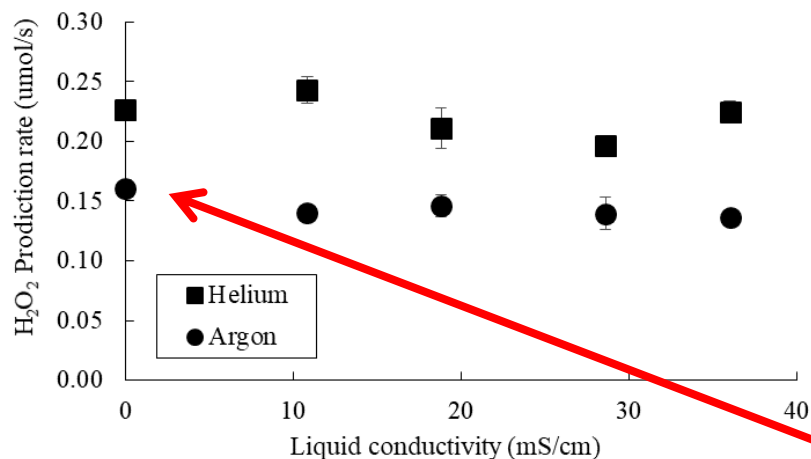
(Airity power supply,
S. Bresch, IPP)

- Trend for H₂ formation similar to those for $\cdot\text{OH}$; H₂ may rapidly escape plasma region.
- H₂O₂ levels off at high frequency, likely due to degradation reactions.
- Formation of O₂ demonstrated from water in argon and helium carrier gases.

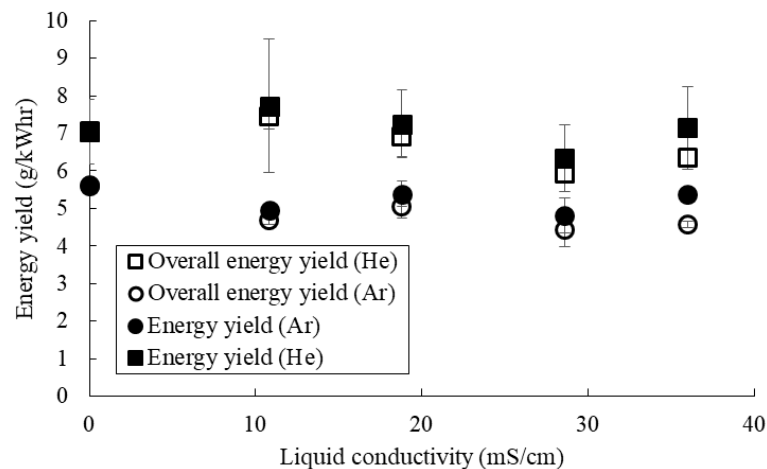
Influence of Liquid Conductivity: H_2O_2

(Eagle Harbor nanopulser)

Production rate

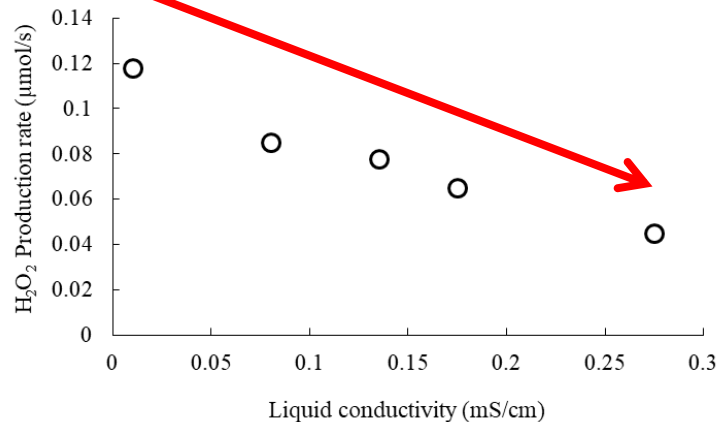


Energy yield



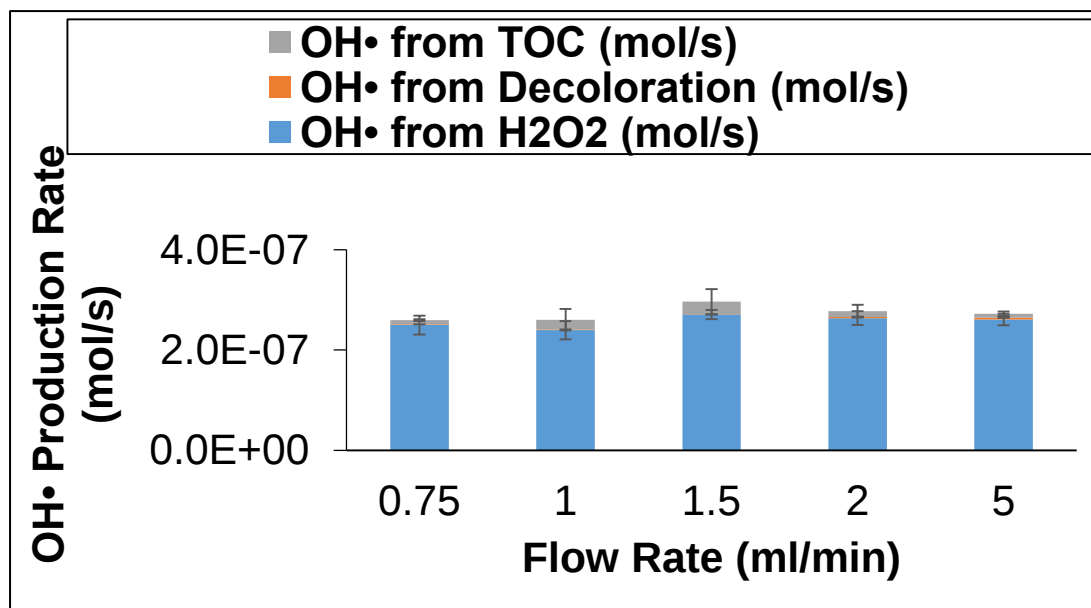
- Relatively small changes in H_2O_2 formation with large changes in liquid conductivity for nanopulser.
- Large range of operation possible with nanosecond pulser but not microsecond power supply.

Microsecond power supply



Liquid phase ·OH Scavenger

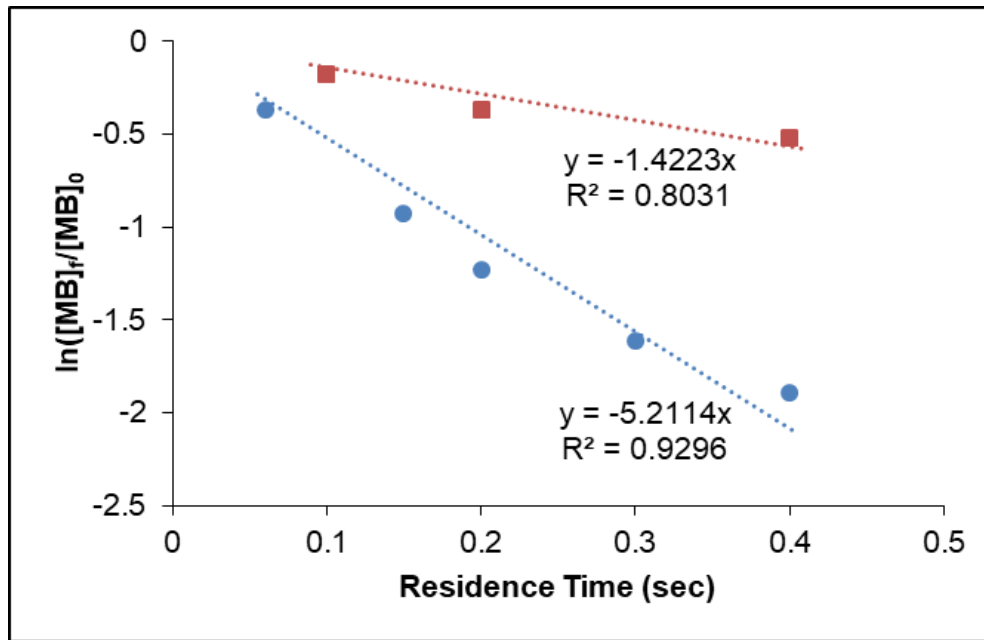
(Methylene Blue – a water soluble organic dye)



OH• production rate	(mol/s)
H ₂ O ₂ from dl H ₂ O	2.40 ± 0.25 x 10 ⁻⁷
H ₂ O ₂ from 0.1 mM MB	2.57 ± 0.12 x 10 ⁻⁷
MB decoloration	2.30 ± 0.13 x 10 ⁻⁹
MB mineralization	1.38 ± 0.67 x 10 ⁻⁸

- Complete MB decoloration has little effect on ·OH (H₂O₂) production.
- MB complete degradation requires 57 moles of ·OH.

Hydroxyl Radicals in Liquid Phase



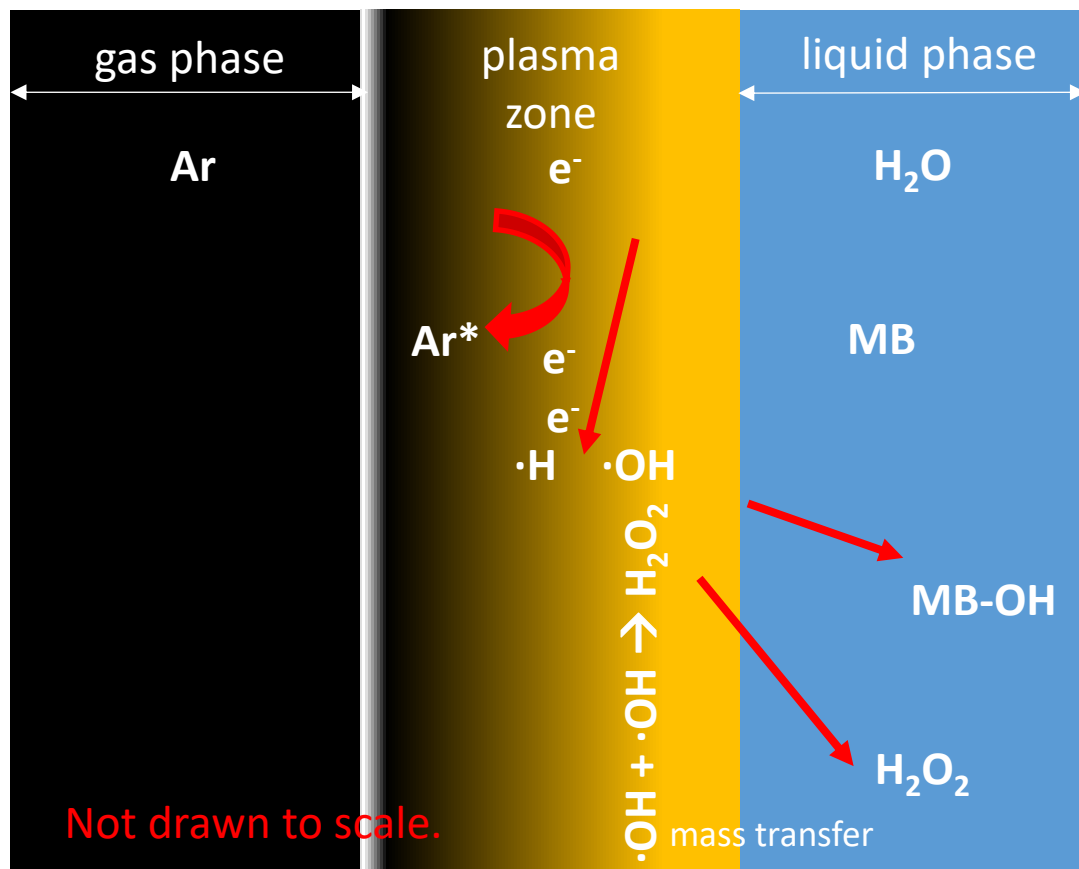
- Based upon non-volatile organic dye decoloration in liquid
- Ignition coil data with argon carrier gas. (Hsieh, 2015)

$$\ln \frac{[MB]}{[MB]_0} = -tk[OH]_{pss}$$

$$[OH]_{pss} = 1.2 \text{ to } 4.3 \times 10^{-10} \text{ M}$$

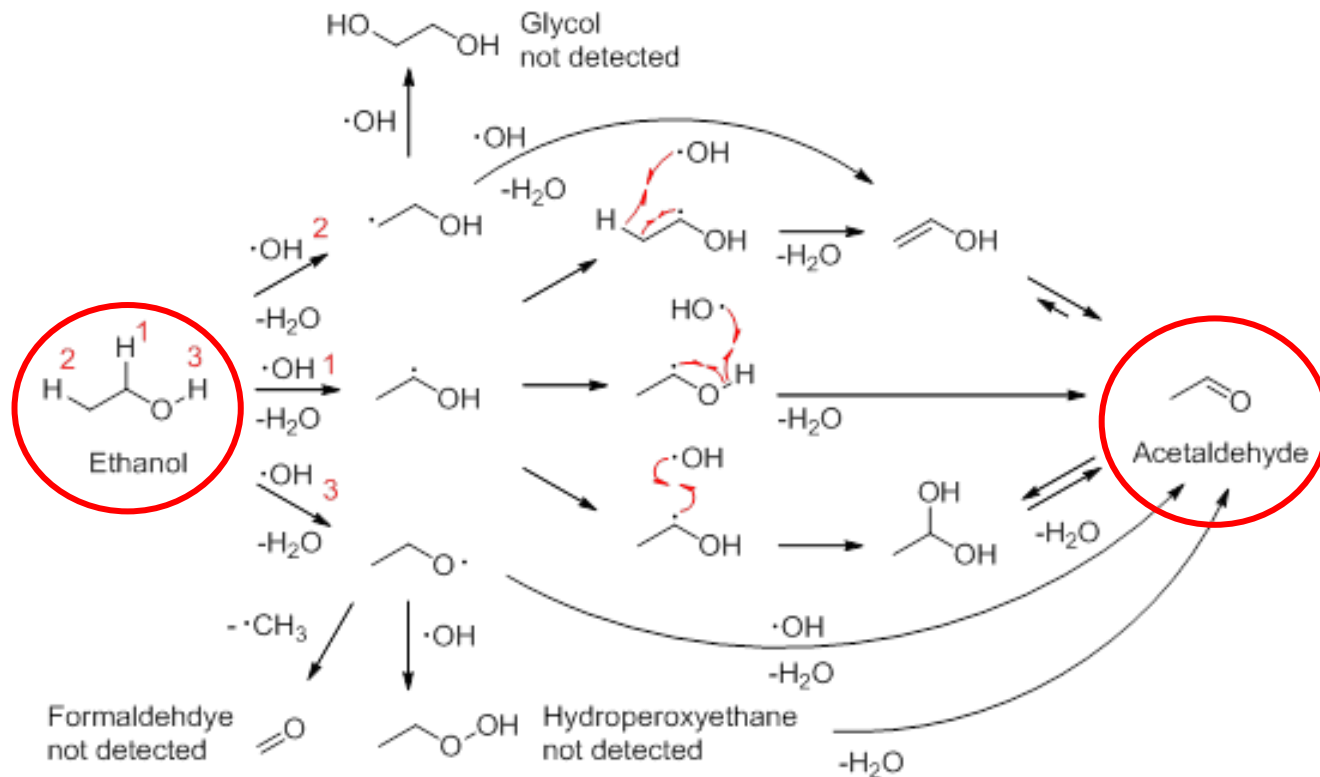
- For comparison - Advanced Oxidation Technologies
 - $\cdot OH$: 10^{-4} to 10^{-1} nM (quasi steady-state due to very high reactivity)

