Chemistry in Plasma Treated Liquids
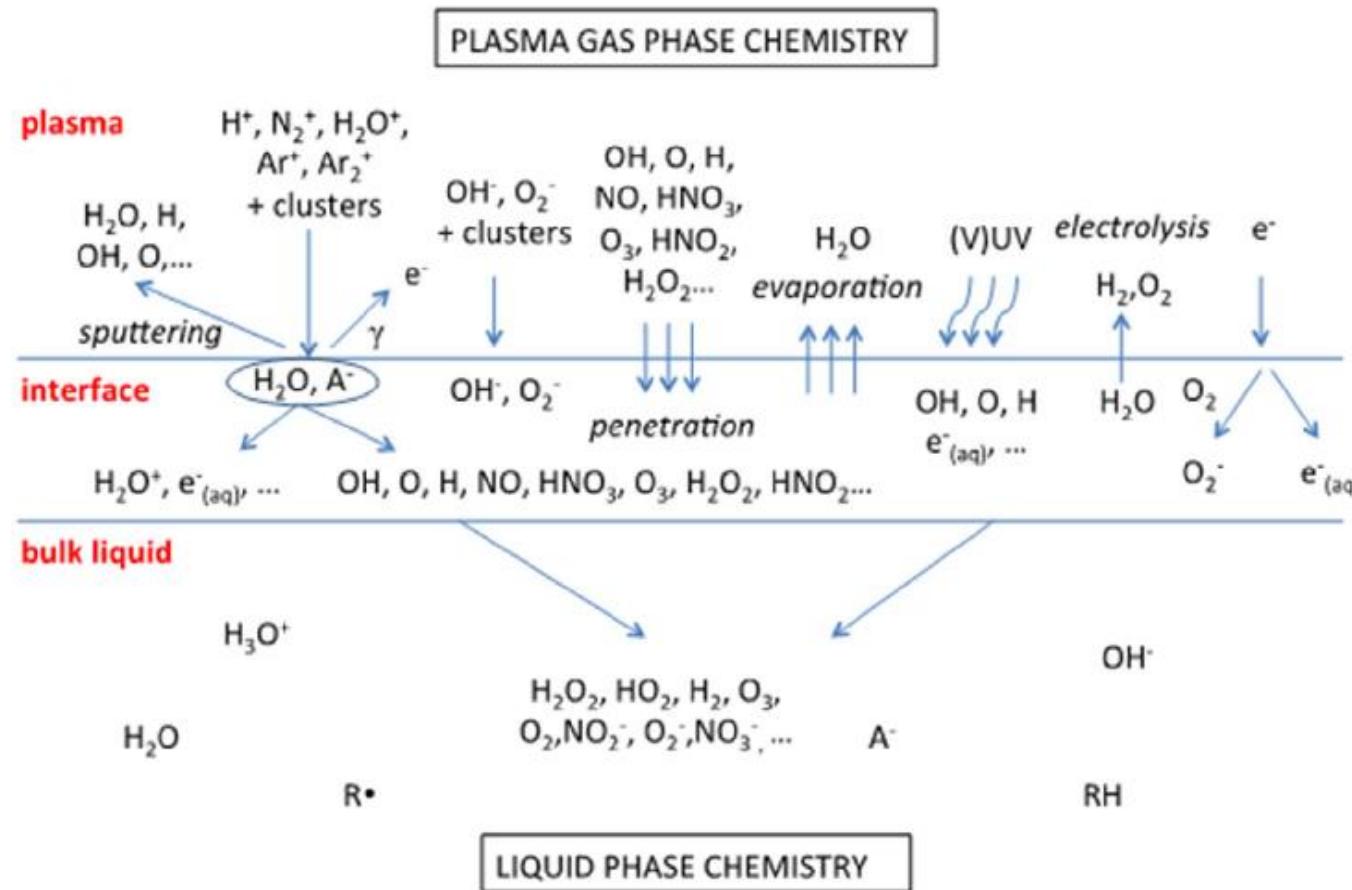
A. von Keudell

Experimental Physics II, Ruhr University Bochum

The plasma liquid interface

PLASMA GAS PHASE CHEMISTRY

plasma

H^+, N_2^+, H_2O^+, Ar^+, Ar_2^+ + clusters

H_2O, H, OH, O,...

OH^-, O_2^- + clusters

OH, O, H, NO, HNO_3, O_3, HNO_2, H_2O_2...

H_2O evaporation

(V)UV

electrolysis e^-

H_2, O_2

sputtering

γ

e^-

interface

H_2O, A^-

OH^-, O_2^-

penetration

OH, O, H

$e^-_{(aq)}$, ...

H_2O

O_2

O_2^-

$e^-_{(aq)}$

H_2O^+, $e^-_{(aq)}$, ...

OH, O, H, NO, HNO_3, O_3, H_2O_2, HNO_2...

bulk liquid

H_3O^+

H_2O

R•

H_2O_2, HO_2, H_2, O_3, O_2, NO_2^-, O_2^-, NO_3^-, ...

A^-

OH^-

RH

LIQUID PHASE CHEMISTRY

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Plasma in liquid chemistry in a nutshell

primary species in the plasma

$$O + O_2 \rightarrow O_3$$
$$2\,H_2O \rightarrow 2\,OH + H_2$$
$$2\,OH \rightarrow H_2O_2$$

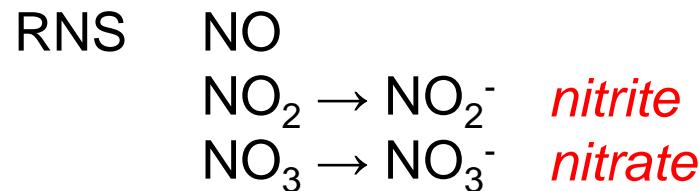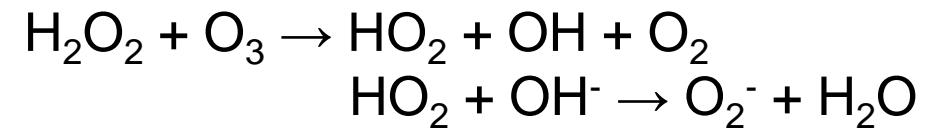$$O_2 + N \rightarrow NO + O$$
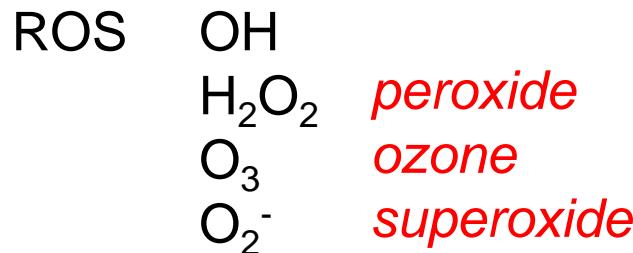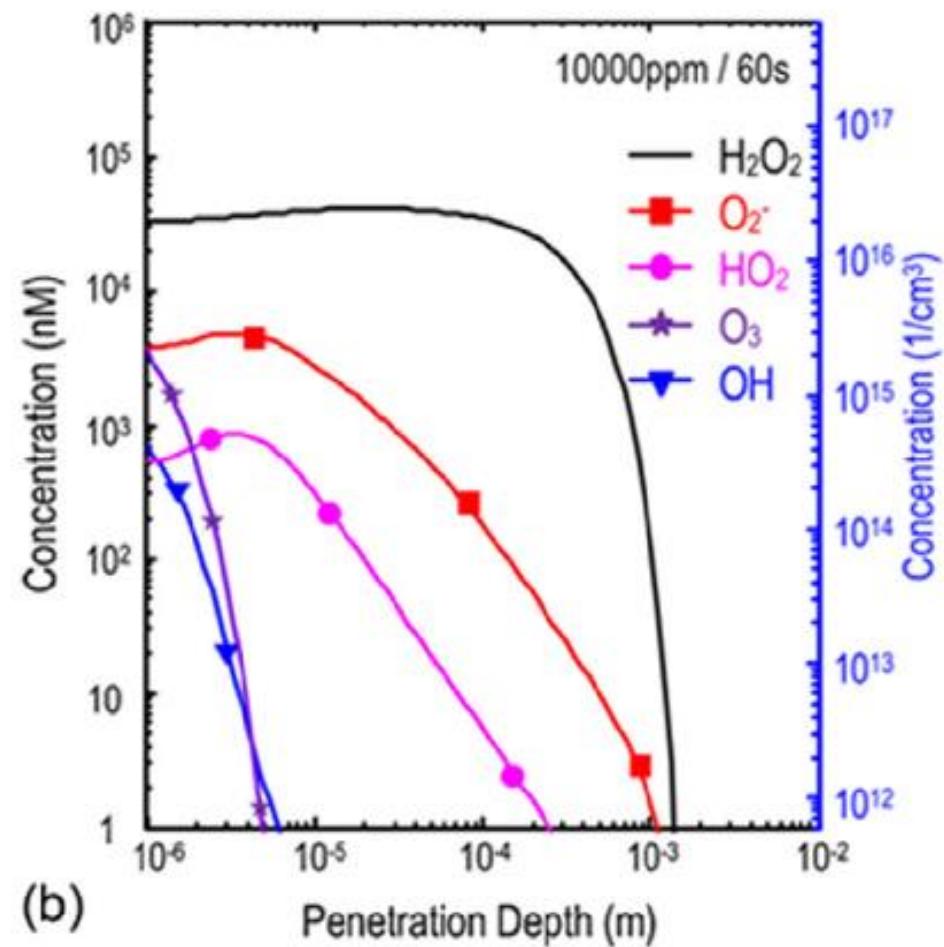$$O + N_2 \rightarrow NO + N$$
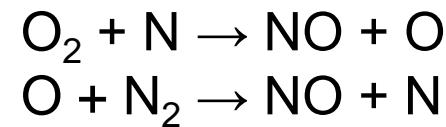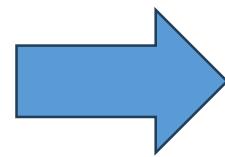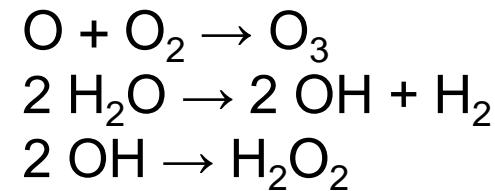
Zeldovich mechanism

Henry
constants
determine
transfer

RONS

primary species in the liquid

ROS   OH
           H_2O_2 *peroxide*
           O_3 *ozone*
           O_2^- *superoxide*

$$H_2O_2 + O_3 \rightarrow HO_2 + OH + O_2$$
$$HO_2 + OH^- \rightarrow O_2^- + H_2O$$

RNS   NO
           $NO_2 \rightarrow NO_2^-$ *nitrite*
           $NO_3 \rightarrow NO_3^-$ *nitrate*

$$NO + O_3 \rightarrow NO_2 + O_2$$
$$NO_2 + O_3 \rightarrow NO_3 + O_2$$
$$NO_2 + H_2O_2 \rightarrow NO_3 + H_2O$$

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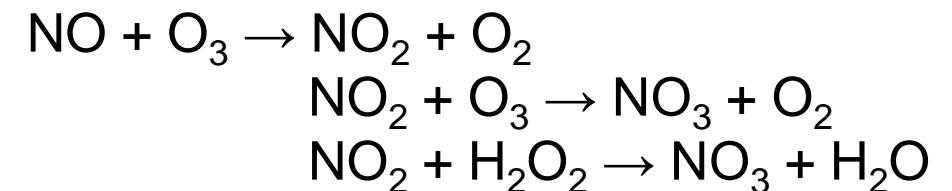
Plasma in liquid chemistry in a nutshell – chemistry modeling

10000ppm / 60s

- H₂O₂
- O₂⁻
- HO₂
- O₃
- OH

(b) Penetration Depth (m)

[188] Chen C, Liu D X, Liu Z C, Yang A J, Chen H L, Shama G and Kong M G 2014 A model of plasma-biofilm and plasma-tissue interactions at ambient pressure *Plasma Chem. Plasma Process.* **34** 403–41

$$H_2O_2 + O_3 \rightarrow HO_2 + OH + O_2$$
$$HO_2 + OH^- \rightarrow O_2^- + H_2O$$

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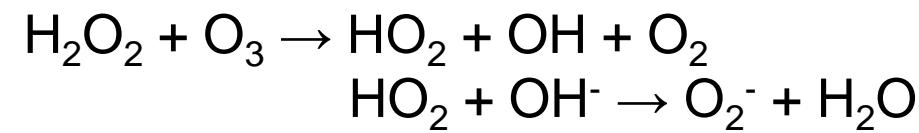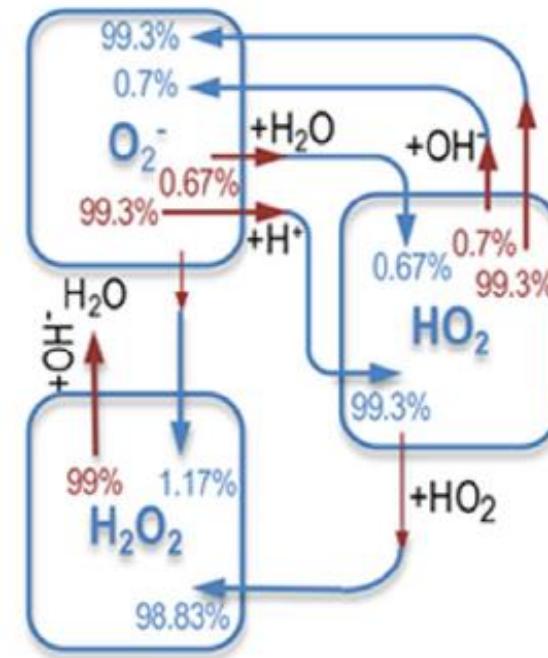
# Plasma activated water – PAW, change in reactivity

(a)
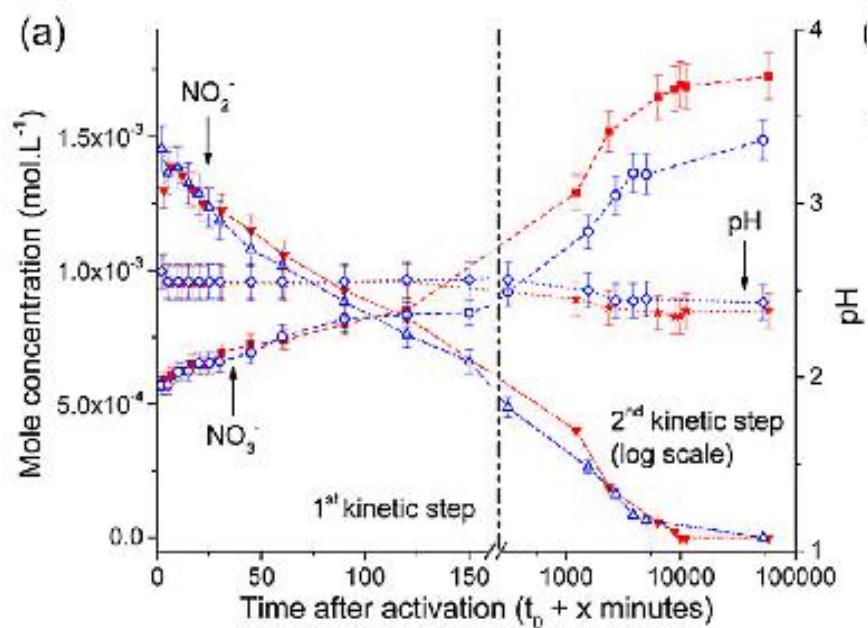
Wartel, M., Faubert, F., Dirlau, I. D., Rudz, S., Pellerin, N., Astanei, D., Burlica, R., Hnatiuc, B., & Pellerin, S. (2021). Analysis of plasma activated water by gliding arc at atmospheric pressure: Effect of the chemical composition of water on the activation. *Journal of Applied Physics, 129*(23), 233301. https://doi.org/10.1063/5.0040035
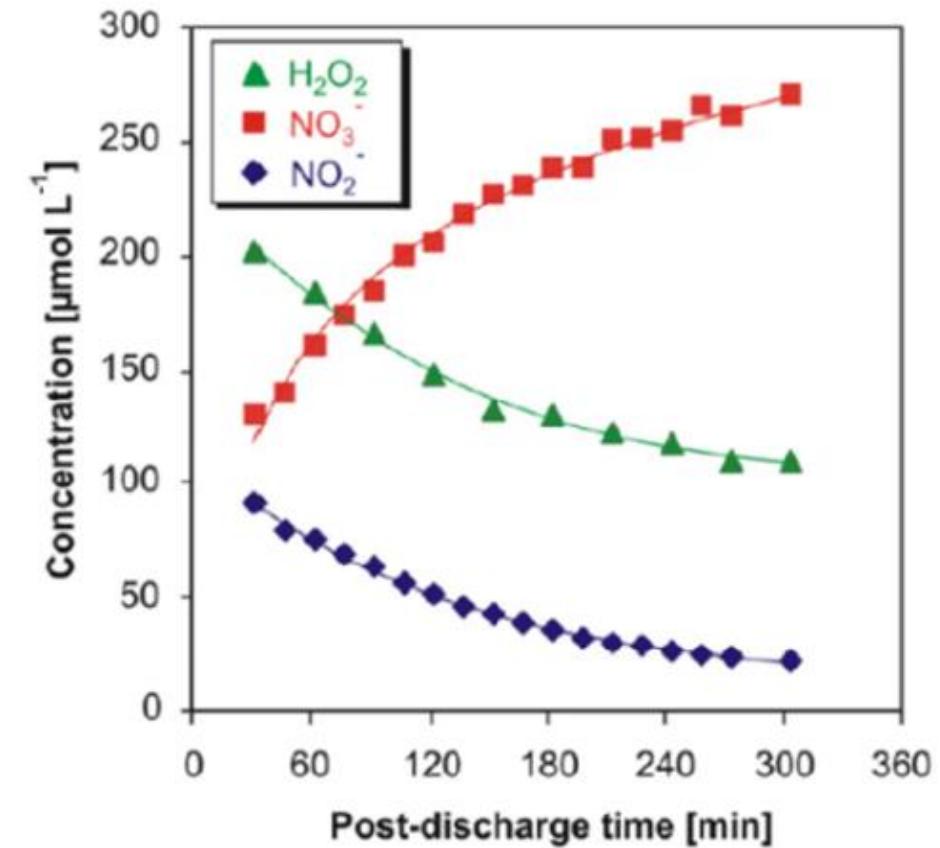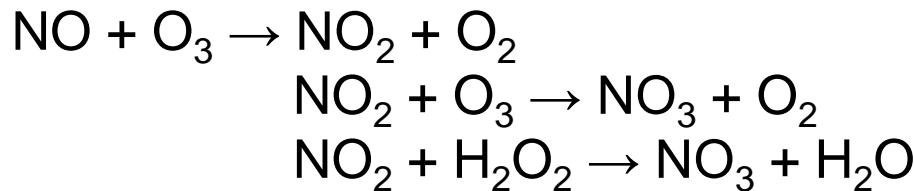

[488] Lukes P, Dolezalova E, Sisrova I and Clupek M 2014 Aqueous-phase chemistry and bactericidal effects from an air discharge plasma in contact with water: evidence for the formation of peroxynitrite through a pseudo-second-order post-discharge reaction of H_2O_2 and HNO_2 *Plasma Source Sci. Technol.* 23 015019

$$NO + O_3 \rightarrow NO_2 + O_2$$
$$NO_2 + O_3 \rightarrow NO_3 + O_2$$
$$NO_2 + H_2O_2 \rightarrow NO_3 + H_2O$$

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Possible plasma arrangements of plasma in liquids

Plasma above the liquid
(liquid electrode)
  → RONS
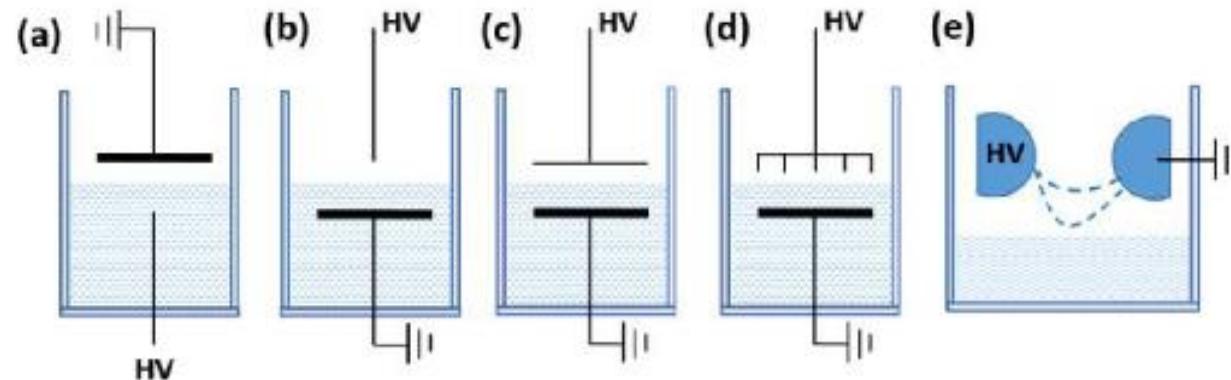
Plasma inside the liquid
  → ROS
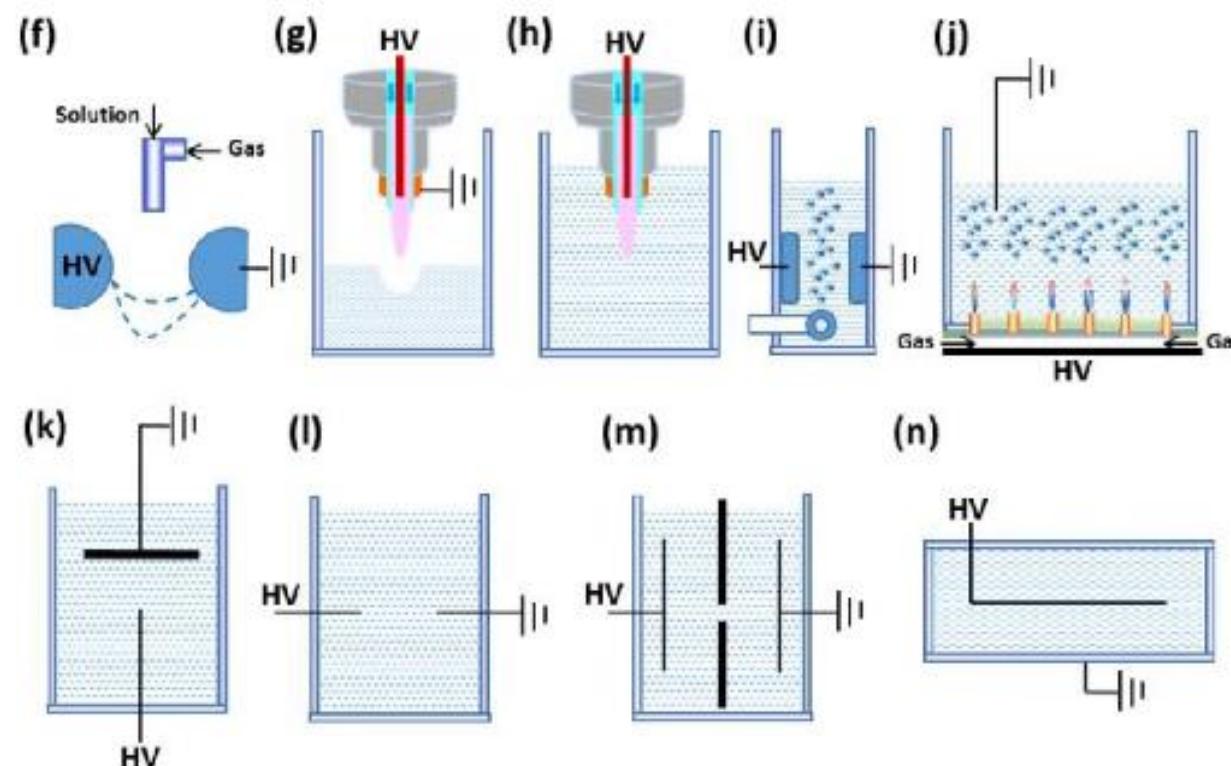
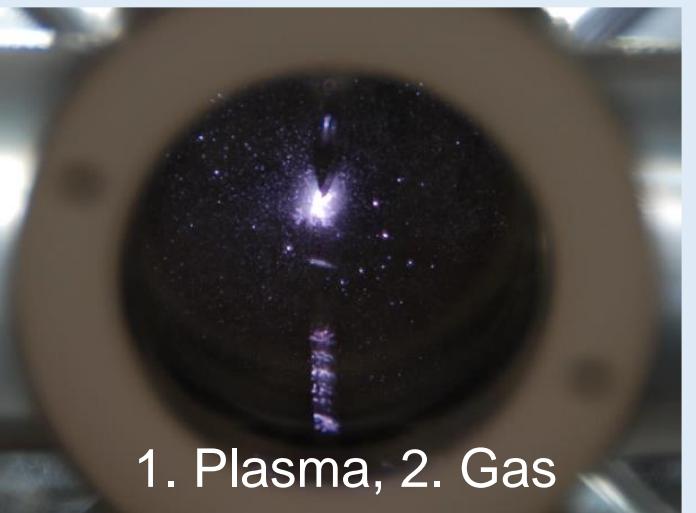: Renwu Zhou et al 2020 J. Phys. D: Appl. Phys. 53 303001