OH Radical Attack with Liquid Scavenger (Methylene Blue)



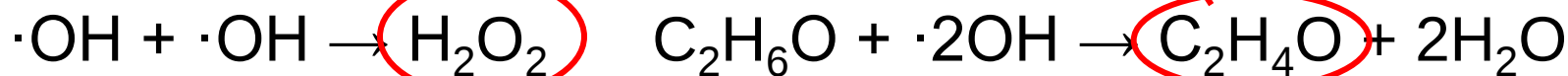
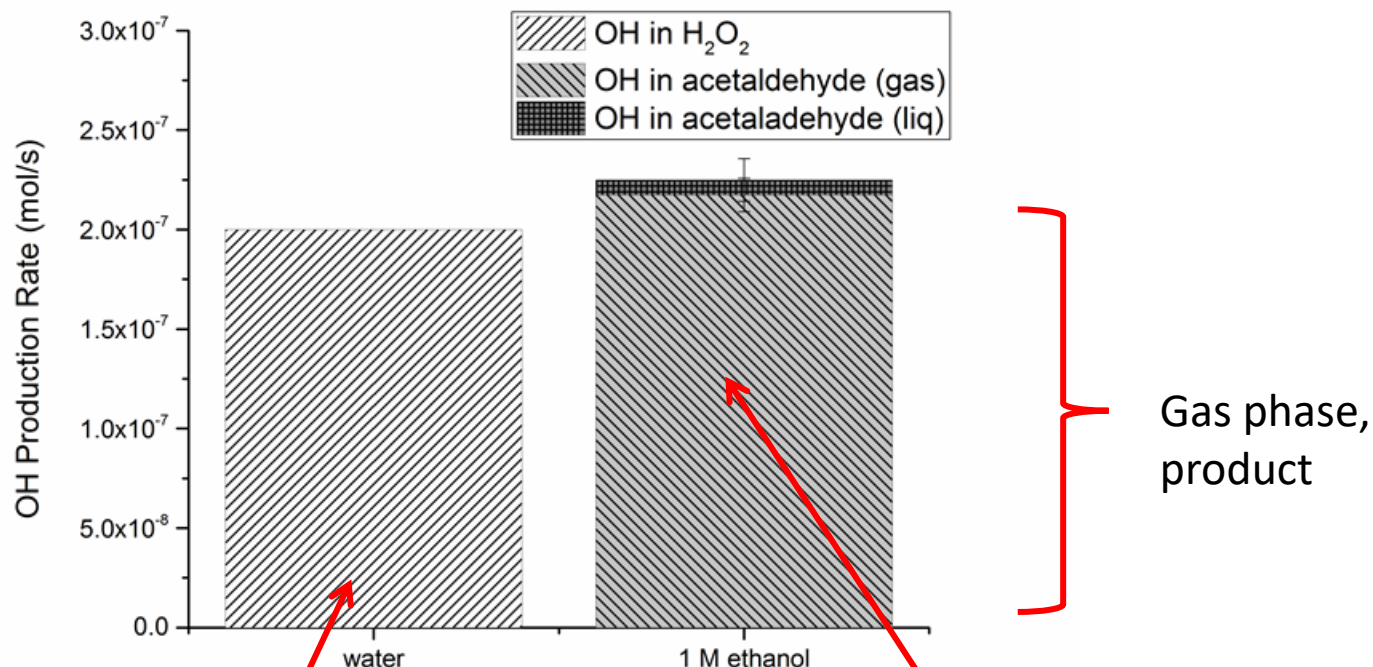
- $\cdot\text{OH}$ reacts in the liquid phase (near interface) with MB
- MB does not affect H_2O_2 formation (in plasma zone)
- Some $\cdot\text{OH}$ is able to go from plasma to liquid interface to degrade MB

OH Radicals from Ethanol



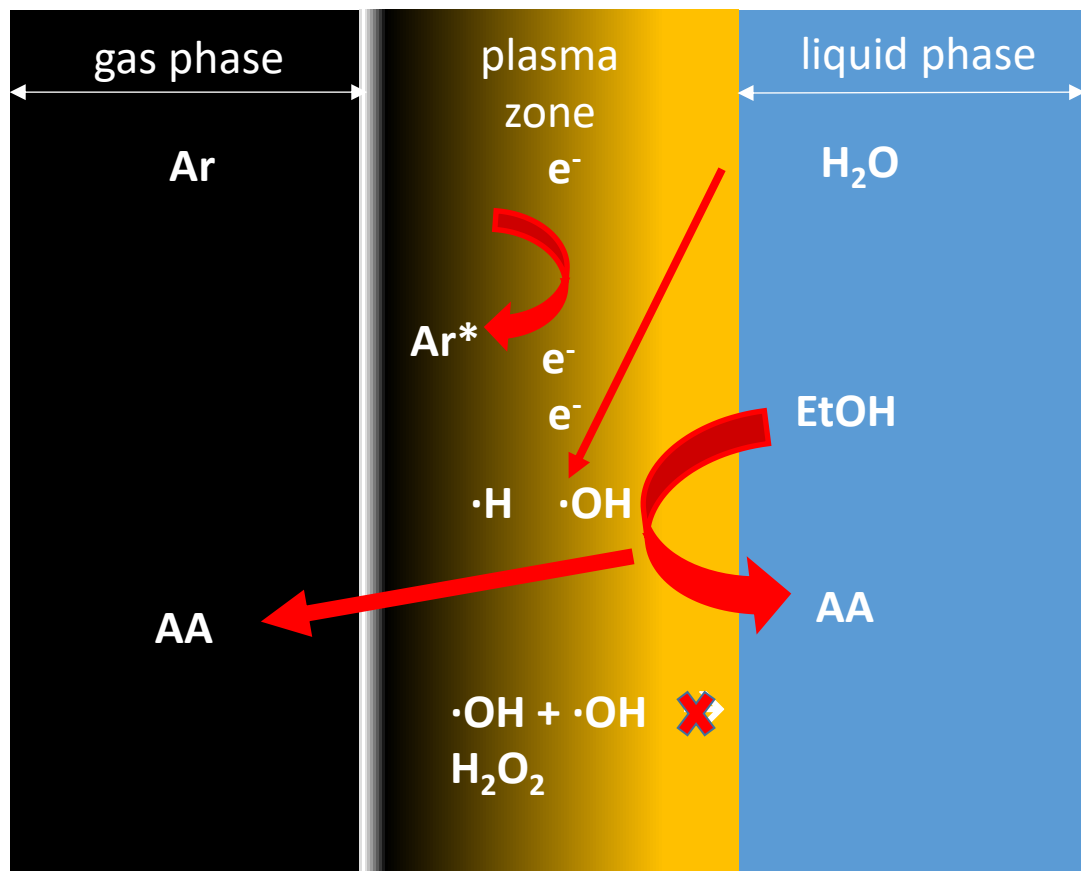
- Overall 2 moles of $\cdot\text{OH}$ to convert ethanol to acetaldehyde.
- Number of $\cdot\text{OH}$ independent of specific pathway.
- Measure reaction product of acetaldehyde.
- Underestimate due to further oxidation of acetaldehyde.

·OH Production Rate from Ethanol



- H₂O₂ completely depleted by ethanol.
- Acetaldehyde accounts for same amount of ·OH as H₂O₂.
- H₂O₂ likely formed in plasma zone near plasma-liquid interface.

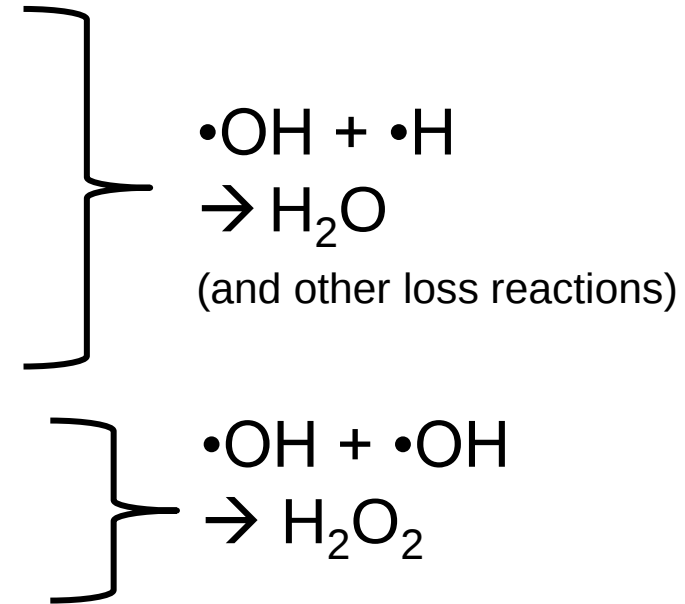
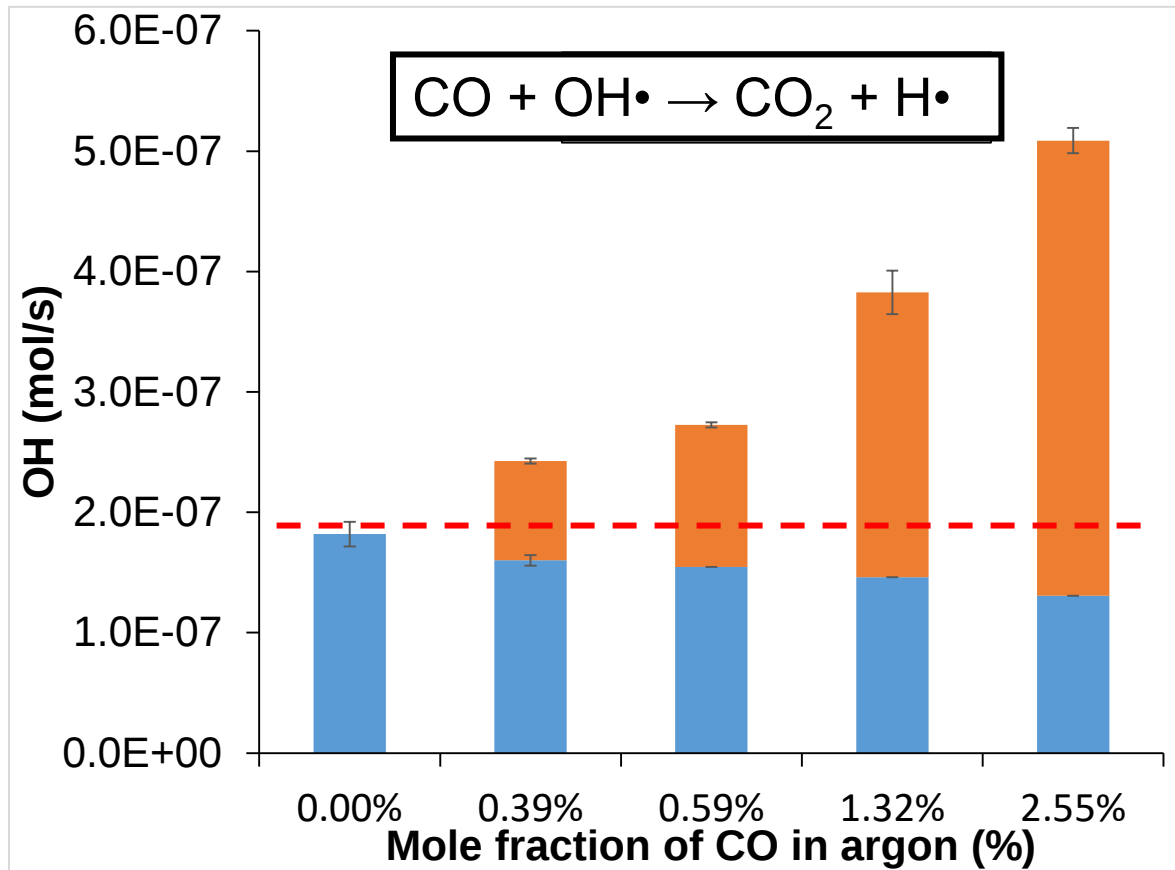
•OH Attack with Gas/Liquid Scavenger (Ethanol)



- Major product acetaldehyde, primarily collected in the gas phase.
- Ethanol can deplete H_2O_2 by competing fully for $\cdot\text{OH}$.
- Ethanol can transfer into the plasma zone (unlike MB which stays in liquid).

OH Radicals from Carbon Monoxide

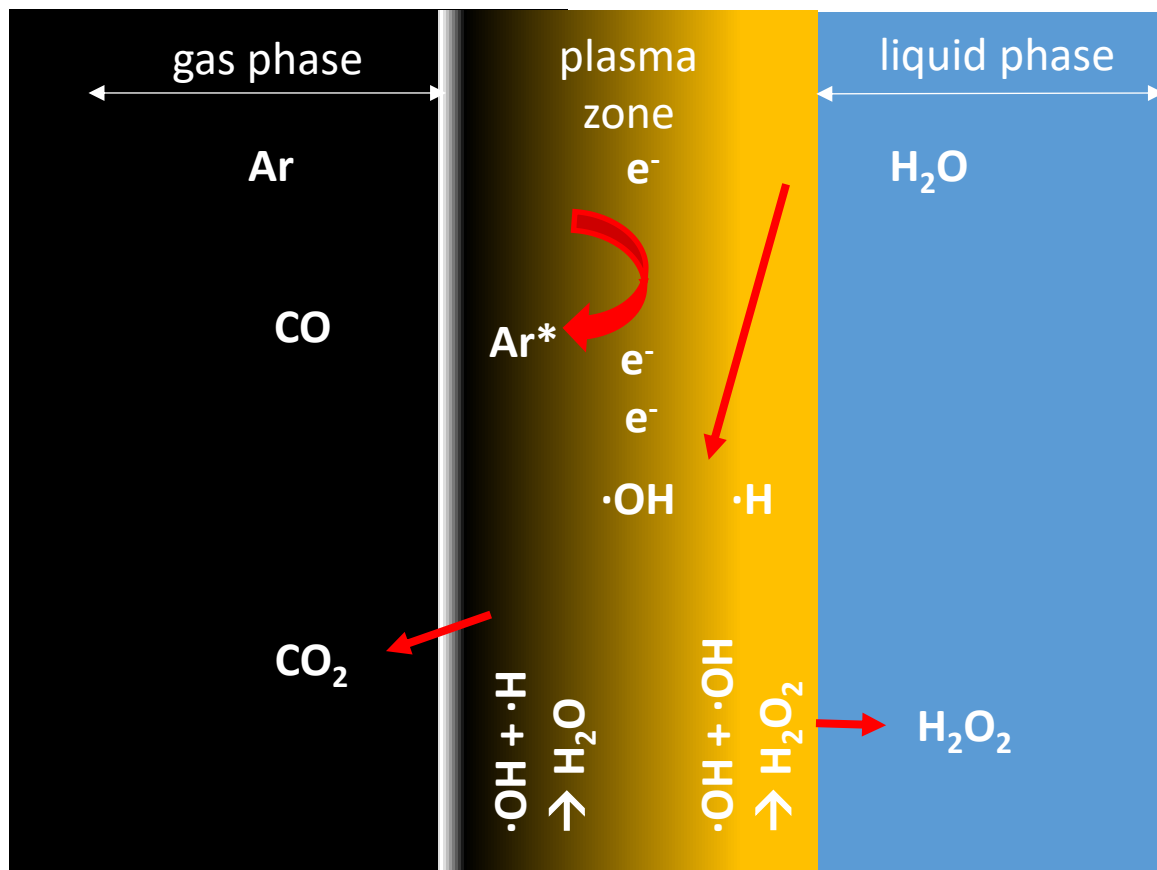
(Gas phase reactions and probe)



- Significant gas phase $\cdot\text{OH}$ that does not form H_2O_2 .
- $\cdot\text{OH}$ available for reactions with gaseous species as well as liquid.
- Requires high CO to affect H_2O_2 .

OH Radical Attack with Gas Scavenger

(Carbon Monoxide)



- CO may be reacting with $\cdot\text{OH}$ that goes to form other species like H_2O .
- Large amounts of CO needed to affect H_2O_2 production. Supports idea that most H_2O_2 is formed in plasma zone near liquid interface.

Hydroxyl Radical Generation from Water

- | | | <u>Yields* (molecules/100 eV)</u> |
|---|---|--|
| • Thermodynamic limit
(from ΔH_r) | $\text{H}_2\text{O} \rightarrow \cdot\text{OH} + \cdot\text{H}$ | 20 |
| • UV light

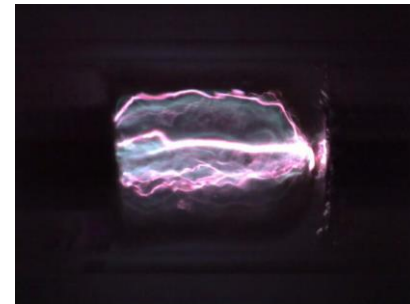
(120 to 190 nm, depends on quantum yields and lamp efficiencies) | $\text{H}_2\text{O} + h\nu \rightarrow \cdot\text{OH} + \cdot\text{H}$ | 2 to 3 (in liquid)
5 to 6 (in gas with vapor) |
| • Radiation

(electron beams, gamma radiation) | $\text{H}_2\text{O} + e^- \rightarrow \cdot\text{OH} + \cdot\text{H} + e^-$ | 2 to 4 (in liquid)
7 to 9 (in gas with vapor) |
| | | Over water |
| • Plasma

Underwater: (Sahni and Locke, 2006)
10^{-2} (primary) 2×10^{-1} (w/ H_2O_2) | $\text{H}_2\text{O} + e^- \rightarrow \cdot\text{OH} + \cdot\text{H} + e^-$ | 2 to 5 (exp, probes, ignition coil)
3 to 7 (exp, probes, nanopulser)
2 to 4 (model, H_2O_2 , nanopulser) |
| • Advanced Oxidation Processes
(O_3 , O_3/UV , $\text{H}_2\text{O}_2/\text{O}_3$, $\text{H}_2\text{O}_2/\text{UV}$, $\text{H}_2\text{O}_2/\text{Fenton}$) | | 2 to 8 (in liquid) |

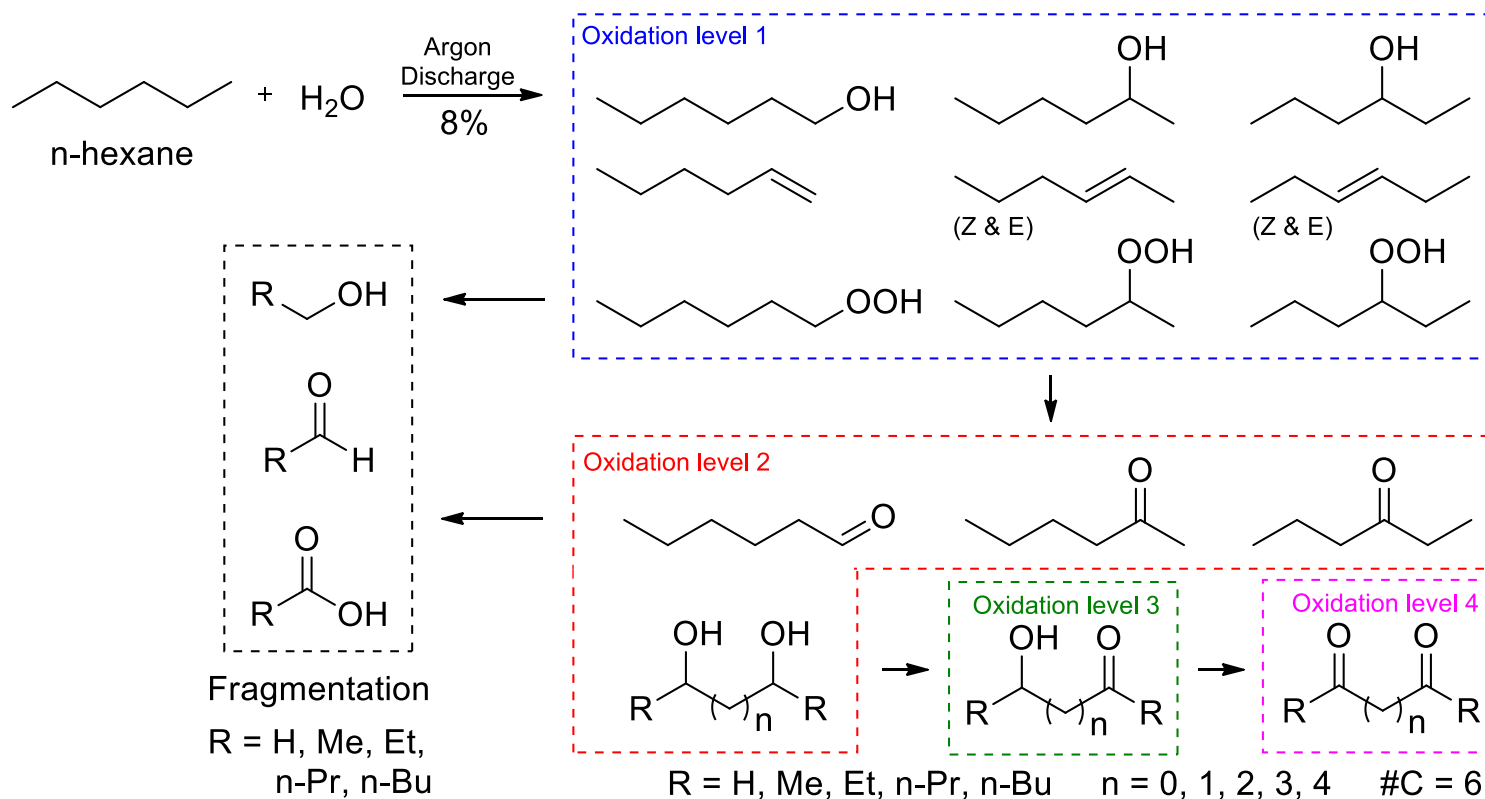
Hexane Oxidation

(Ignition coil, gas phase reactant)



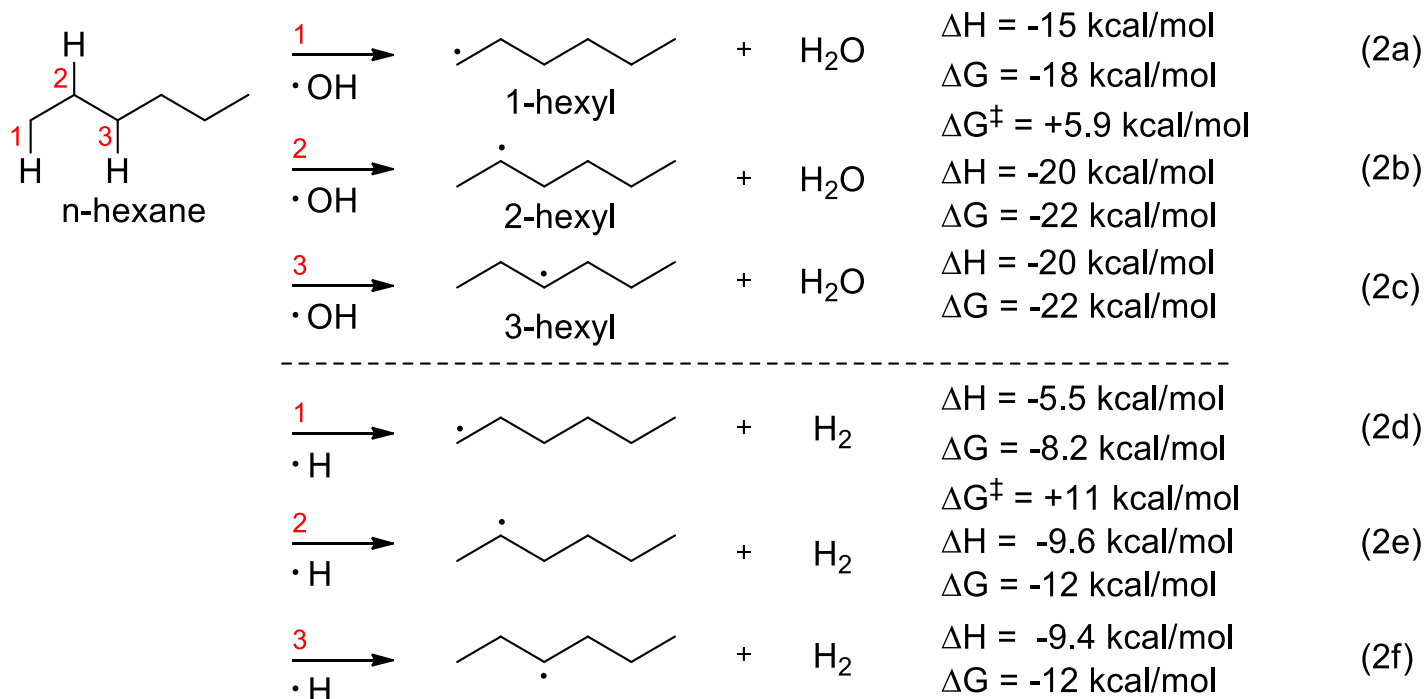
Experiments and modeling show products due to $\cdot\text{OH}$ and $\cdot\text{H}$ reactions

- Hexane fed as gas – dilute amount to prevent polymerization.
- Products in liquid and gas
- Quantum chemical calculations using Gaussian 03



(Bresch et al., 2015)

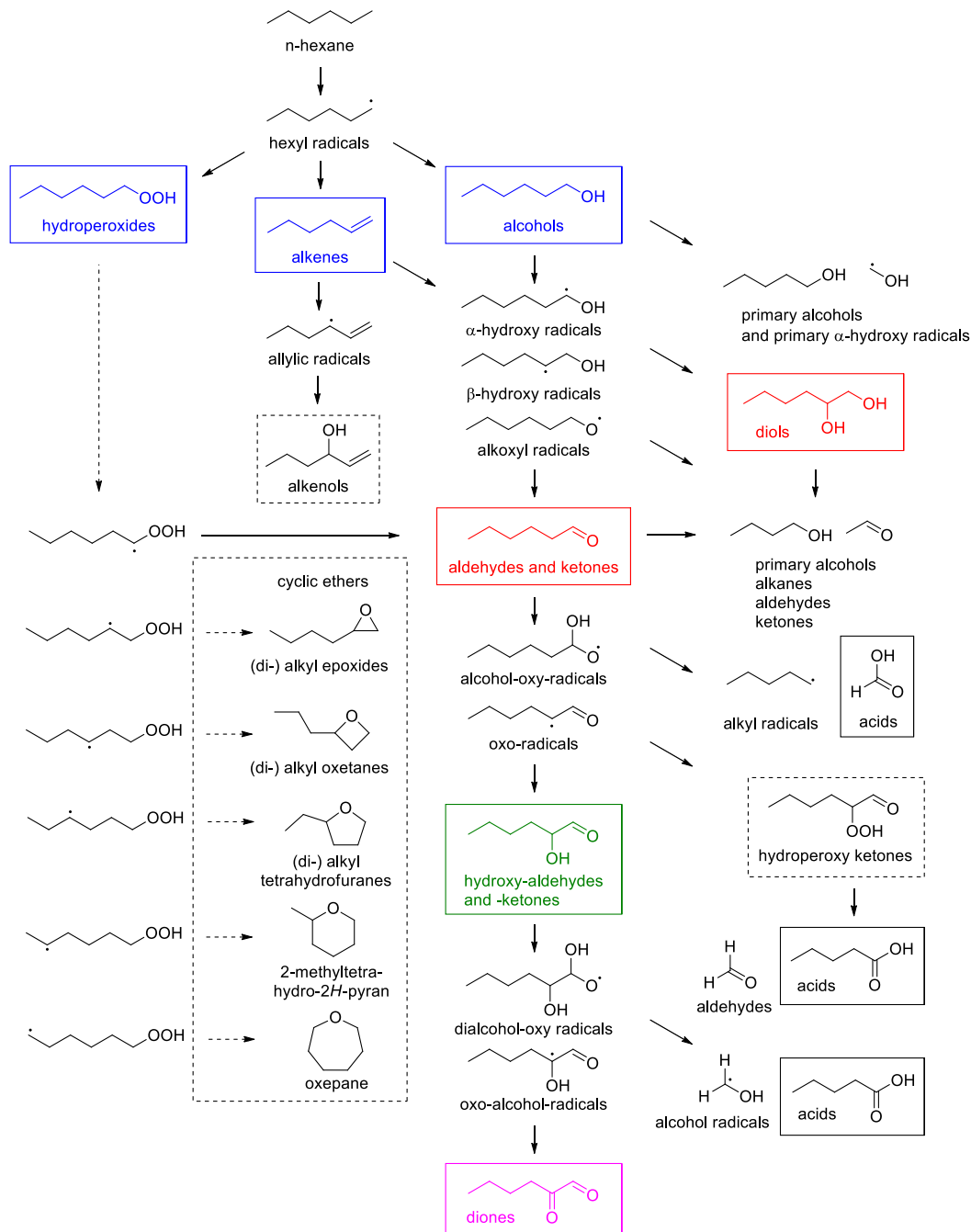
Initial Reaction Steps



- Although both $\cdot\text{OH}$ and $\cdot\text{H}$ reactions possible
- $\cdot\text{OH}$ reactions generally more likely based upon ΔG (and products – see next slide)