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Solvated electrons in liquids induced by plasmas
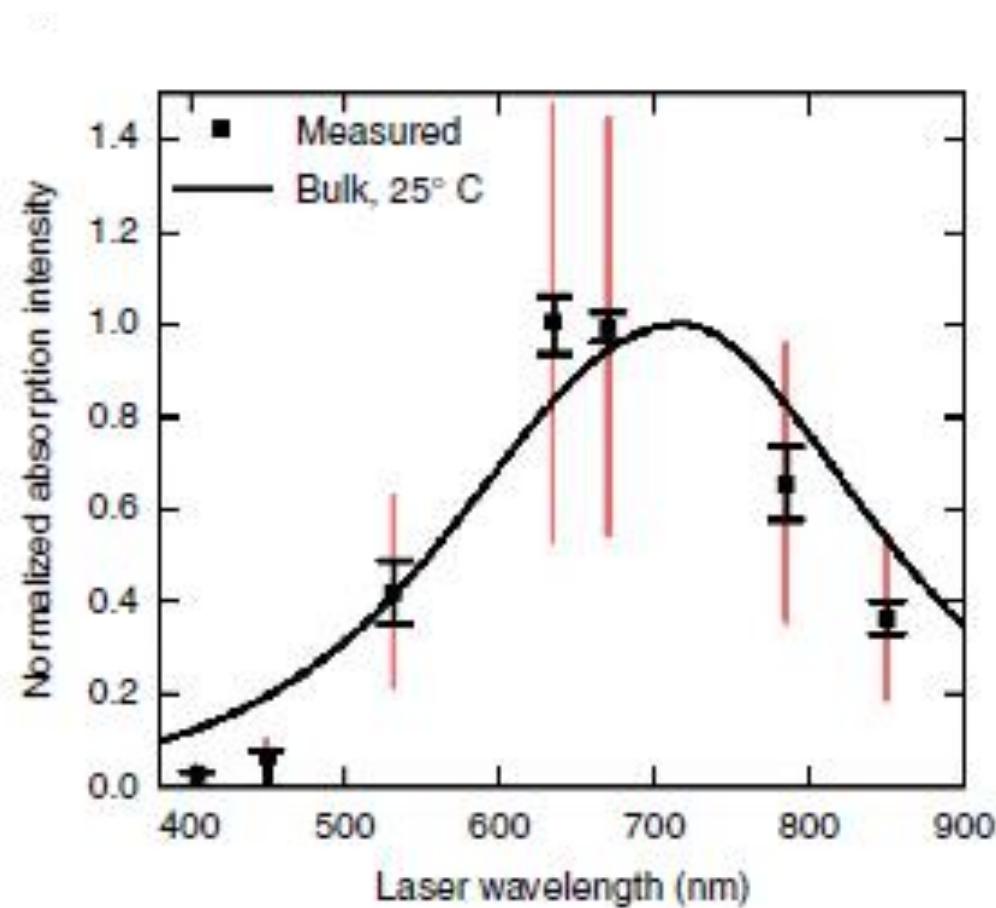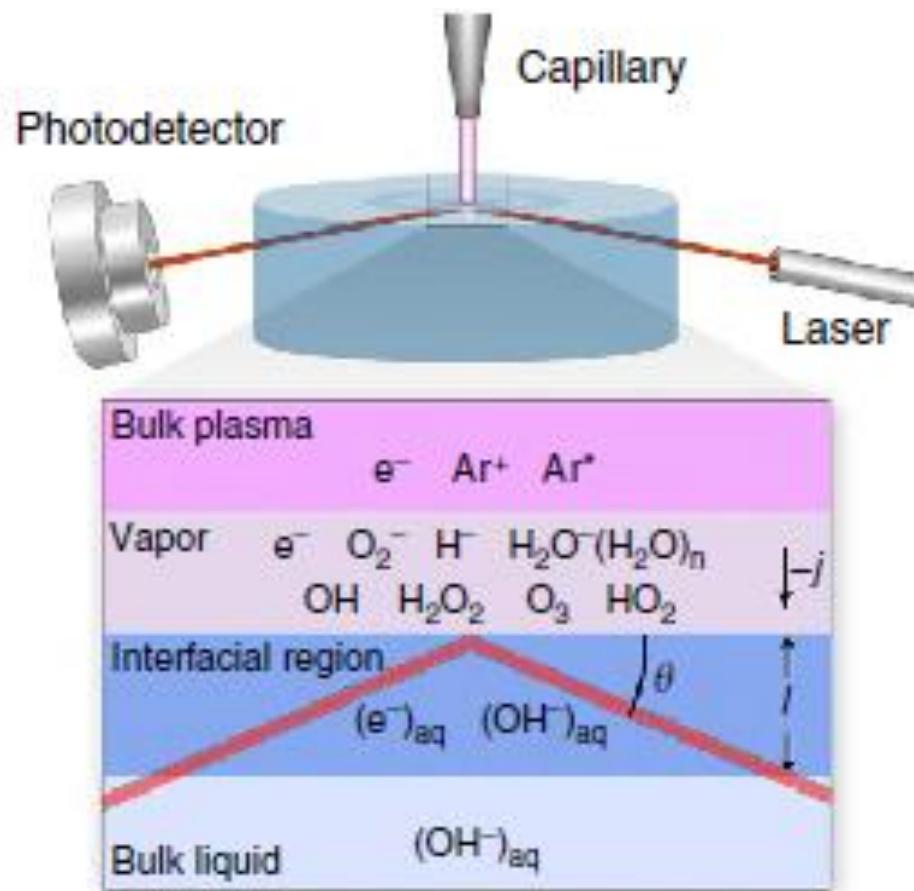
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Plasma Chemistry in liquids – example H_2O_2 generation
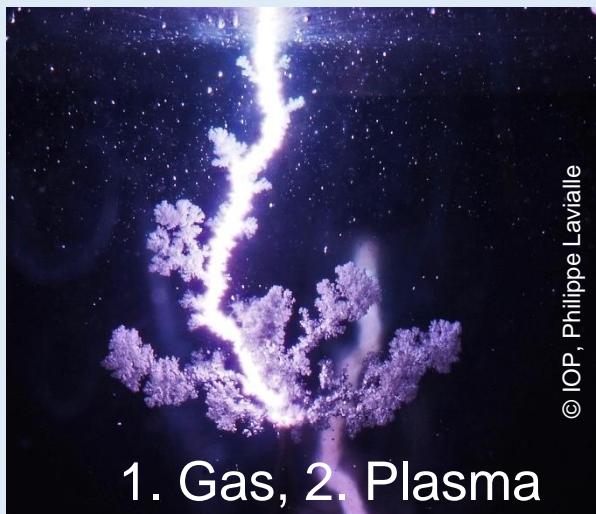
Nanosecond plasmas

1. Plasma, 2. Gas

- Short nanosecond pulses
- Pulses too short for formation of a gas bubble
- Plasma ignition inside the liquid

Extremely high pressures and temperatures 10000 bar, 50000 K

Microsecond plasmas
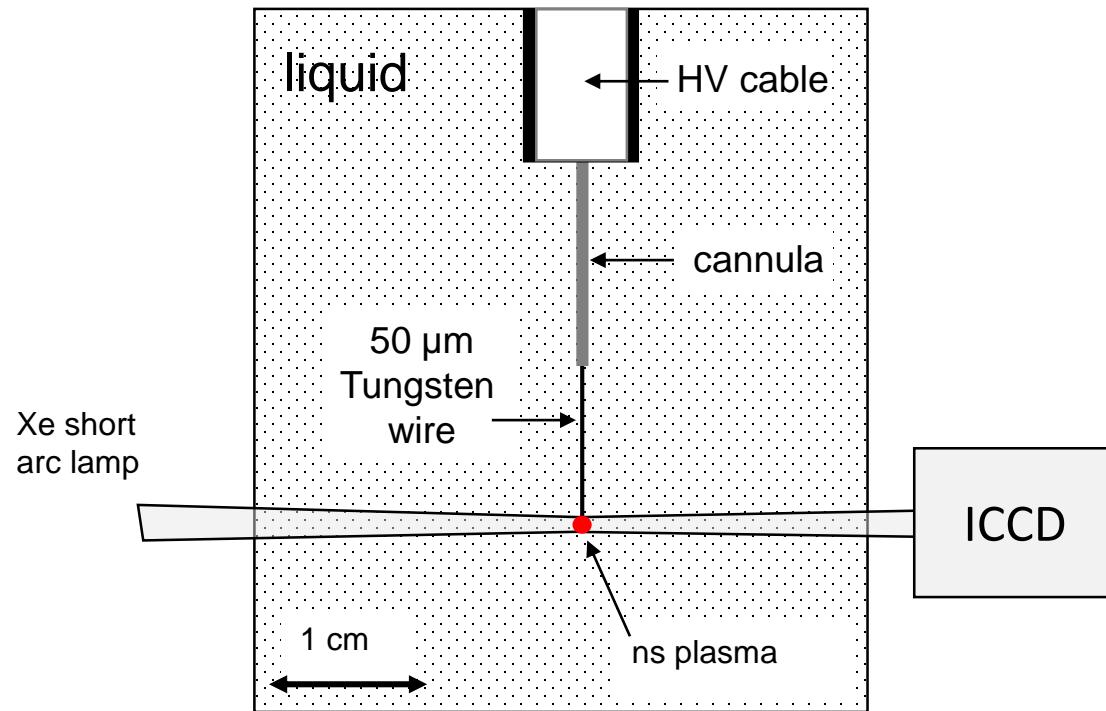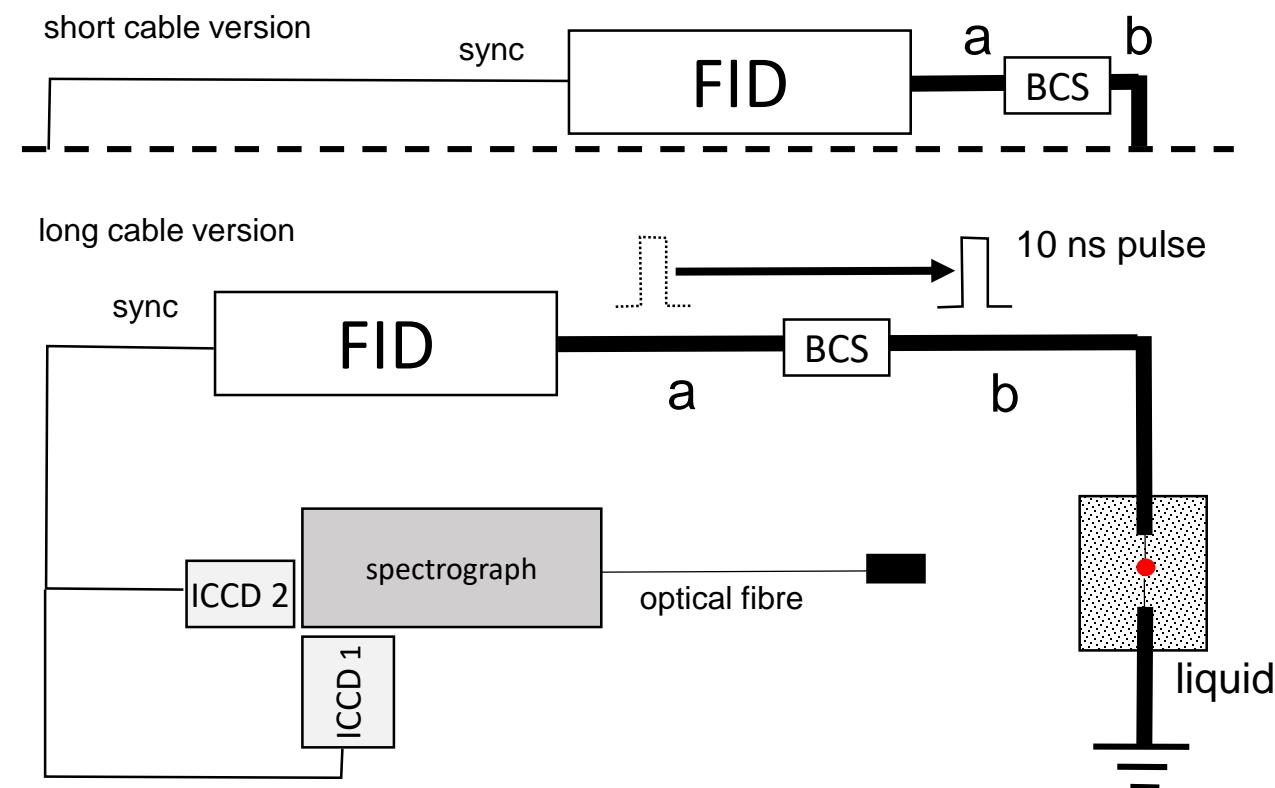

© IOP, Philippe Lavialle

1. Gas, 2. Plasma

- Long microsecond pulses
- Initial formation of a gas bubble due to Ohmic heating or E-field rupture
- Plasma ignition inside the water vapor in the bubble

Moderate high pressures and temperatures 10 bar, 20000 K

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Plasma Chemistry in liquids – example H_2O_2 generation

- 10 ns pulses, 14…30 kV, distilled water
- Shadowgraphy 2 ns … 70 ns gate widths
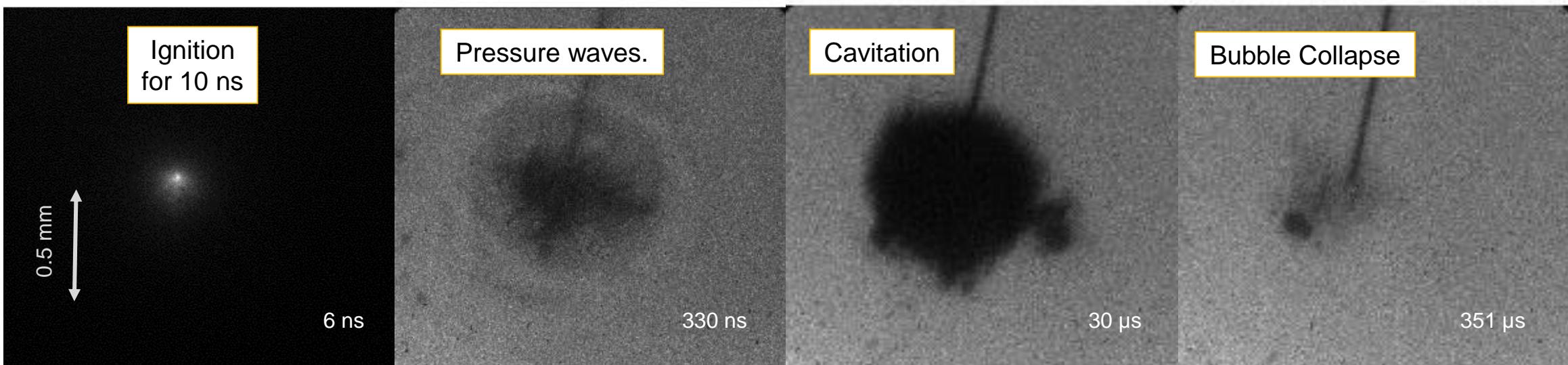- Optical emission spectroscopy with 2ns and 30 ns gate time

Goals:
- reactive liquid production
- regeneration of catalysts for plasma enhanced electrolysis

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Plasma Chemistry in liquids – example H_2O_2 generation
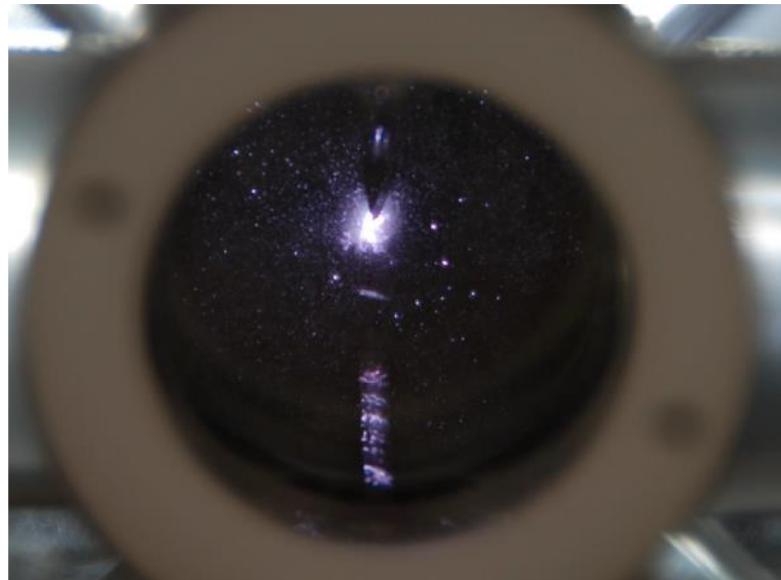
Temporal evolution of the discharge