(Bresch et al., 2015)

Hexane production Distribution



- Colored boxes – products observed (NMR, GCMS)
- $\cdot\text{OH}$ products observed

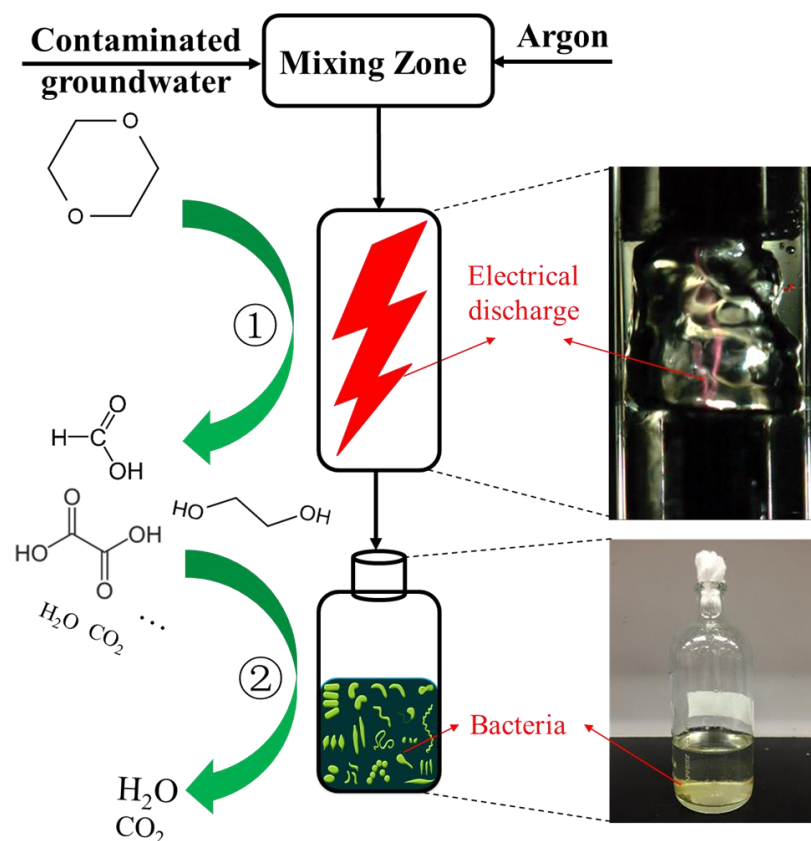
(Bresch et al., PCPP, 2015)

Post-plasma Considerations

-1,4 dioxane degradation-

Example Application

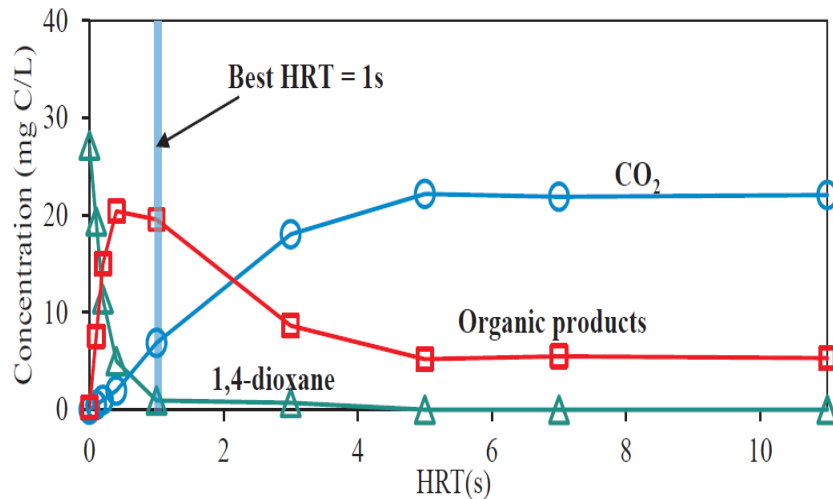
- Partial degradation of 1,4 dioxane by plasma
 - 1,4 dioxane highly water soluble, non-volatile
 - Emerging groundwater contaminant found in combination with chlorinated contaminants
- Mineralization in bioreactor after plasma reactor
- Seeking to improve overall efficiency by reducing overall energy cost by combining plasma for initial degradation with bioreactor for complete mineralization of products from plasma.



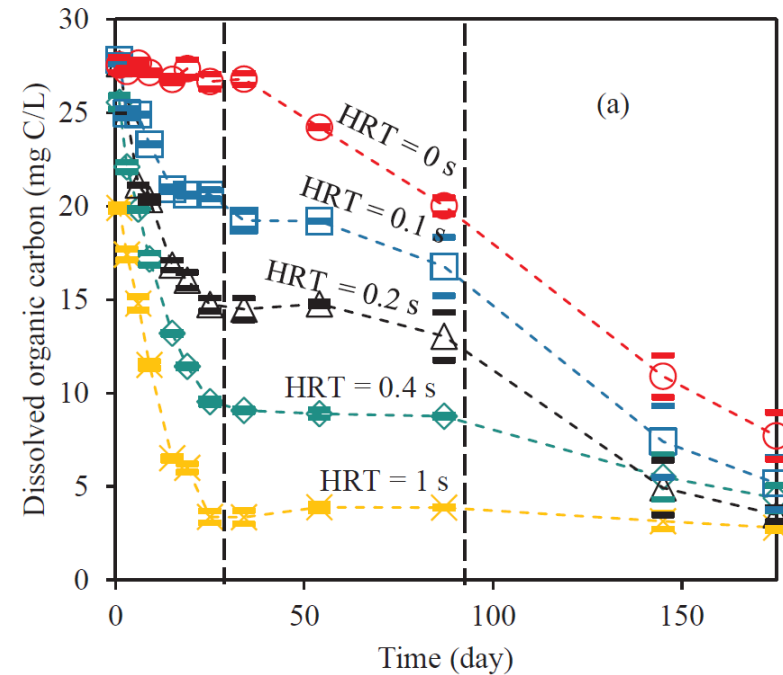
(Xiong et al., 2019)

Plasma/Bioreactor Treatment Performance

Plasma reactor performance

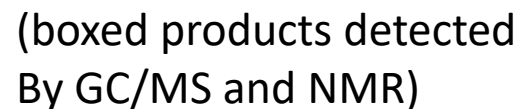


Bioreactor performance



- Optimum HRT in plasma reactor occurs when majority of dioxane is converted to intermediates in plasma reactor, but organic products remain
- Plasma degrades 1, 4 dioxane; bioreactor degrades remaining products.
- Plasma/bioreactor utilizes 5 times less power than plasma alone and bioreactor is about 5 times faster than without plasma.
- Bioreactor alone can only partially remove 1, 4 dioxane and organic carbon.

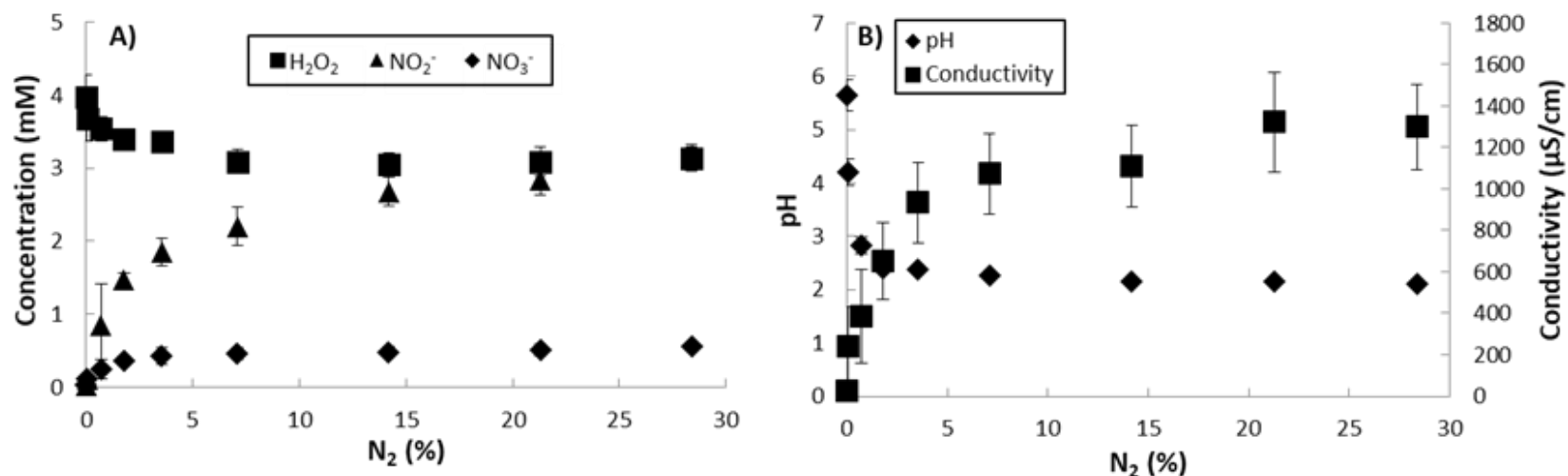
(liquid phase, $\cdot\text{OH}$ based)



Products from 1, 4 dioxane suggest oxidation by $\cdot\text{OH}$.

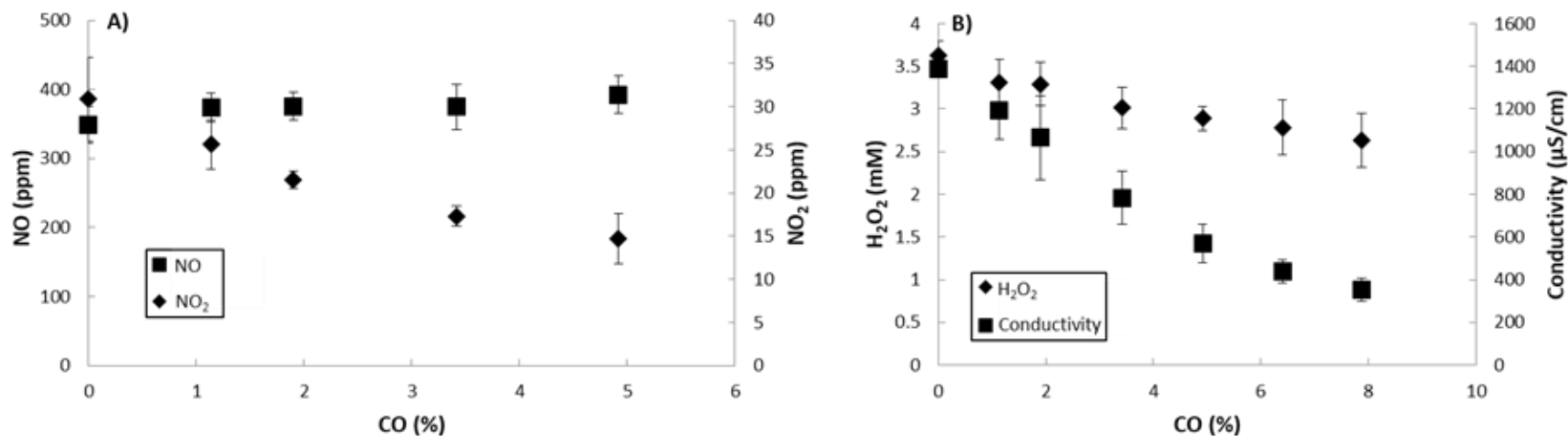
Formation of Nitrogen Oxides in Ar/N₂

Liquid Phase Results



- Increasing N₂
 - NO₃⁻ saturates and NO₂⁻ continues to increase gradually w/ N₂
 - Limitation of ·OH supply likely
- Increasing N₂ in argon up to 3% reduces H₂O₂ about 25%.
 - Note ·OH is still present to form H₂O₂, but H₂O₂ not largely suppressed by high N₂ (like CO probe shown previously).

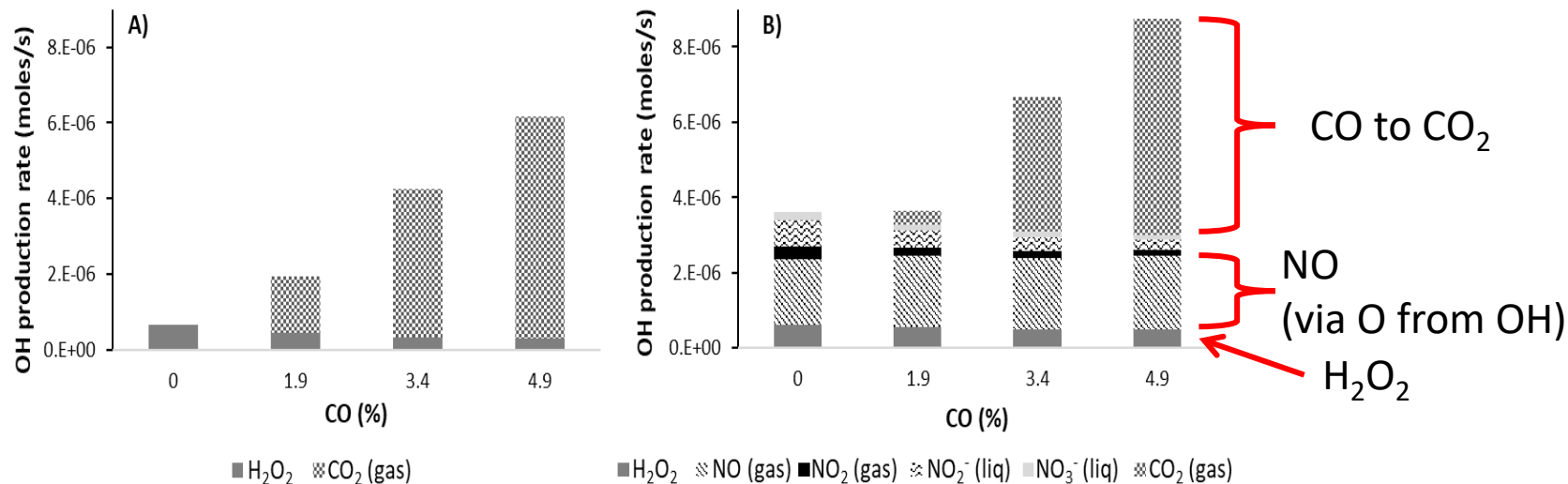
Gas Phase CO as $\cdot\text{OH}$ Scavenger in Ar/N₂



- Increasing CO:
 - Does not affect NO formation
 - Lowers NO₂, H₂O₂, NO₂⁻, and NO₃⁻
- Reactions: $\text{CO} + \cdot\text{OH} \rightarrow \text{CO}_2 + \cdot\text{H}$
 - $\cdot\text{OH} + \cdot\text{OH} \rightarrow \text{O} + \text{H}_2\text{O}$ (more likely source of O for NO formation)
 - $\text{NO} + \cdot\text{OH} \rightarrow \text{HNO}_2$ (decreased due to CO quenching $\cdot\text{OH}$)
 - $\text{NO}_2 + \cdot\text{OH} \rightarrow \text{HNO}_3$ (decreased due to CO quenching $\cdot\text{OH}$)

Hydroxyl Radicals in Ar/N₂ Plasma

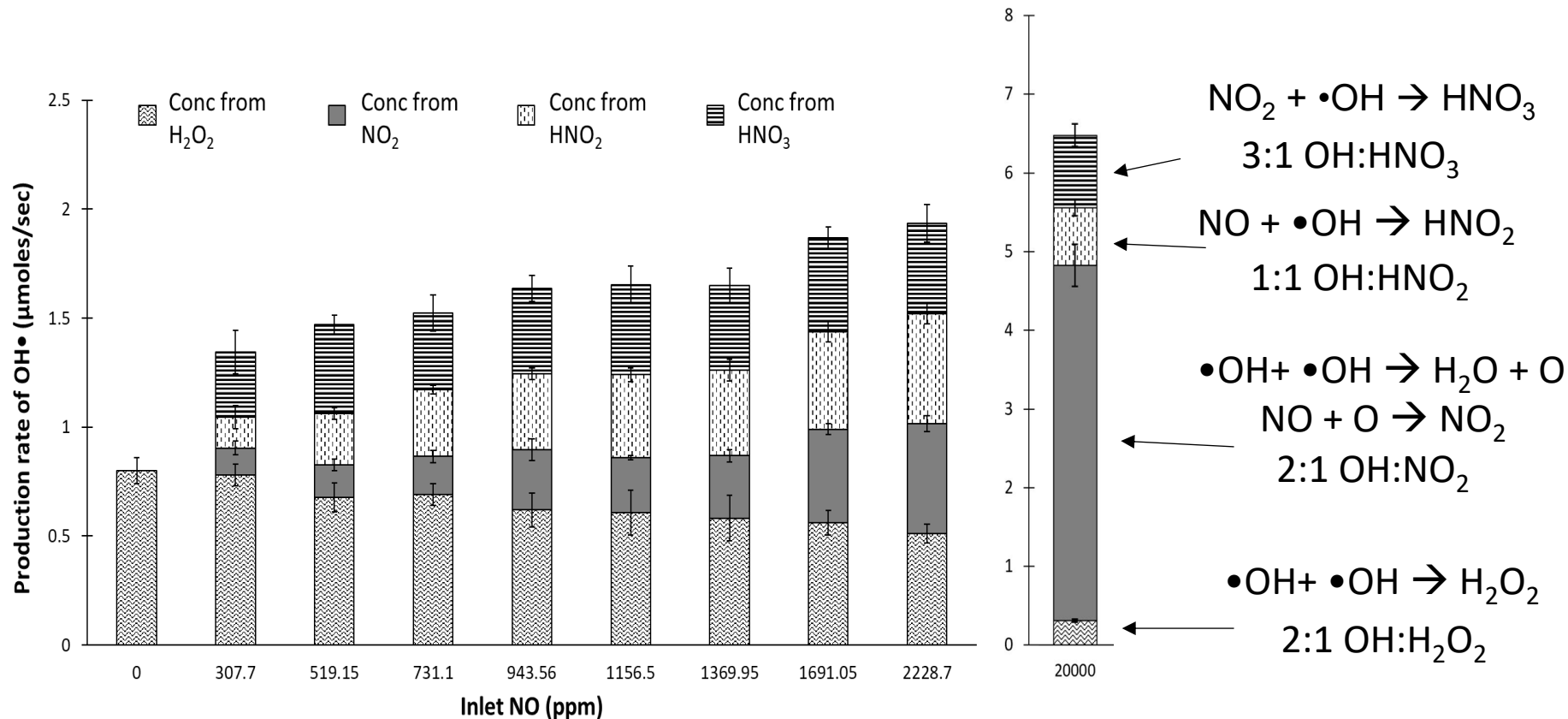
CO scavenging $\cdot\text{OH}$



- Significantly more $\cdot\text{OH}$ in CO reactions than in total H₂O₂ and NO_x.
 - Implies room for improvement in plasma oxidation reactions
- $\cdot\text{OH}$ energy yield 6.7 eV/100 molecules provides information on “primary” formation of $\cdot\text{OH}$

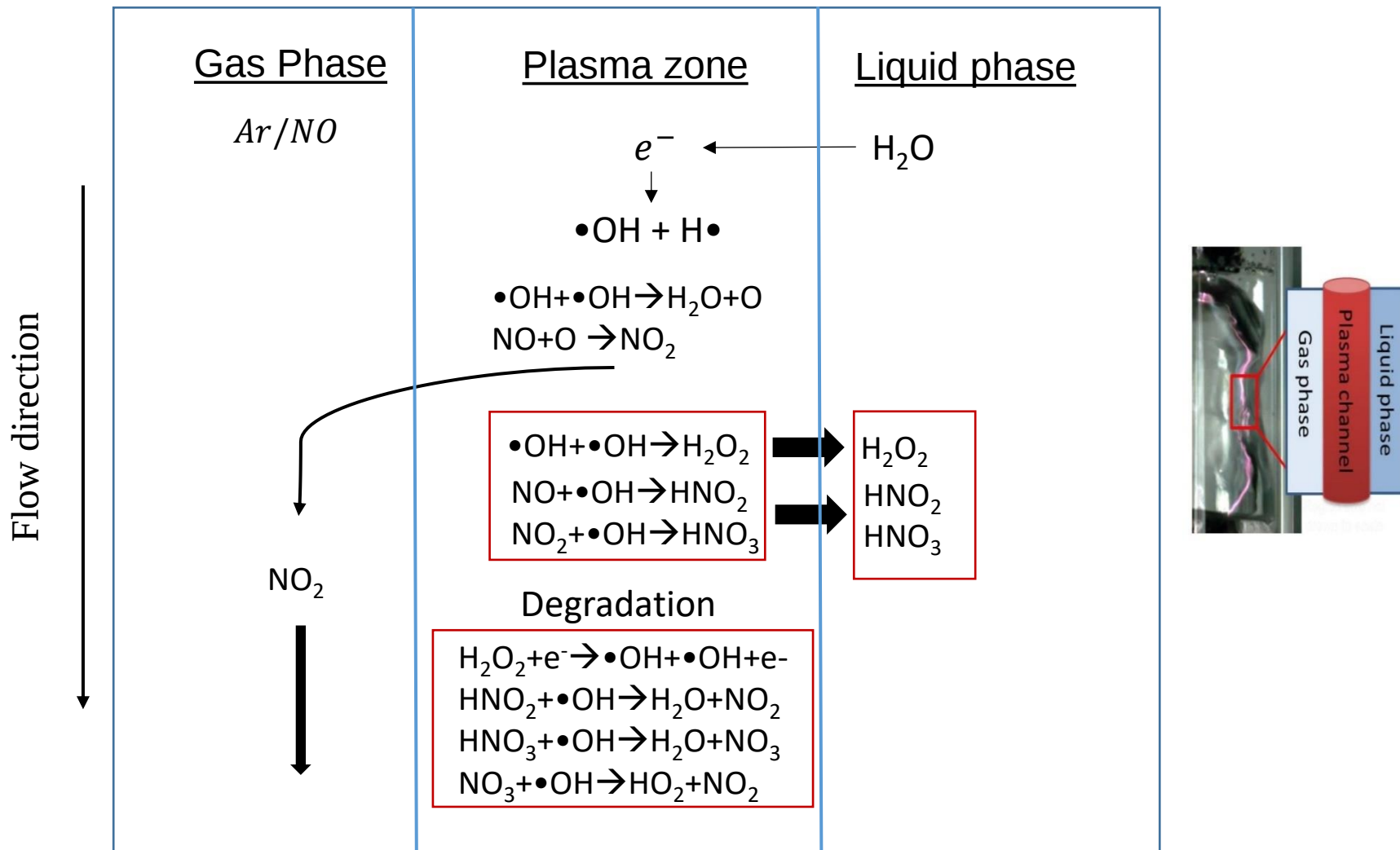
Hydroxyl Radicals in Ar/N₂ Plasma

NO scavenging of ·OH



- Experimental data suggests ·OH controls formation of HNO₂, HNO₃ and atomic oxygen
- HNO₂ and HNO₃ production limited by back reactions with increase in inlet NO

Summary of Nitrogen Species Reaction Pathways



Conclusions

- Gas-liquid reactor utilized here characterized with respect to
 - Geometry of gas and liquid volumes and interface
 - Hydrodynamic flow patterns, pressure, and mass transfer characteristics
 - Effects of power supply type (microsecond vs nanopulser)
 - Plasma gas temperature, electron density, and electron energy
 - Effects of solution conductivity, pulse frequency, power supply type
 - Nanopulser (fast rise) operates to near seawater conductivity without large drop in H_2O_2 .
 - Formation of hydroxyl radicals, hydrogen peroxide, oxidation products of several organic compounds including liquid phase, gas phase, and volatile compounds
- Relatively high efficiency for $\cdot\text{OH}$ formation demonstrated
 - $\cdot\text{OH}$ (primary) energy yields comparable to all other AOPs
 - $\cdot\text{OH}$ reactions/reaction products found in both gas phase and liquid phase
 - $\cdot\text{OH}$ reactions
 - Reactions of many organic compounds in the liquid and gas phases
 - Control formation of nitrogen oxides, particularly formation of acids
 - Control formation of hydrogen peroxide
 - Degradation reactions (reverse and others) can reduce efficiencies

Recent Collaborators



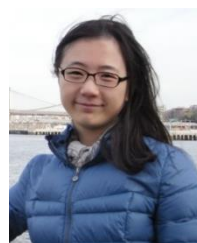
Dr. Kevin Hsieh
(ChE PhD 2015)



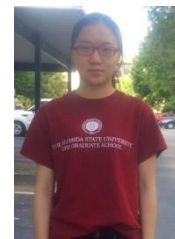
Dr. Stefan Bresch
(Chem PhD 2015)



Robert Wandell
(ChE PhD 2016)



Huihui Wang
(ChE PhD 2018)



Yi Xiong
(CEE PhD candidate)



Radha Bulusu
(ChE PhD candidate)



Prof. Igor Alabugin
(Chem/Biochem)



Prof. Youneng Tang
(Civil Envir. Engr.)



Prof. Radu Burlica
(Iasi Univeristy)



Kosuke Tachibana
(PhD, Tokyo Inst. Tech.
Oita University)



Dr. Jan Voráč
(Masaryk University)

- Undergraduates

- Basiel Makled
- Parastou (Mandy) Shahzeidi
- David Reece
- Rachel Gallan
- Qiao Zhang (BS/MS)

- Others

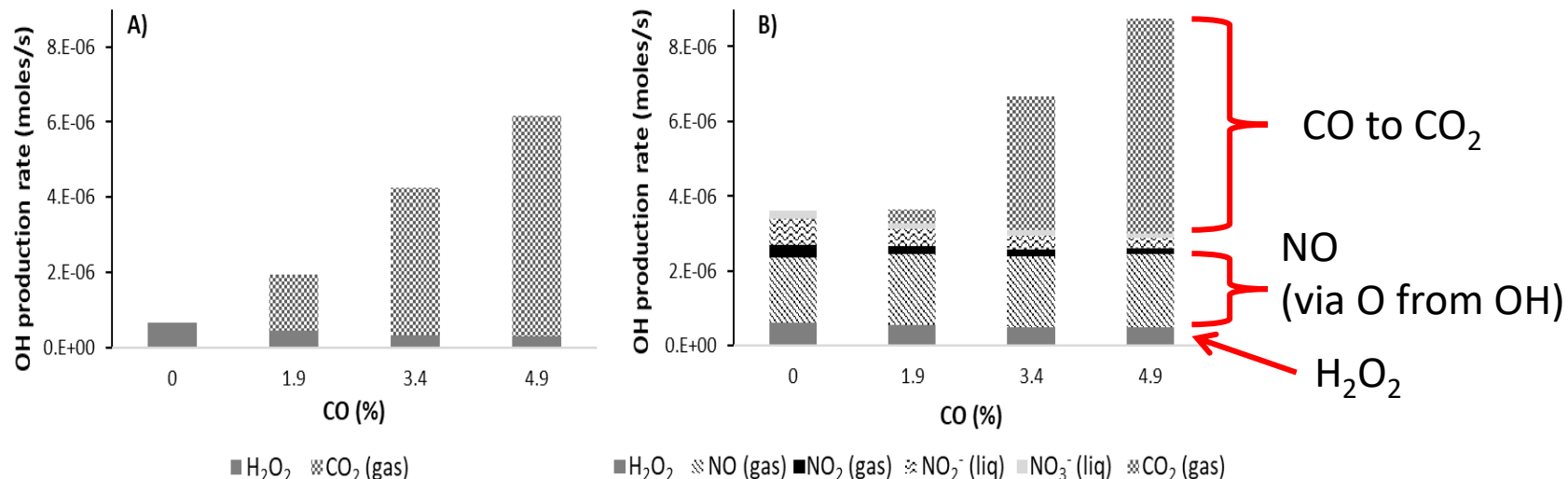
- Eagle Harbor Technologies
- Patrick Breslend, FSU
- Dr. Pavel Dvorak, Masaryk Univ.