4 phases
- Ignition (Streamer)
- Pressure waves propagate
- Conversion of water into plasma and vapor
- Expansion of a cavitation bubble
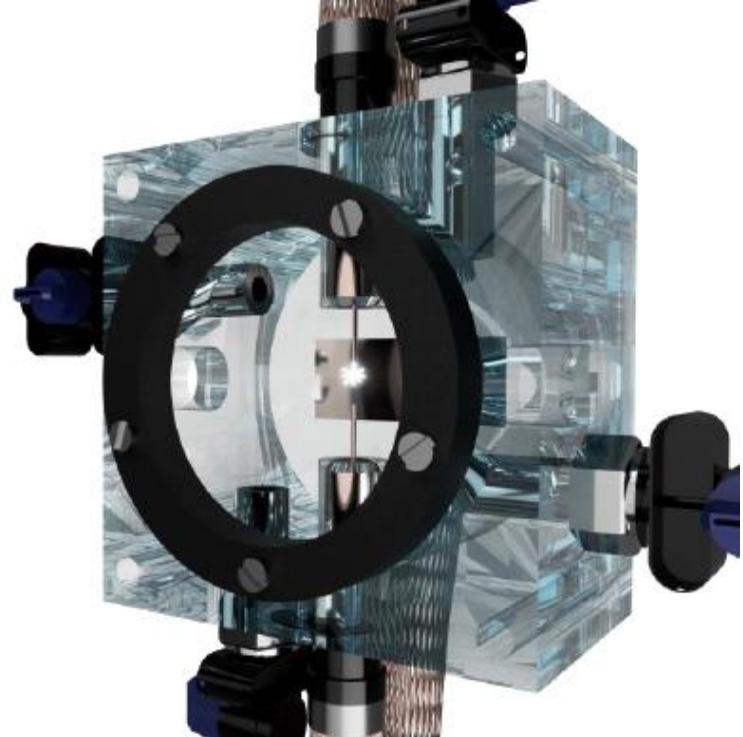
Ignition for 10 ns	Pressure waves.	Cavitation	Bubble Collapse
0.5 mm			
6 ns	330 ns	30 µs	351 µs

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Plasma Chemistry in liquids – example H₂O₂ generation

Temporal evolution of the discharge

441.00ns
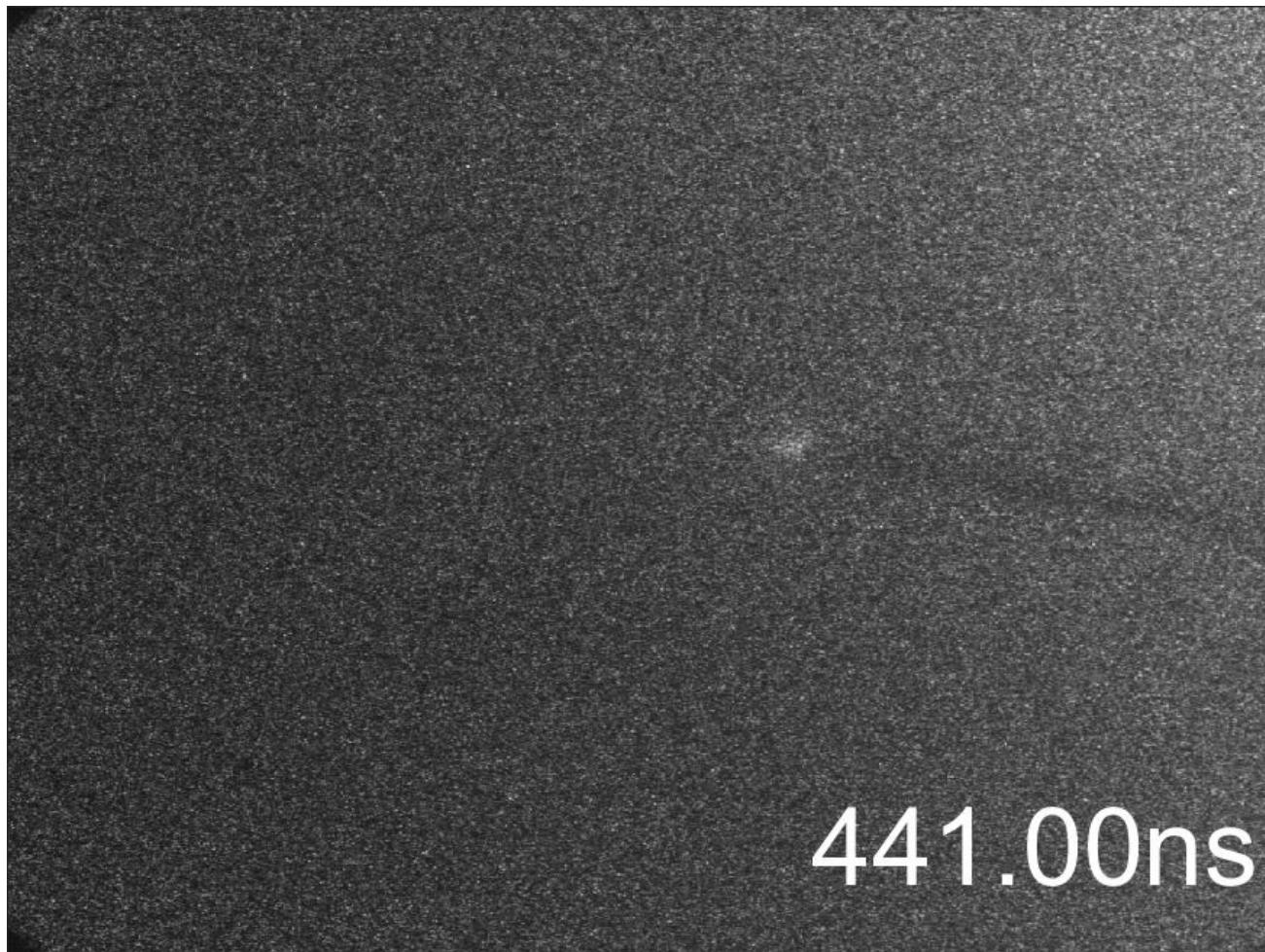
H alpha emission after the plasma pulse

60 ns gate, 30 ns steps

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Monitoring Bubble Expansion with Shadowgraphy – monitoring sound waves and cavitation
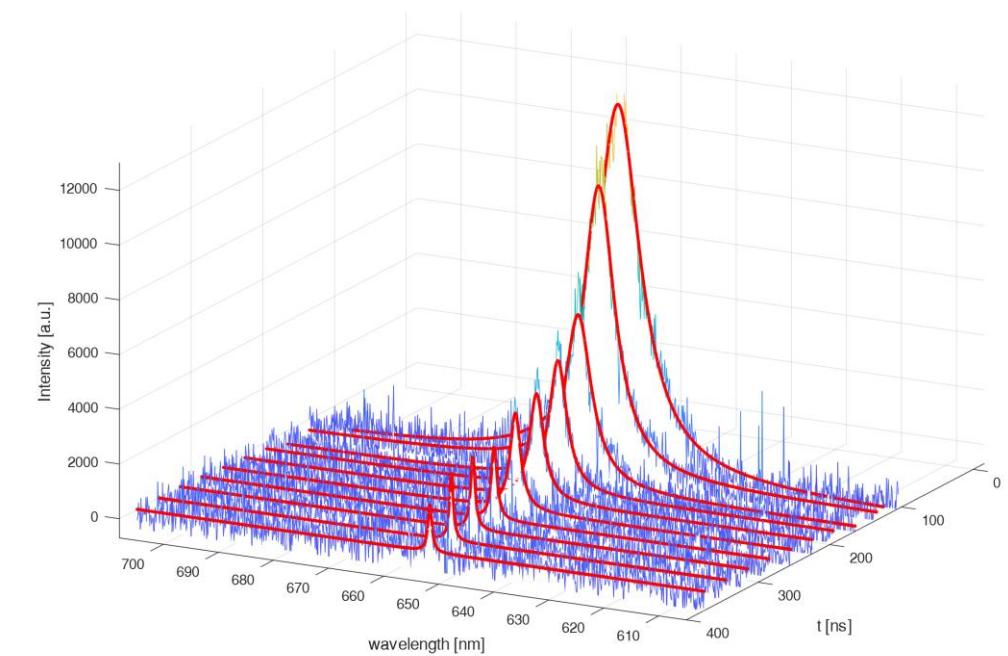

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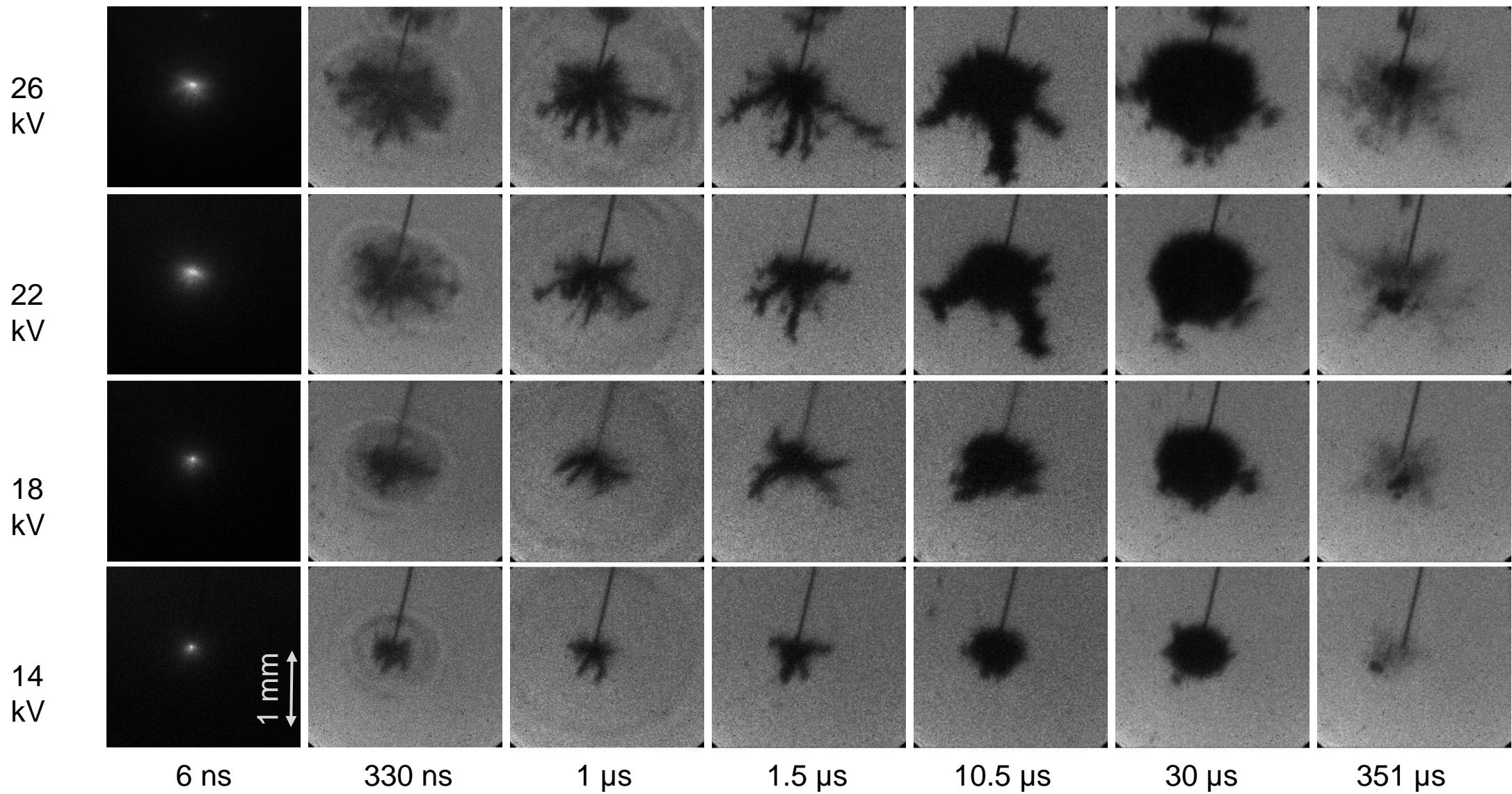
Comparison of Bubble Expansion with cavitation theory

Rayleigh Plesset equation:

$$R\ddot{R}\left(1 - \frac{\dot{R}}{c}\right) + \frac{3}{2}\dot{R}^2\left(1 - \frac{\dot{R}}{3c}\right) = h\left(1 + \frac{\dot{R}}{c}\right) + \left(1 - \frac{\dot{R}}{c}\right)\frac{R}{c}\frac{\partial h}{\partial t}$$

| 6 ns | 330 ns | 10.5 µs | 30 µs | 351 µs |

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Solution for R(t) assuming a compressible liquid and condensation of vapor species

Balance between
surface flux and
volume loss depending
on R,
β=sticking coeff. = 1

$$\frac{1}{4}nv_{therm}4\pi R^2\beta = \frac{4\pi}{3}R^3 n\frac{1}{\tau}$$

$$\tau = \frac{4R}{3v_{therm}\beta}$$

$$p_0 \rightarrow p_0\exp\left(-\frac{t}{\tau}\right)$$

$$p(t) \rightarrow p_0\exp\left(-\frac{t}{\tau}\right)\left(\frac{R_0}{R}\right)^{3\gamma}$$

super
critical
water

0.5 mm

44 ns

1 mm

1µs

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Transition of the water vapor in the bubble through the phase diagram of water

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Plasma in a bubble expansion

everything to scale

Ignition sequence

20 bar
5 µm
240 bar

25 bar @ 300 K
5 µm

10 000 bar @ 150000 K

sound wave

r_{max} =600 µm
t=60 µs

r_{min} =5 µm
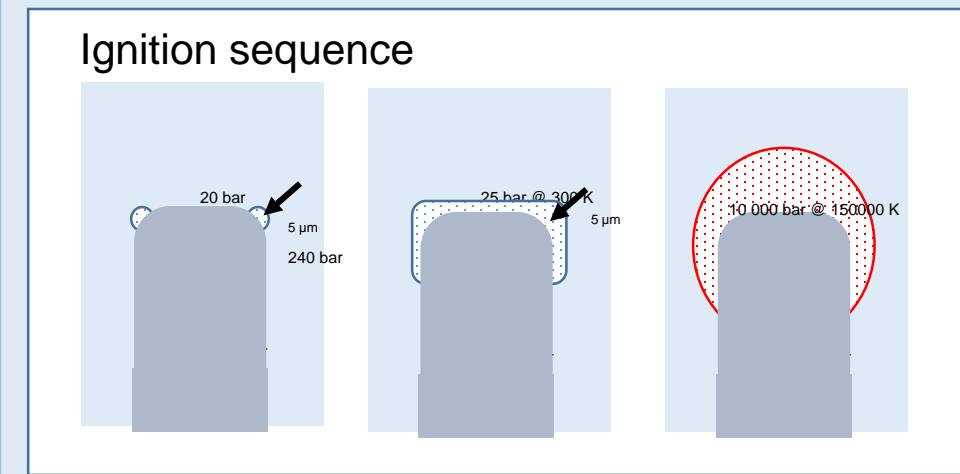t=100 µs

r = 5 µm	r = 25 µm	r = 50 µm	r = 80 µm	r = 100 µm
t = 1ns	t = 10ns	t = 100 ns	t = 200 ns	t = 400 ns

collapse

gas

sound wave

Ignition plasma

supercrit. vapor

conden- sation

re-heated

re-heated

re-heated

$n_0 = 3 \cdot 10^{28}$ m^{-3}
$n_e = 3 \cdot 10^{28}$ m^{-3}
$p = 10^{11}$ Pa

$n_0 = 3 \cdot 10^{28}$ m^{-3}
$p = 5 \cdot 10^{8}$ Pa
T = 1200 K

$n_0 = 2.6 \cdot 10^{27}$ m^{-3}
$n_e = 10^{25}$ m^{-3}
$p = 2 \cdot 10^{7}$ Pa
T = 550 K

$n_0 = 1.6 \cdot 10^{27}$ m^{-3}
$n_e = 10^{23}$ m^{-3}
$p = 10^{7}$ Pa
T = 450 K

$n_0 = 2.8 \cdot 10^{26}$ m^{-3}
$p = 10^{6}$ Pa
T = 260 K

$n_0 = 1.4 \cdot 10^{24}$ m^{-3}
$p = 10^{3}$ Pa
T = 50 K

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Temperatures from emission spectra of the plasma into the UV

Spectrum (first 50 ns, time resolution 2 ns)
- Recombination
- H_2, H_2O recomb. continuum
- OH, OH^+, H_2O, H_2O^+ bands
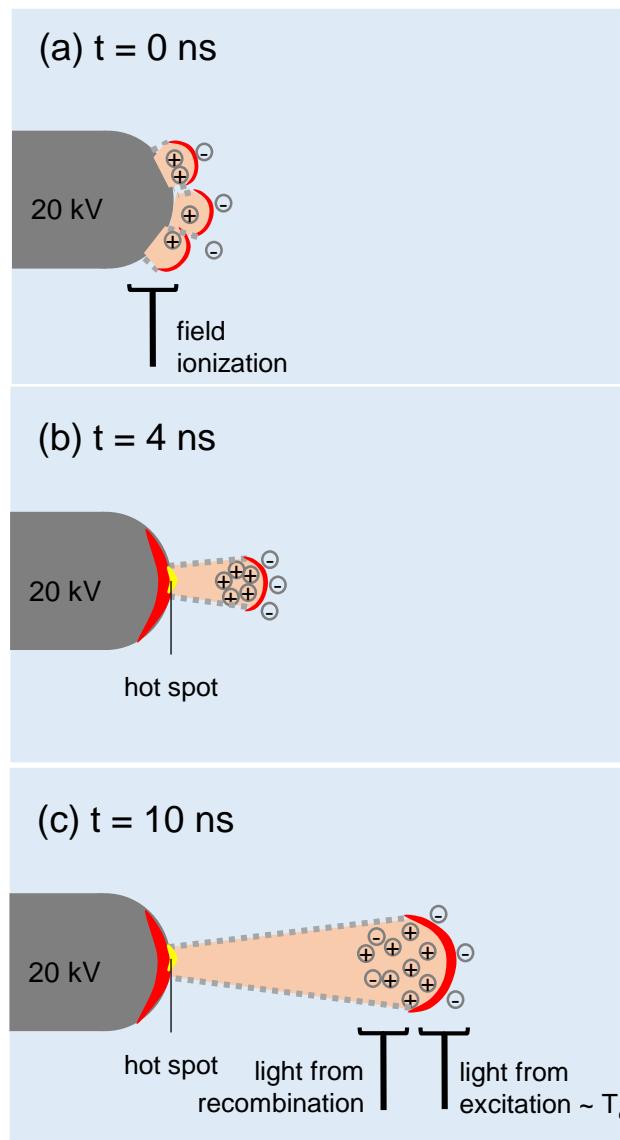- Black body radiation (W)
- H_α
- $O_{(777nm)}$

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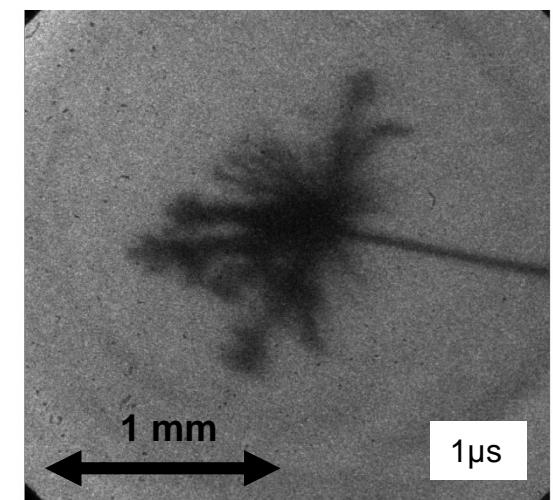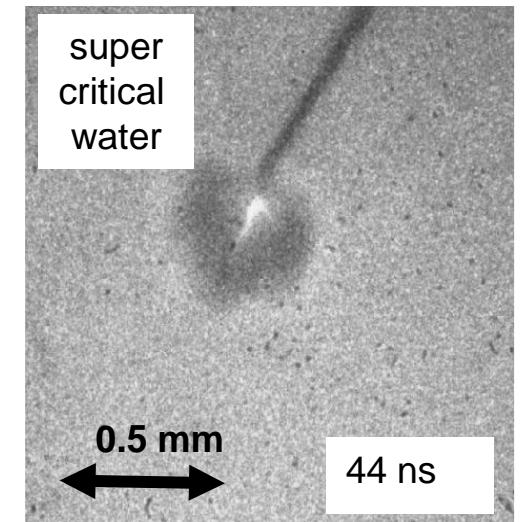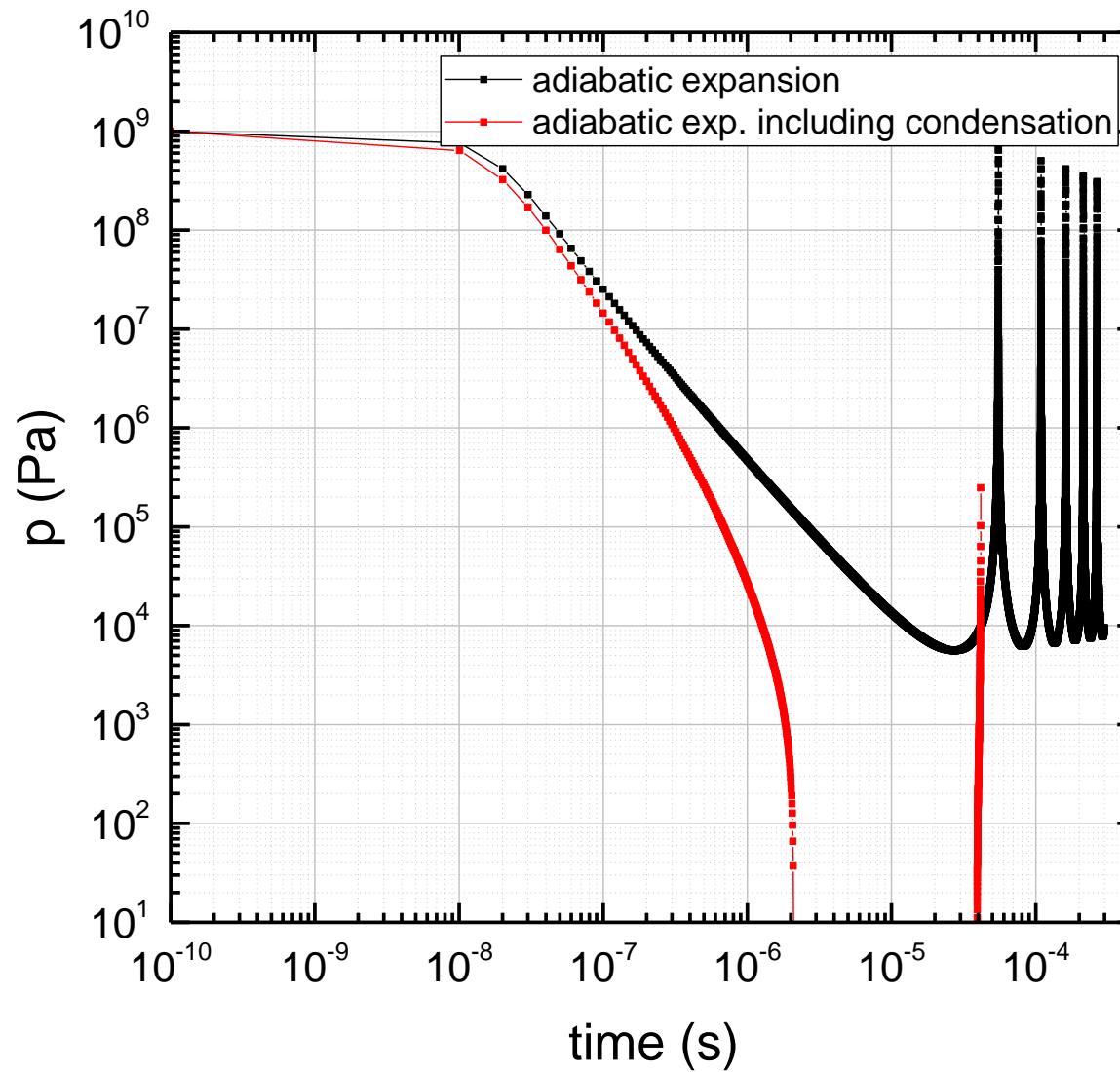
Line emission – Ionization front propagates Hydrogen Balmer Series

(a) t = 0 ns

20 kV

field ionization

(b) t = 4 ns

20 kV

hot spot

(c) t = 10 ns

20 kV

hot spot   light from recombination   light from excitation ~ T_e

self absorption of Halpha from the ionization region disappears, ionization front steepens

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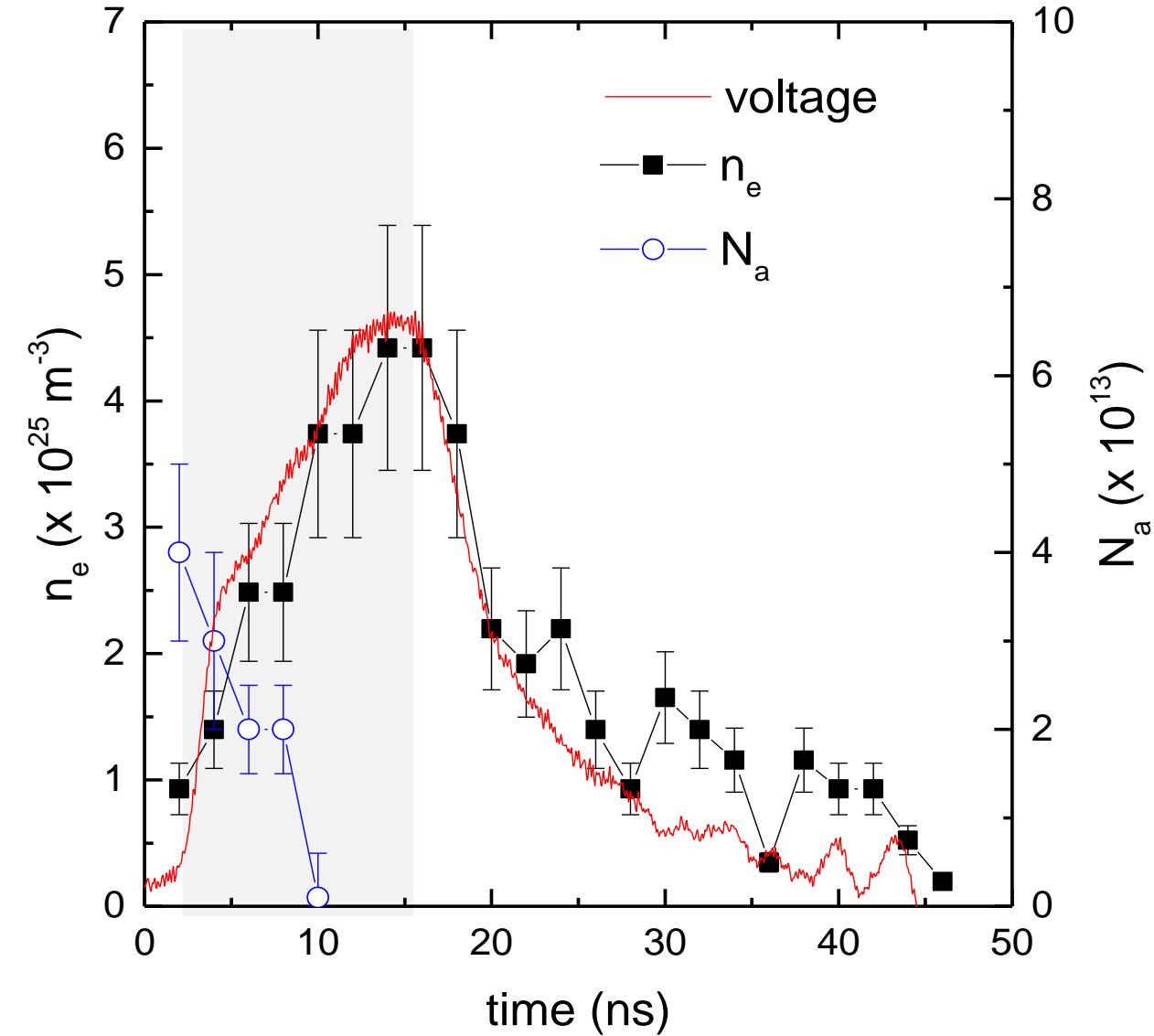
Efficiency to create H_2O_2 with these plasmas
Modeling the chemistry