- Institute of Plasma Physics, Prague

- Dr. P. Lukes, Dr. V. Jirasek
- Dr. V. Babicky, Dr. M. Clupek
- Dr. M. Simek

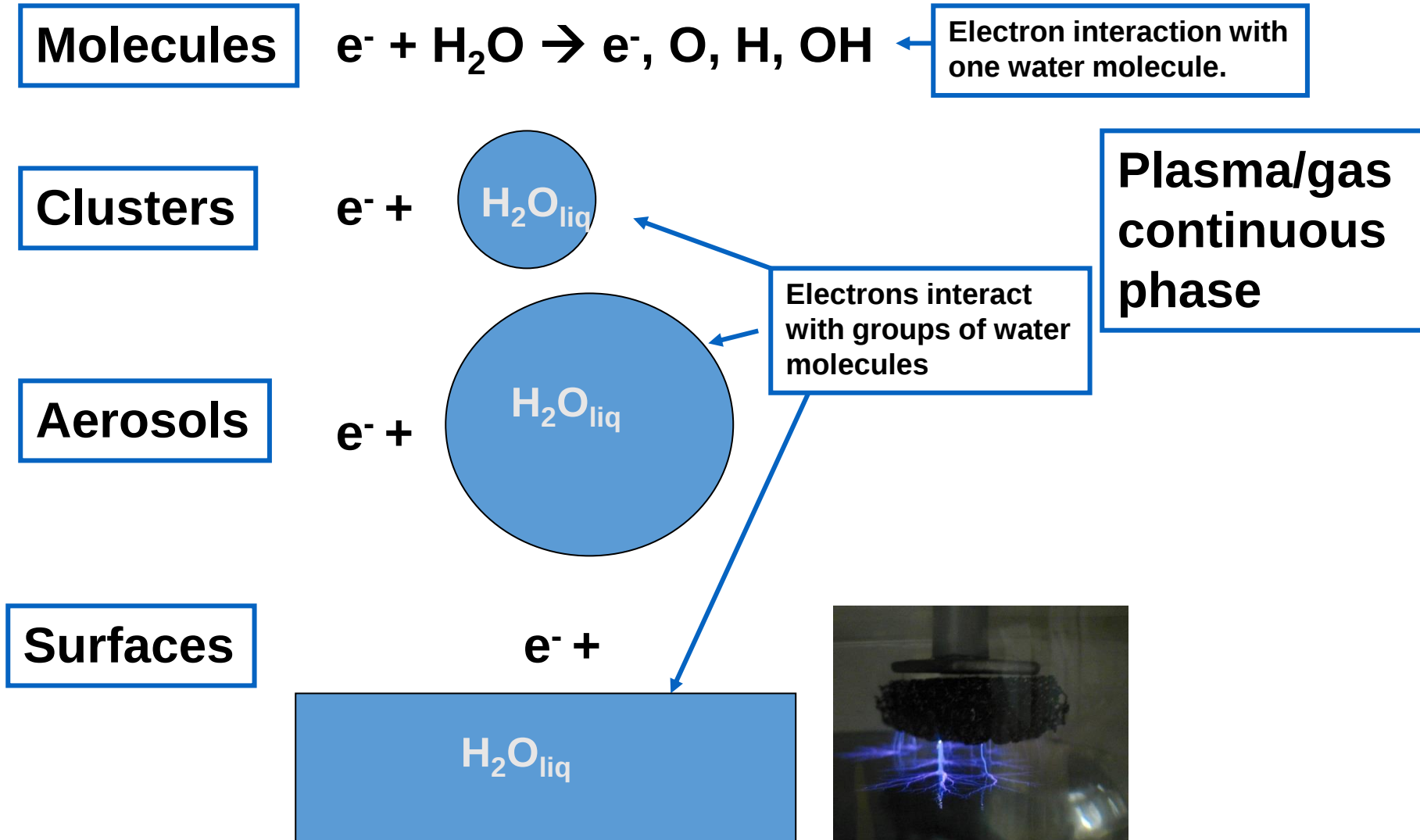
Thank you for your interest.

Hydroxyl Radicals in N₂/Ar Plasma



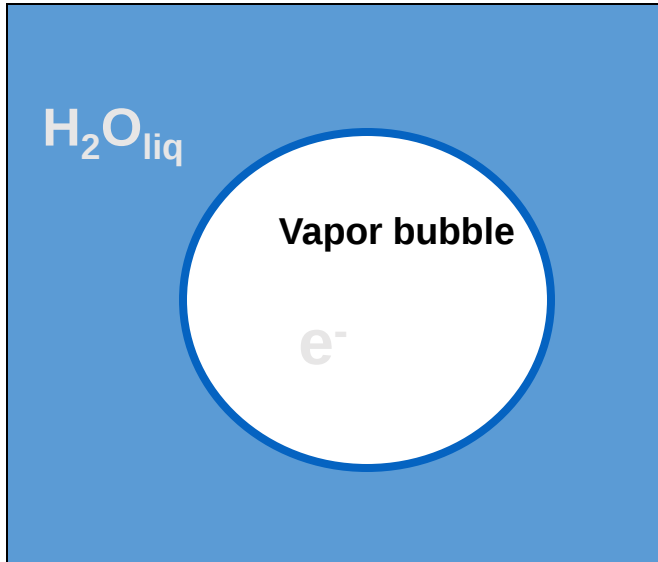
- Significantly more •OH in CO reactions than in total H₂O₂ and NO_x.
 - Implies room for improvement in plasma oxidation reactions
- •OH energy yield 6.7 eV/100 molecules provides information on “primary” formation of •OH

Water Plasma (electron) Interactions

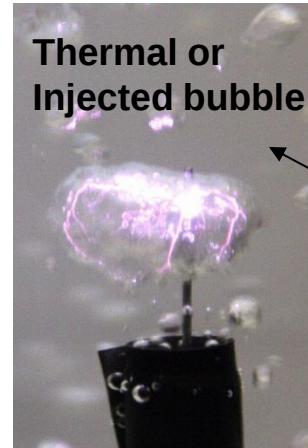
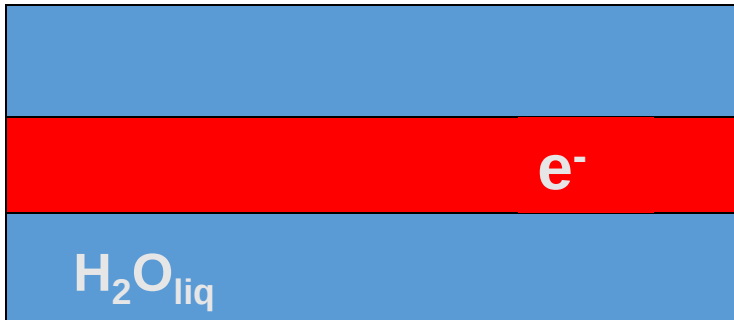


Water Plasma (electron) Interactions

Bubbles



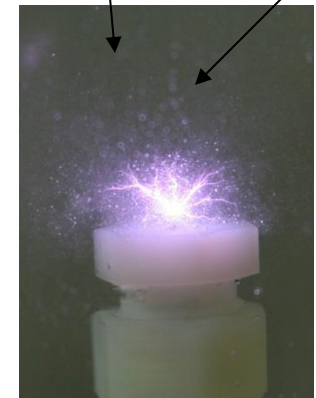
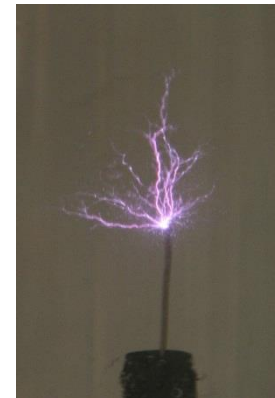
Plasma Channels



Liquid is continuous phase

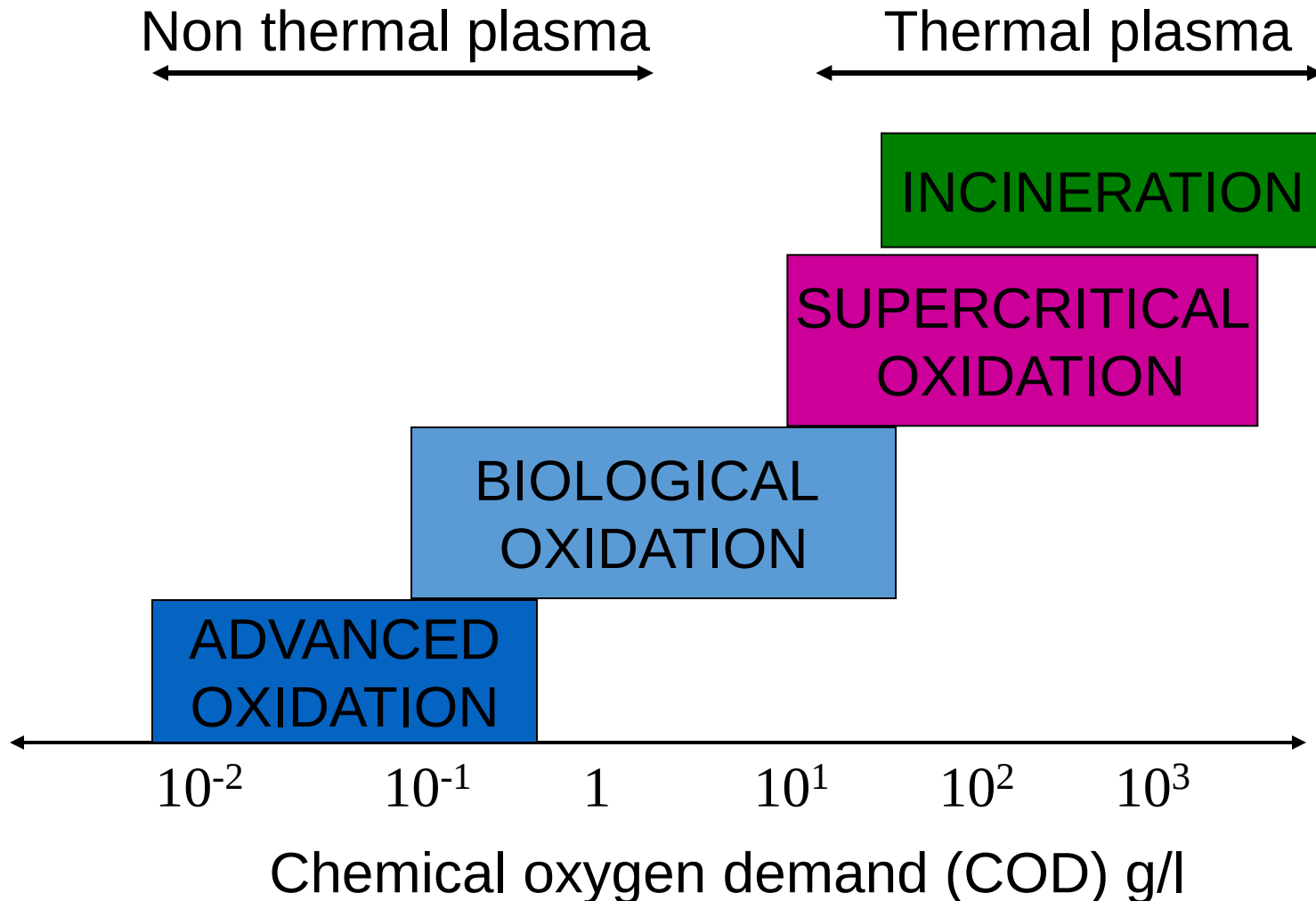
Increasing photographic time exposure

Fine bubbles formed



Treatability Ranges

(adapted from Tarr, 2003)



Predicted generation of $\cdot\text{OH}$ by various AOPs

Process	assumed						estimated
	O_3	H_2O_2	UV	O_3	UV	H_2O_2	OH yield
	g/kWh	g/kWh	eV/photon	mole O_3 / mole OH	mole photon/ mole OH	mole H_2O_2 / mole OH	molecules/ 100 eV
O_3	50			1.5			1.9
O_3	100			1.5			3.7
O_3/UV	50		1	1.5	0.5		1.8
O_3/UV	50		6	1.5	0.5		1.8
O_3/UV	100		1	1.5	0.5		3.6
O_3/UV	100		6	1.5	0.5		3.3
$\text{O}_3/\text{H}_2\text{O}_2$	50	50		1		0.5	2.1
$\text{O}_3/\text{H}_2\text{O}_2$	100	50		1		0.5	3.3
$\text{H}_2\text{O}_2/\text{UV}$		50	1		0.5	0.5	7.6
$\text{H}_2\text{O}_2/\text{UV}$		50	6		0.5	0.5	6.4
H_2O_2 Fenton		50				1	3.9
H_2O_2 Fenton		100				1	7.9

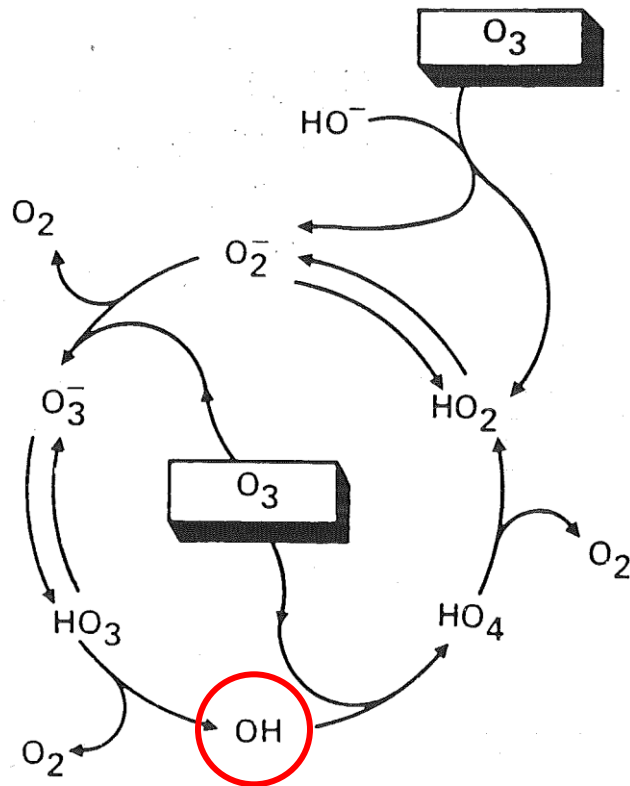
- Stoichiometry taken from Glaze, 1987
- Does not account for low O_3 solubility and mass transfer
- Idealized view due to solution (pH, scavengers, etc.) conditions