- Starting point
  gas density 3×10^{22} cm^{-3}

- Starting Temperature T = 20000 K
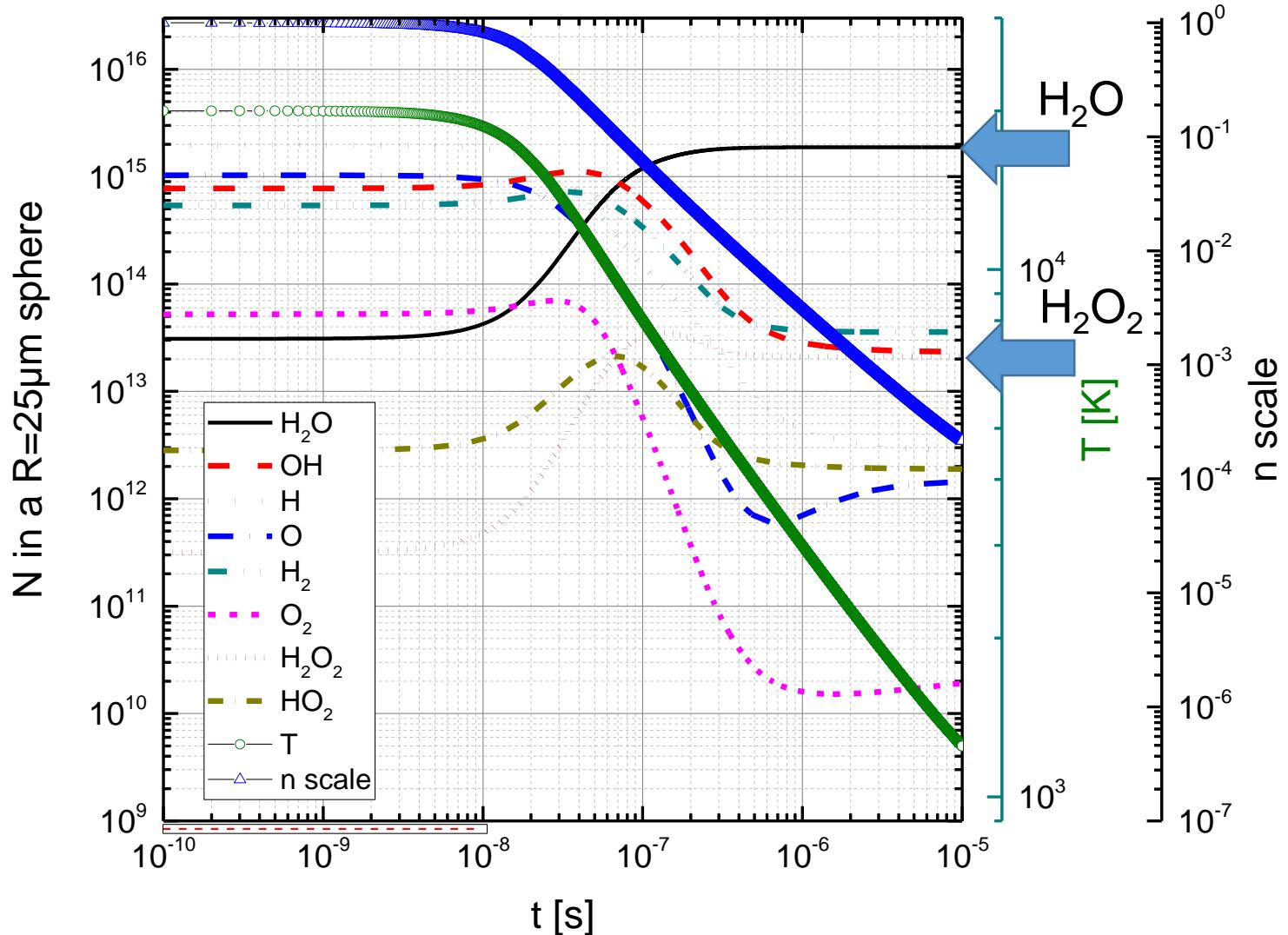
- **H_2O_2/H_2O ratio at 10 µs ~ 10^{-2}**

Hot phase:

- $H_2O \rightarrow OH + H$

recombination phase

- $OH + OH \rightarrow H_2O_2$
- $H + H \rightarrow H_2$
- $OH + H \rightarrow H_2 + O$

*S. Mededovic, B. Locke
JPD 40, 7734 (2007)
PCPP 32, 875 (2012)

In the expanding phase, chemistry freezes out, $H_2O \rightarrow H_2O_2 + H_2 + O + H$

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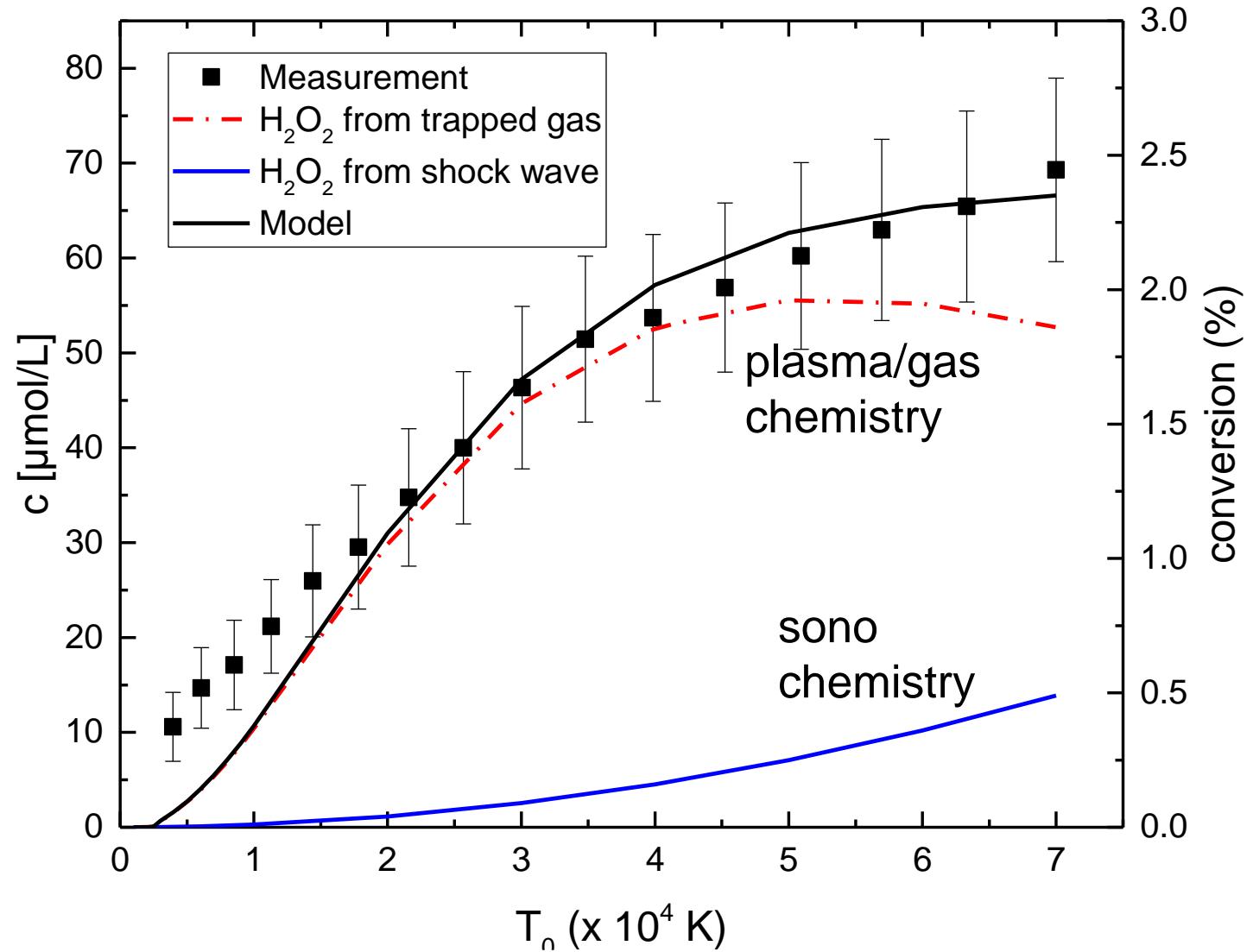# Efficiency to create H_2O_2 with these plasmas
Modeling the chemistry

- Take T_0 from cavitation
- calculate time development of the chemistry until 10 µs
- determine H_2O_2 concentration after 10 µs in the model

<u>efficiency 1.1%</u>
<u>@ 20 kV (20000 K)</u>
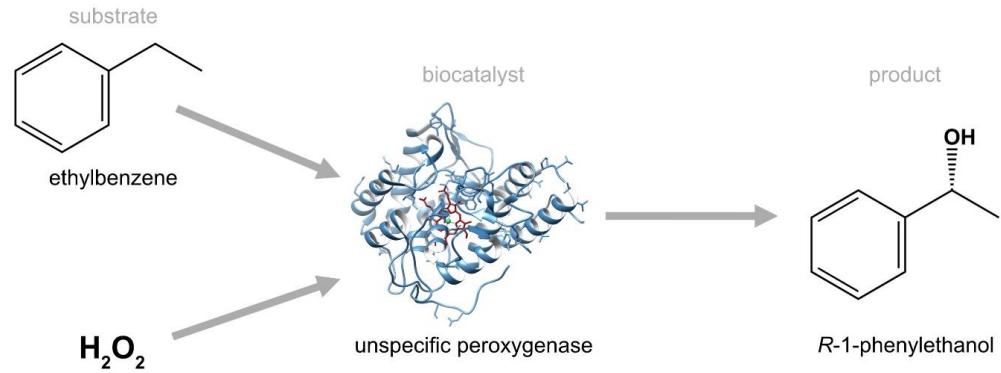
- At high voltages/T_0, contribution due to sonochemistry becomes significant

46 g H_2O_2/kWh
(most other plasma methods only a few g/kWh)

Legend:
- ■ Measurement
- —·— H_2O_2 from trapped gas
- ——— H_2O_2 from shock wave
- ——— Model

plasma/gas chemistry

sono chemistry

y-axis: c [µmol/L]
right y-axis: conversion (%)
x-axis: T_0 (x 10^4 K)

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Biocatalysis (Bandow group @ RUB)

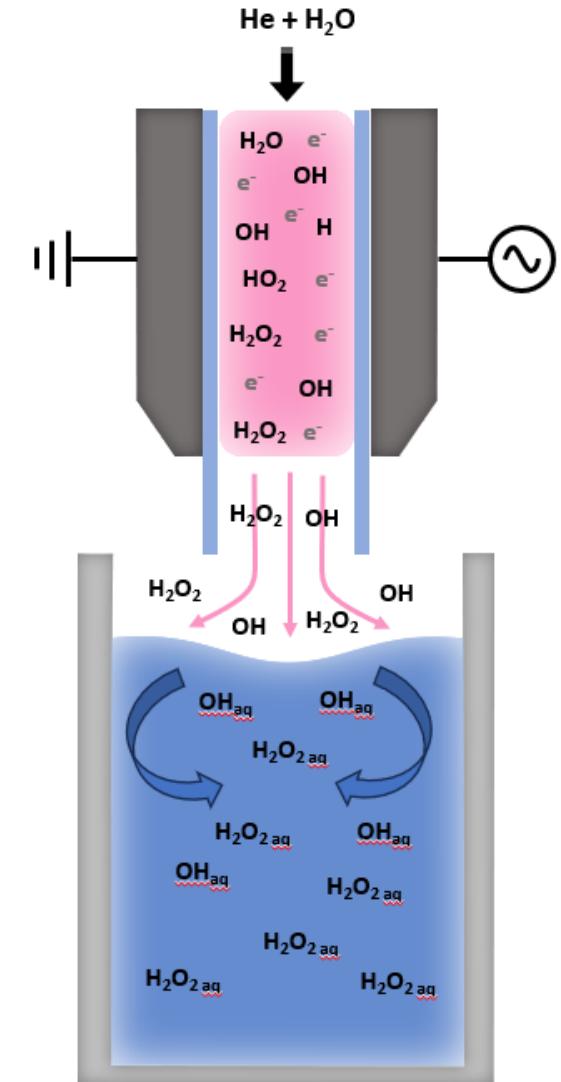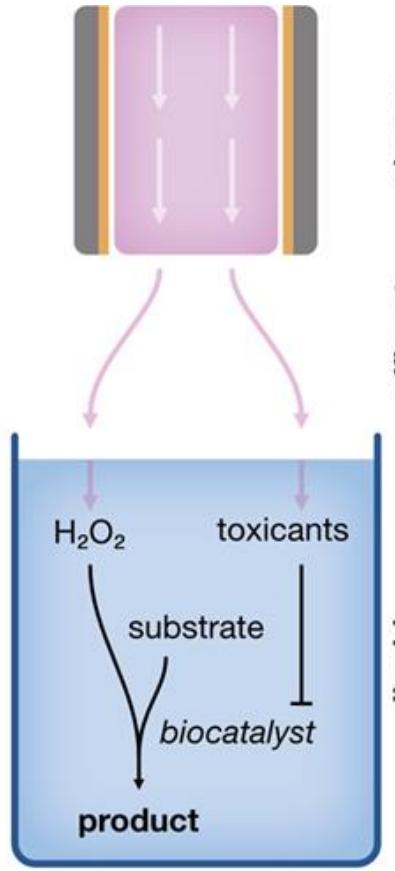**advantages of** enzymatic reactions
- mild conditions
- less by-products / waste
- chemo- and stereo-selectivity

substrate

ethylbenzene

H_2O_2

biocatalyst

unspecific peroxygenase

product

R-1-phenylethanol

advantages of **plasma**
- easily turned on/off
  - H_2O_2 is also toxic for enzymes
- non-invasive
- not increasing the reaction volume