Hydroxyl Radicals from AOPs

Process	Overall reactions
O₃	Molecular: O ₃ + reactant → product Radical: O ₃ ... → ·OH
H₂O₂ - Fenton	H ₂ O ₂ + Fe ²⁺ → Fe ³⁺ + ·OH + OH ⁻
O₃/H₂O₂	H ₂ O ₂ + 2O ₃ → 2 ·OH + 3O ₂
UV	Reactant + hν → products
O₃/UV	O ₃ + H ₂ O + hν → 2 ·OH + O ₂
UV/H₂O₂	H ₂ O ₂ + hν → 2 ·OH
O₃/UV/H₂O₂	2O ₃ + H ₂ O ₂ + hν → 2 OH + 3 O ₂

Key species: input – O₃, H₂O₂, UV major reactant - ·OH

Ozone Reactions in Water



(Staehlin and Hoigne, 1985)

1) $\text{O}_3 + \text{reactant} \rightarrow \text{products}$

2) $\text{O}_3 \dots \rightarrow \cdot\text{OH}$

(net 1.5 moles O_3 to 1 mole $\cdot\text{OH}$)

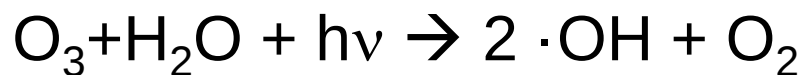
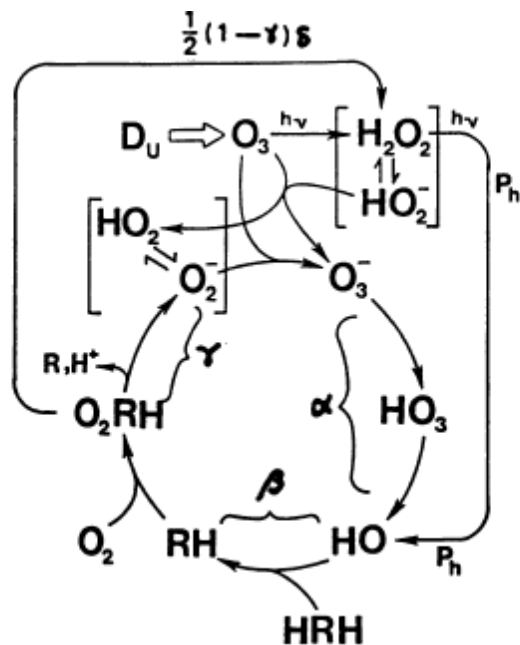
$\cdot\text{OH} + \text{reactant} \rightarrow \text{products}$

Limitations

- Ozone solubility in water
- Mass transfer
- Solution properties, e.g. scavengers

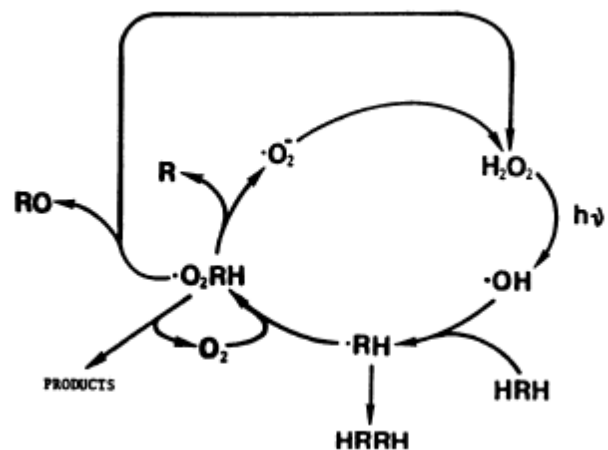
UV and Chemical Pathways

Ozone + UV



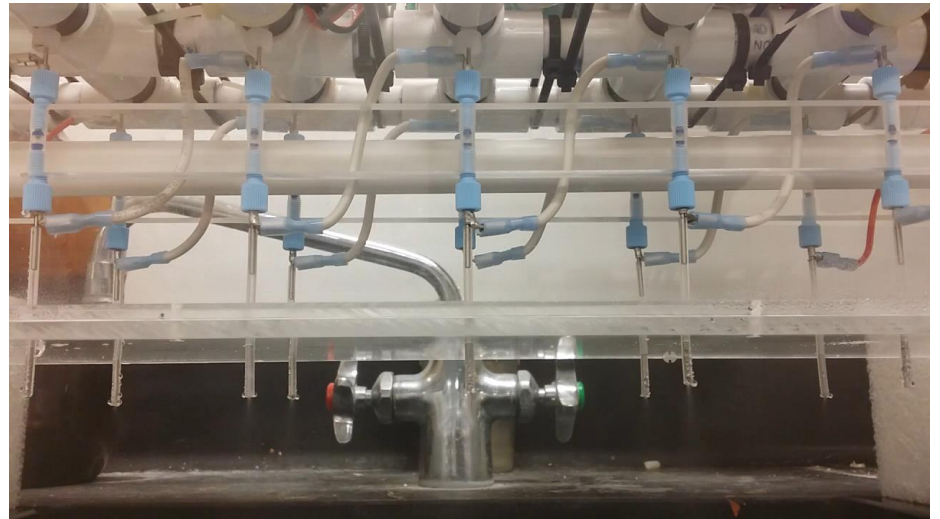
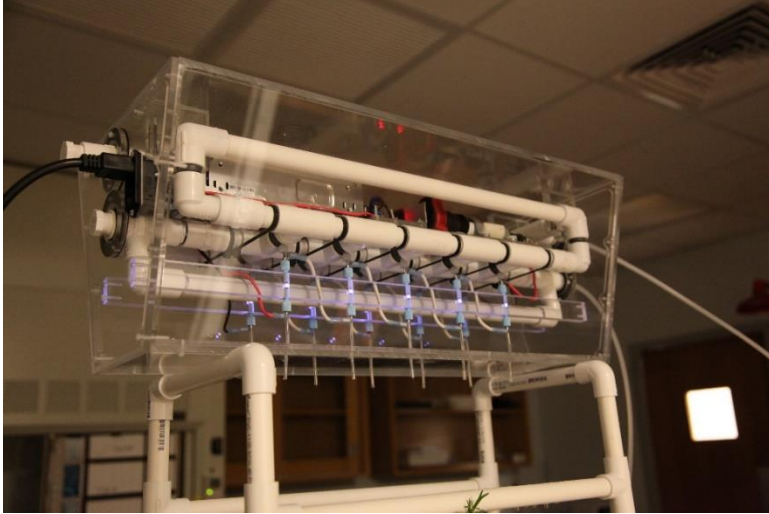
(Peyton/Glaze 1988)

H_2O_2 + UV



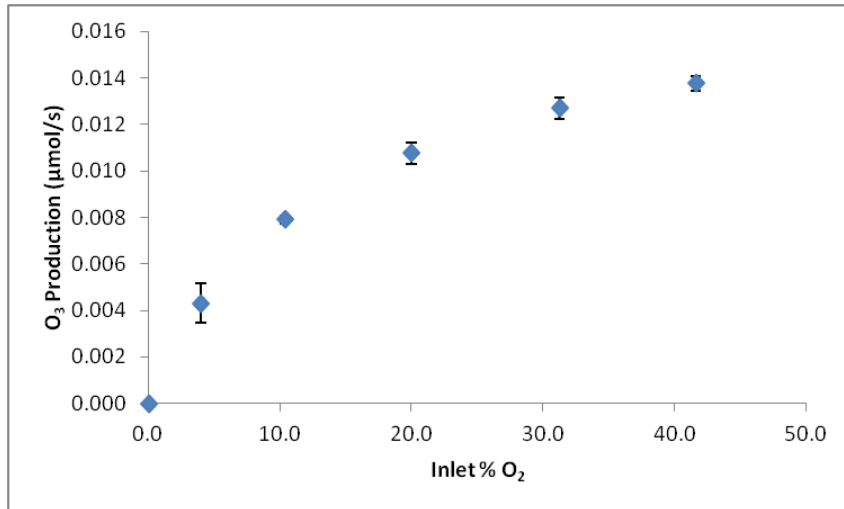
(Peyton 1990)

Scaled-up Prototype

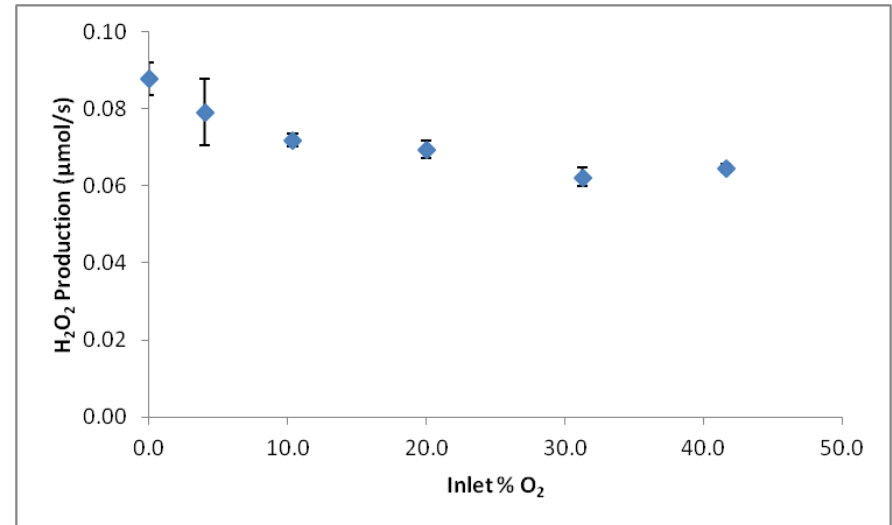


Oxygen Addition

Ozone production



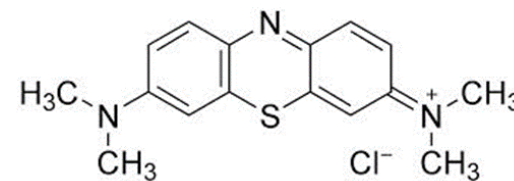
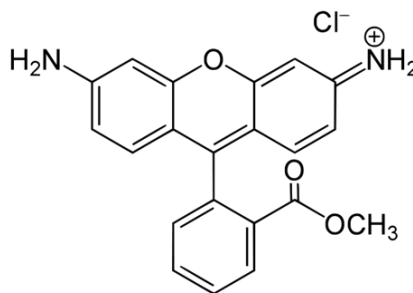
Hydrogen peroxide formation



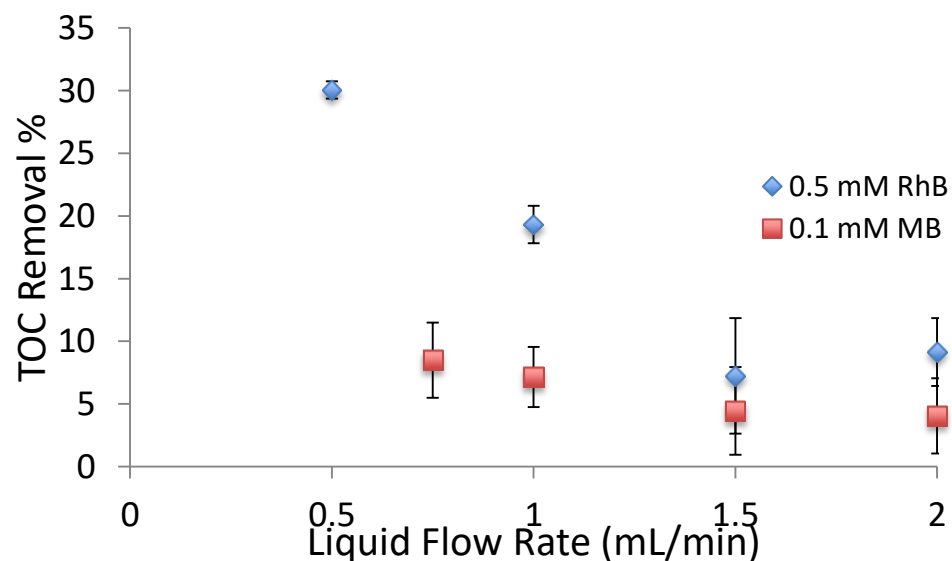
- Oxygen addition leads to significant ozone formation in the gas phase.
- Oxygen addition only slightly decreases H₂O₂ formation.
- Oxygen addition has no effect on MB decoloration in liquid.
 - Suggests ozone transfer to liquid and reactions is liquid slow.

Dye Removal

Reactor	Energy Yield g/kWh
Pulsed discharge in water	0.08 to 0.2
DC discharges in air over water film	4.9
Plasma jet discharge with argon	0.4
PCD in water with O ₂ bubbling	0.59
Water film reactor with argon (this work)	2.3 to 4.0
Laminar jet with bubbling (Thagard)	11.4
Water spray in PDBD with O ₂	45
UV/H ₂ O ₂	0.1
Ultrasound	0.2
Photocatalysis	0.2
Ozonation	0.3



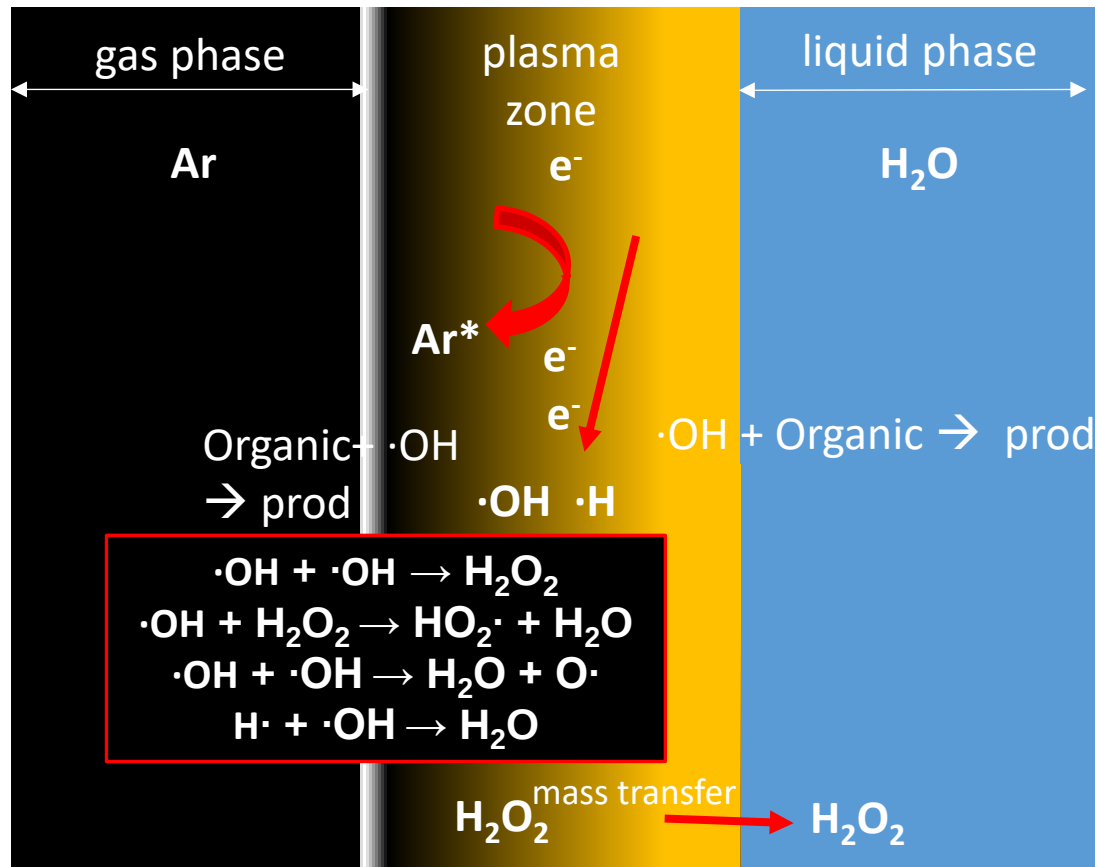
Total Organic Carbon Removal



Key issues

- Can we control the chemical reactions by changing the input conditions?
 - How affect efficiency and selectivity?
- Do the input pulse parameters affect plasma properties such as electron density, electron temperature, and plasma temperature?
- Do these plasma properties affect chemistry?
- What is the role of liquid water?
 - Source of reactants: from liquid to plasma
 - H_2O : $\cdot\text{OH}$ oxidant, H reductant
 - Interface and transport of mass and energy
 - Second phase improves plasma, thermal, and chemical quenching and increases gradients at phase boundary
 - Magnitudes of the gradients in temperature and concentration at interface
 - How do gradients affect chemical reactions?
 - Which reactive species transfer between plasma and liquid?
 - Collects products: from plasma to liquid
 - H_2O_2 , alcohols, aldehydes,...