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Biocatalysis (Bandow

product inhibition/
substrate limitation

CPJ

50 nM immobilized r*Aae*UPO in 5 ml KPi
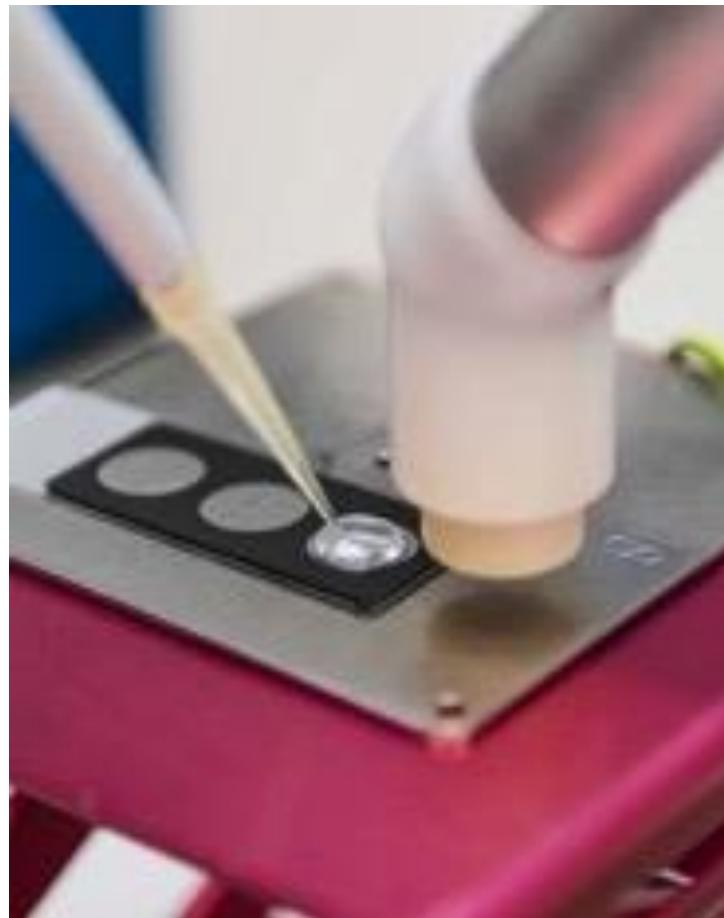(100 mM, pH 7) with 50 mM ETBE

ReliZyme *beads*
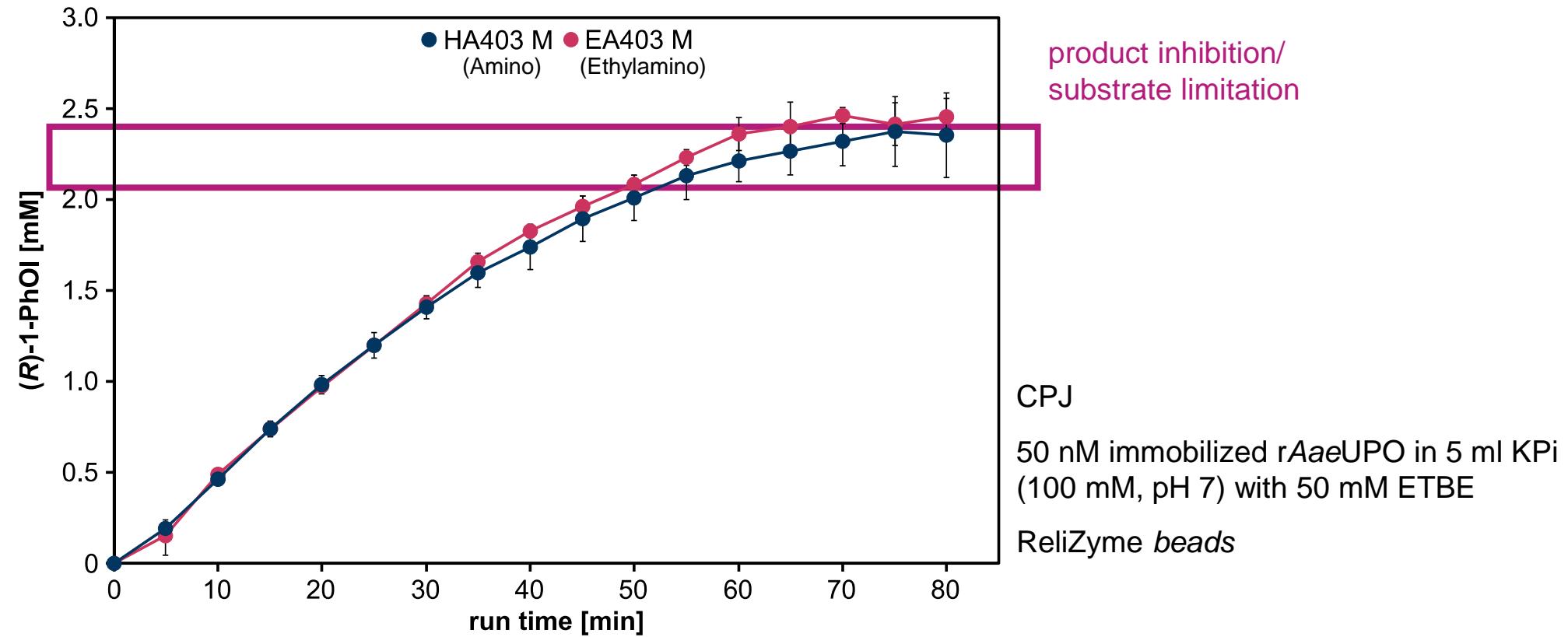
> **HA403M, EA403 M on the same level of product formation → more bead types usable in biocatalysis (further tested beads not on the same level)**
> **plateau reached (probably due to product inhibition and substrate limitation)**

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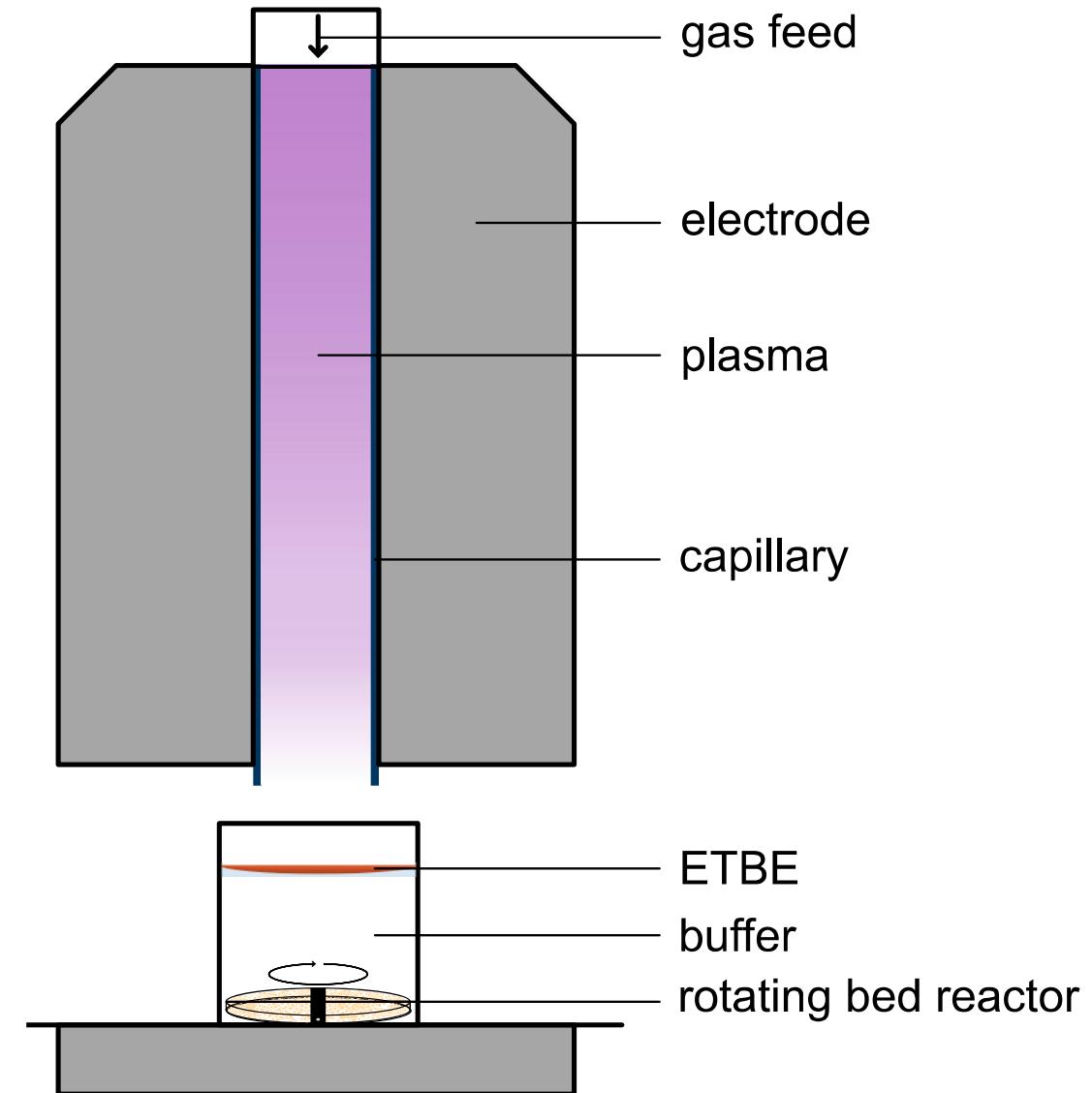
Different plasma sources (Bandow, Golda, Gibson group @ RUB)

DBD

Capillary jet

Capillary jet, rotating bead reactor
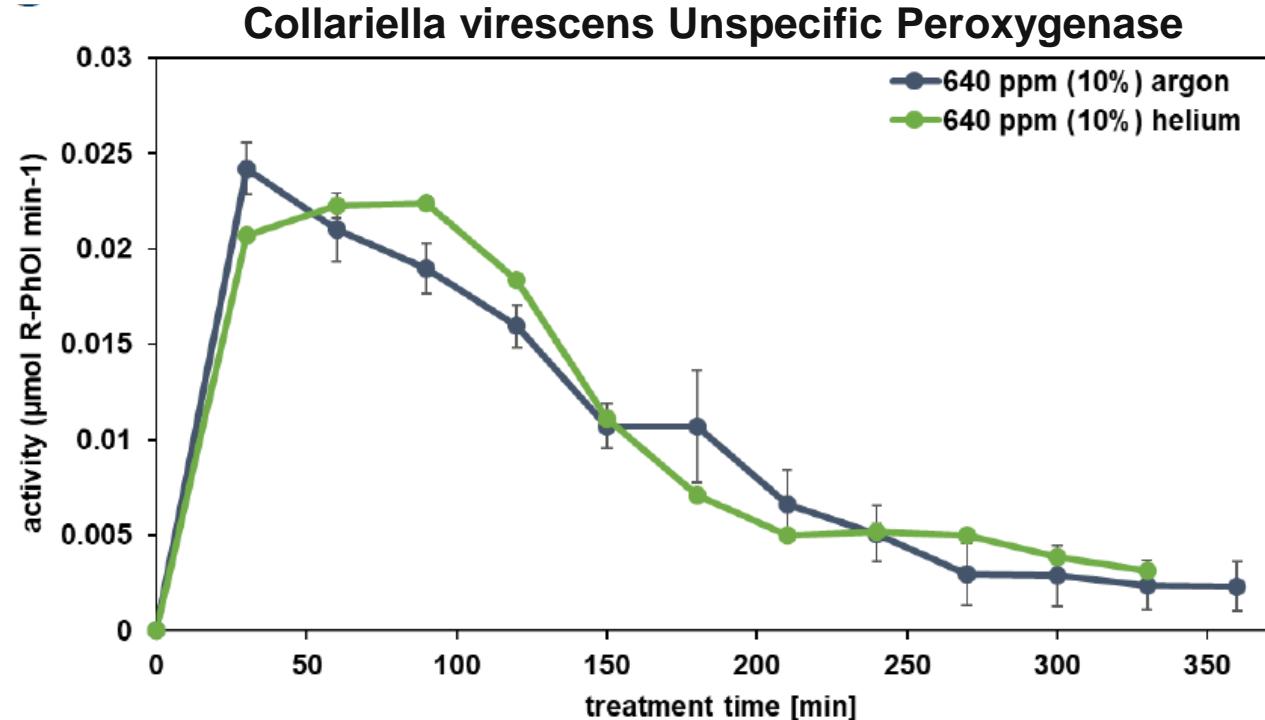

- gas feed
- electrode
- plasma
- capillary
- ETBE
- buffer
- rotating bed reactor

Yayci e*t al.* (2020) *ChemSusChem.*

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Plasma driven biocatalysis (group Bandow @ RUB)

ethylbenzene
substrate

biocatalyst
AaeUPO

H_2O_2

product
OH
R-1-phenylethanol

gas flow
electrode
capillary
plasma
effluent
buffer
immobilized enzyme in rotating bed reactor

2 slm | 640 ppm water vapor (argon/helium) | 6 W

Agrocybe (Cyclocybe) aegerita Unspecific Peroxygenase
AaeUPO

Legend:
- helium 640 ppm (10%)
- argon 640 ppm (10%)

y-axis: activity [µmol R-PhOI min-1], from 0 to 0.5
x-axis: treatment time [min], from 0 to 120

Argon and **Helium | 640 ppm water vapor (10%)**

→ No significant difference in product concentration after plasma-driven biocatalysis with **argon** and **helium** as feed gas

Plasma driven biocatalysis (group Bandow @ RUB)

substrate → biocatalyst → product

ethylbenzene

H_2O_2

CviUPO

R-1-phenylethanol

electrode
capillary
plasma
gas flow
effluent
buffer
immobilized enzyme in rotating bed reactor