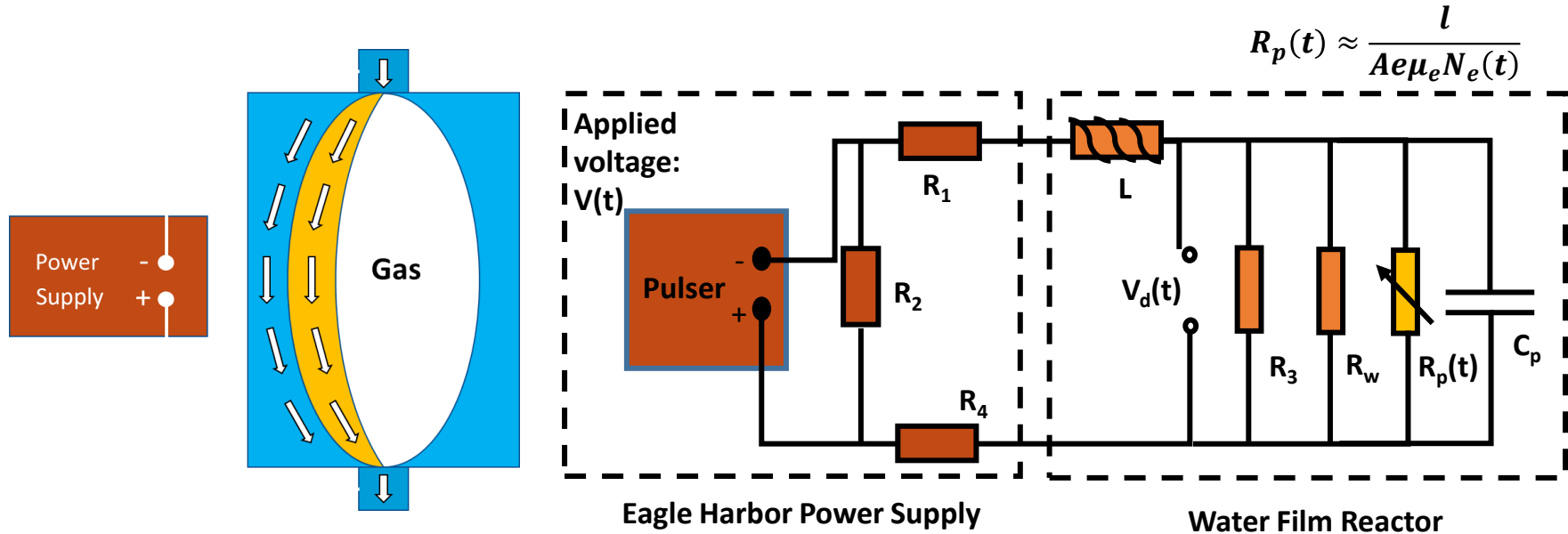
Summary



- Organic compounds in gas phase: hexane, CO, ethanol
- Organic compounds in the liquid phase: MB, ethanol

Electrical Circuit Model for Conductivity Effects

(Eagle Harbor nanopulser)



$R_p, R_w, R_{1,2,3,4}$: Resistance of plasma, water film, and resistors in the circuit

C_p : Capacitance of reactor

A : Cross-section area of plasma channel

e : Elementary charge

μ_e : Mobility of electron

N_e : Electron density

l : Electrode gap

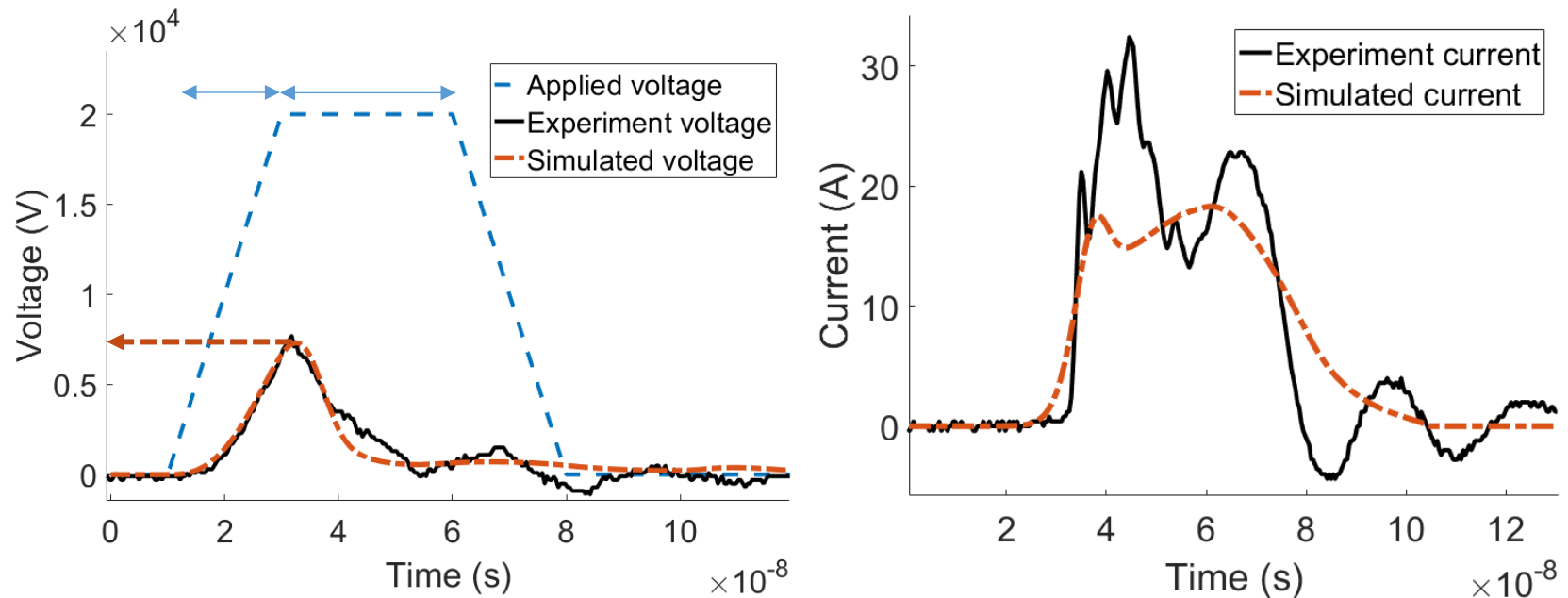
L : Inductance of wire

- $N_e(t)$ – assumed to follow current pulse.

(Wang et al., 2019)

Simulating Discharge Voltage and Current

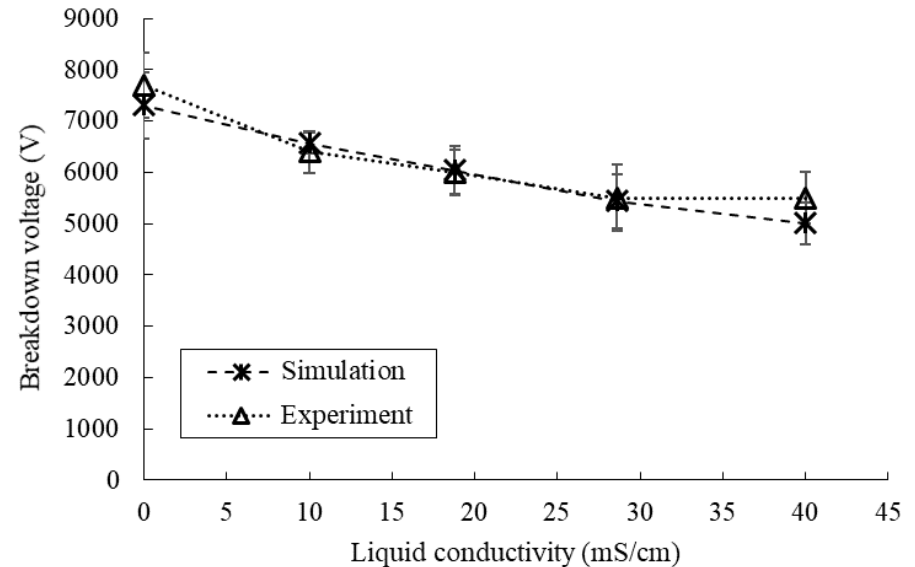
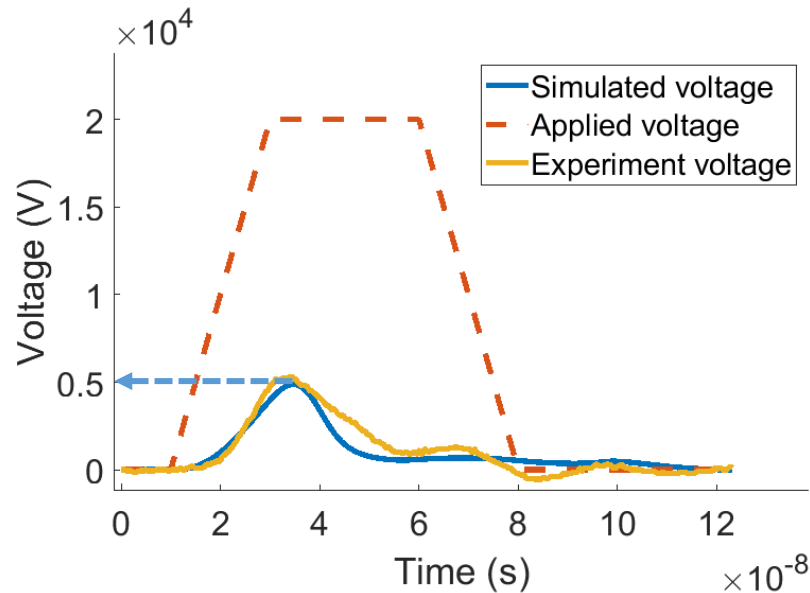
(Eagle Harbor nanopulser)



(Power Supply: 20 kV, 2kHz, 50ns; DI water 1mL/min; Argon)

Liquid Conductivity and Breakdown Voltage

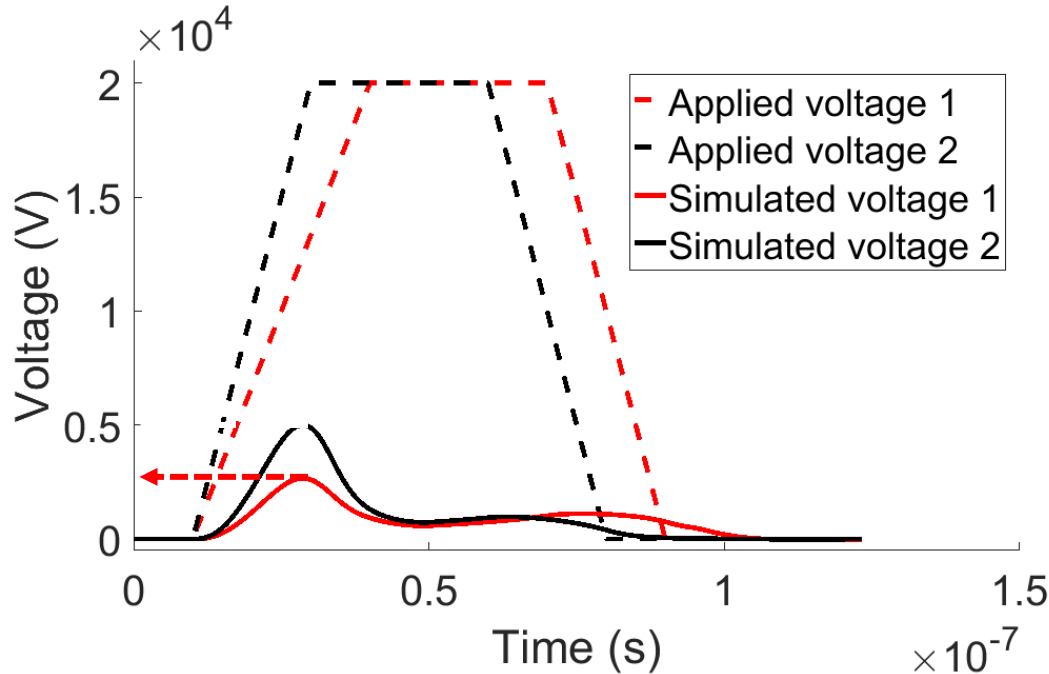
(Eagle Harbor nanopulser)



- Power Supply: 20 kV, 2kHz, 50ns; 40 mS/cm, 1mL/min; Argon
- Breakdown voltage drops with liquid conductivity

(Wang et al., 2019)

Influence of Applied Voltage on Breakdown



Conditions/Assumptions:

- 40mS/cm KCl solution
- Carrier gas: Argon
- Electron density was assumed unchanged with applied voltage
- Two applied voltages with different pulse rise time were used

- Longer rise times lead to lower breakdown voltages.
- Ignition coil power supply rise time 4 μ s insufficient to generate discharge at high conductivity.
- Eagle Harbor power supply rise time 20 ns works very well.