2 slm | 640 ppm water vapor (argon/helium) | 6 W

Collariella virescens Unspecific Peroxygenase

- 640 ppm (10%) argon
- 640 ppm (10%) helium
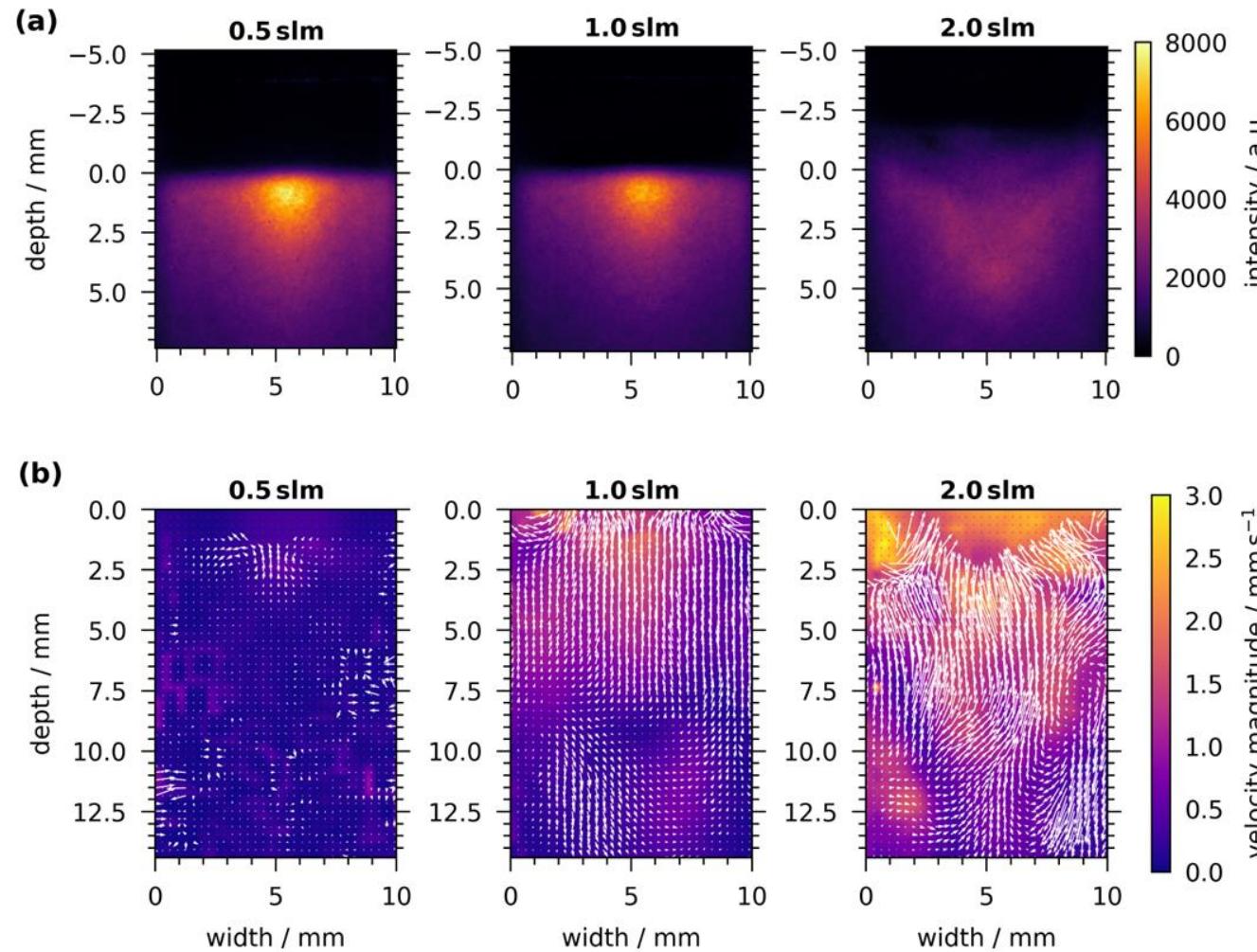
activity (μmol R-PhOl min-1) vs treatment time [min]
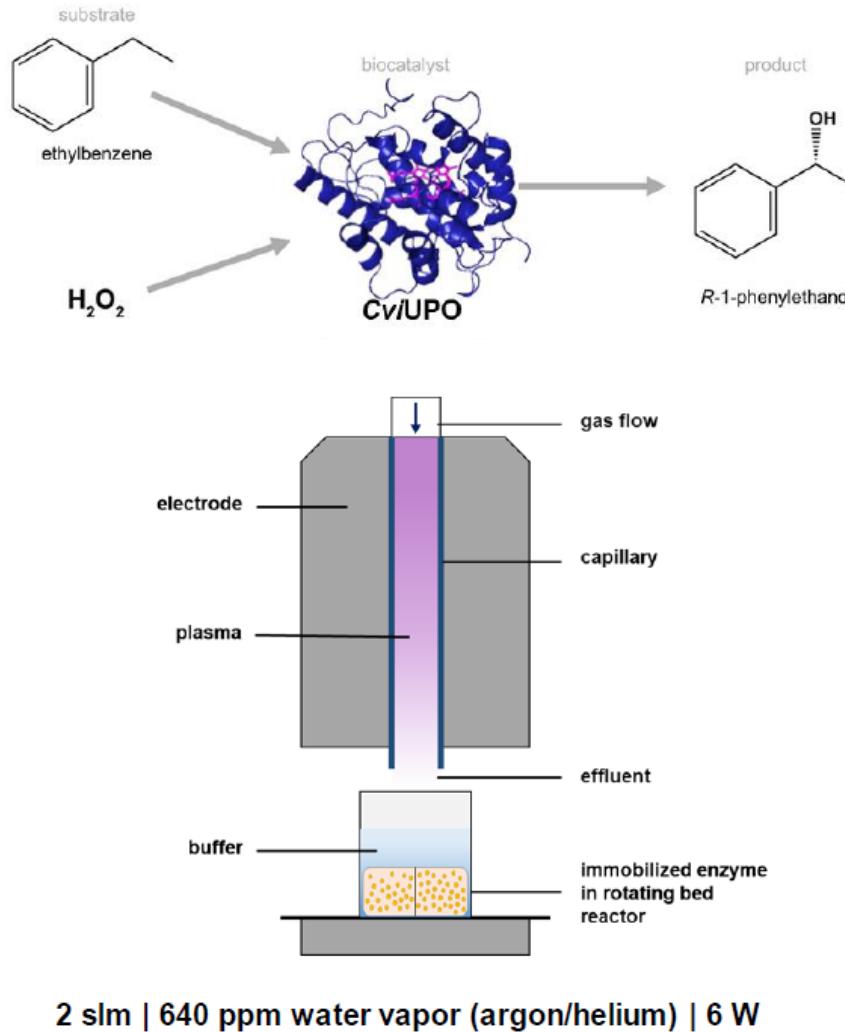
The use of **argon as feed gas in plasma-driven biocatalyis** is possible and leads to similar product formation

Helium → 0.004 μmol R-Phol min^{-1} after 350 min

**Argon** → 0.003 μmol R-Phol min^{-1} after 360 min

Diffusion of OH and convective transport (Golda group @ RUB)

- CL of luminol
  → Main signal at the liquid surface
- Decrease in CL signal deeper than 2.5 mm
- OH is mainly distributed at the liquid surface

- PIV measurements → Visualization of convective transport
- Enhanced convective transport at higher gas flow rates
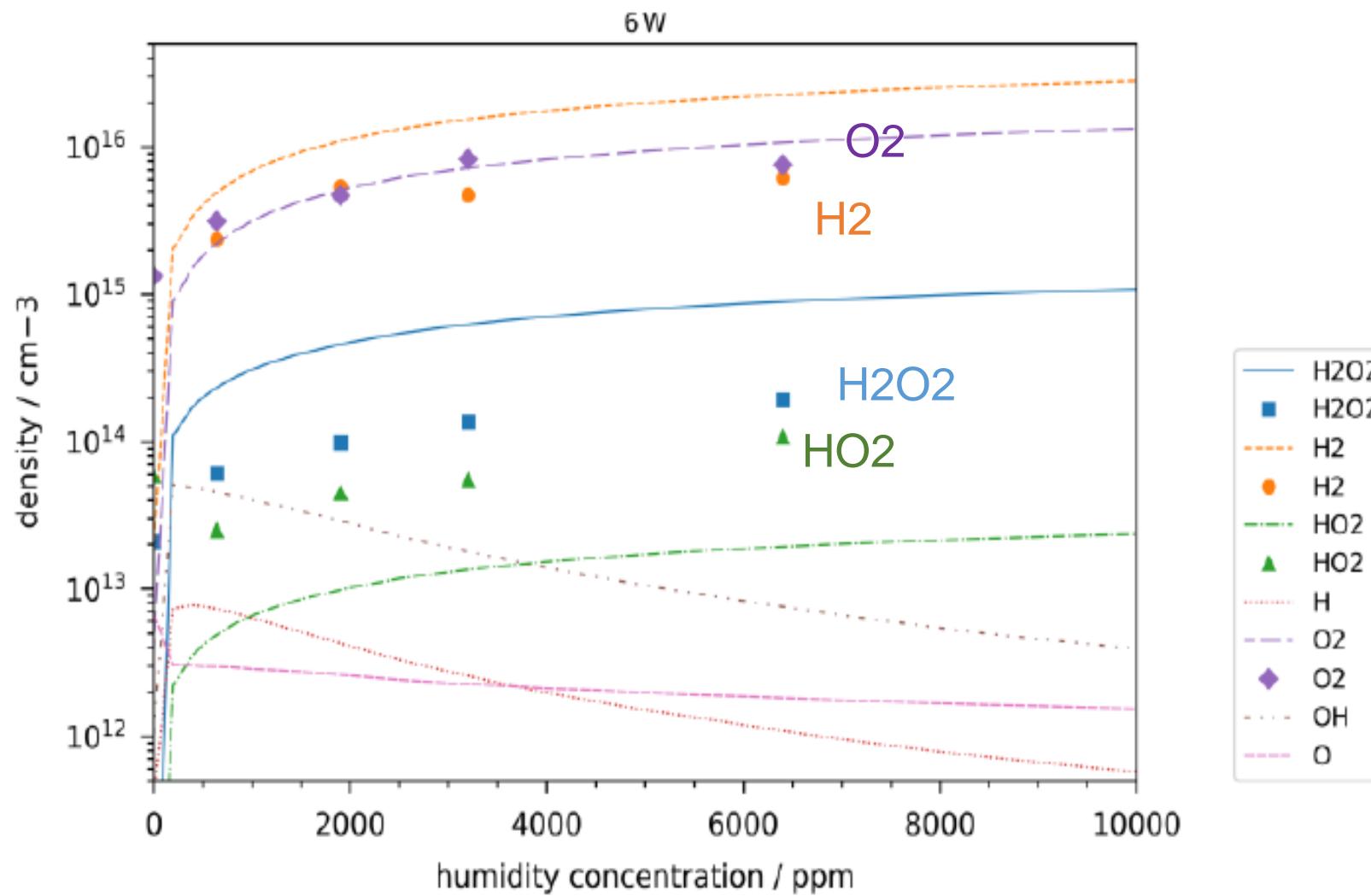- At 0.5 slm and lower → Almost no convective transport

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Plasma driven biocatalysis (group Benedikt @ RUB)
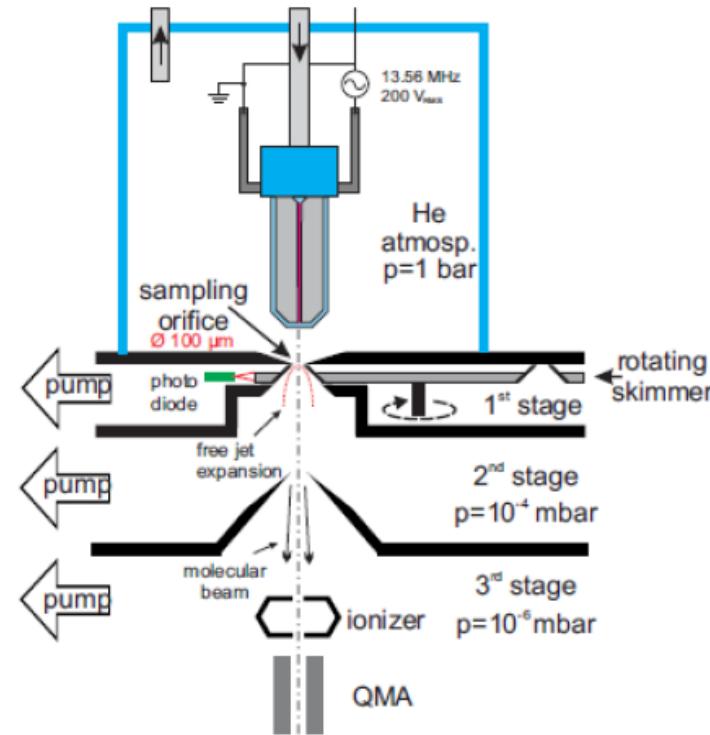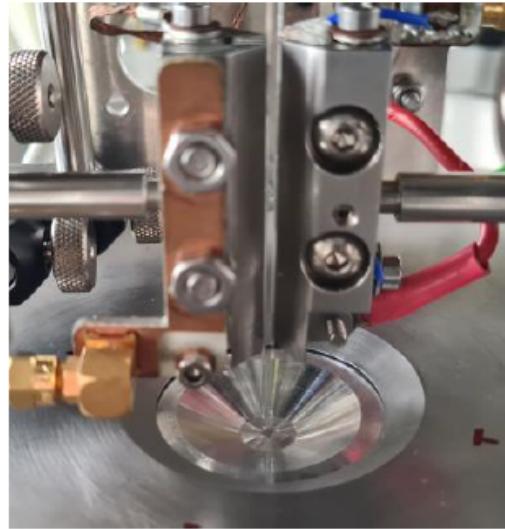
Dissertation Gert Willems, Ruhr-University Bochum (2016)

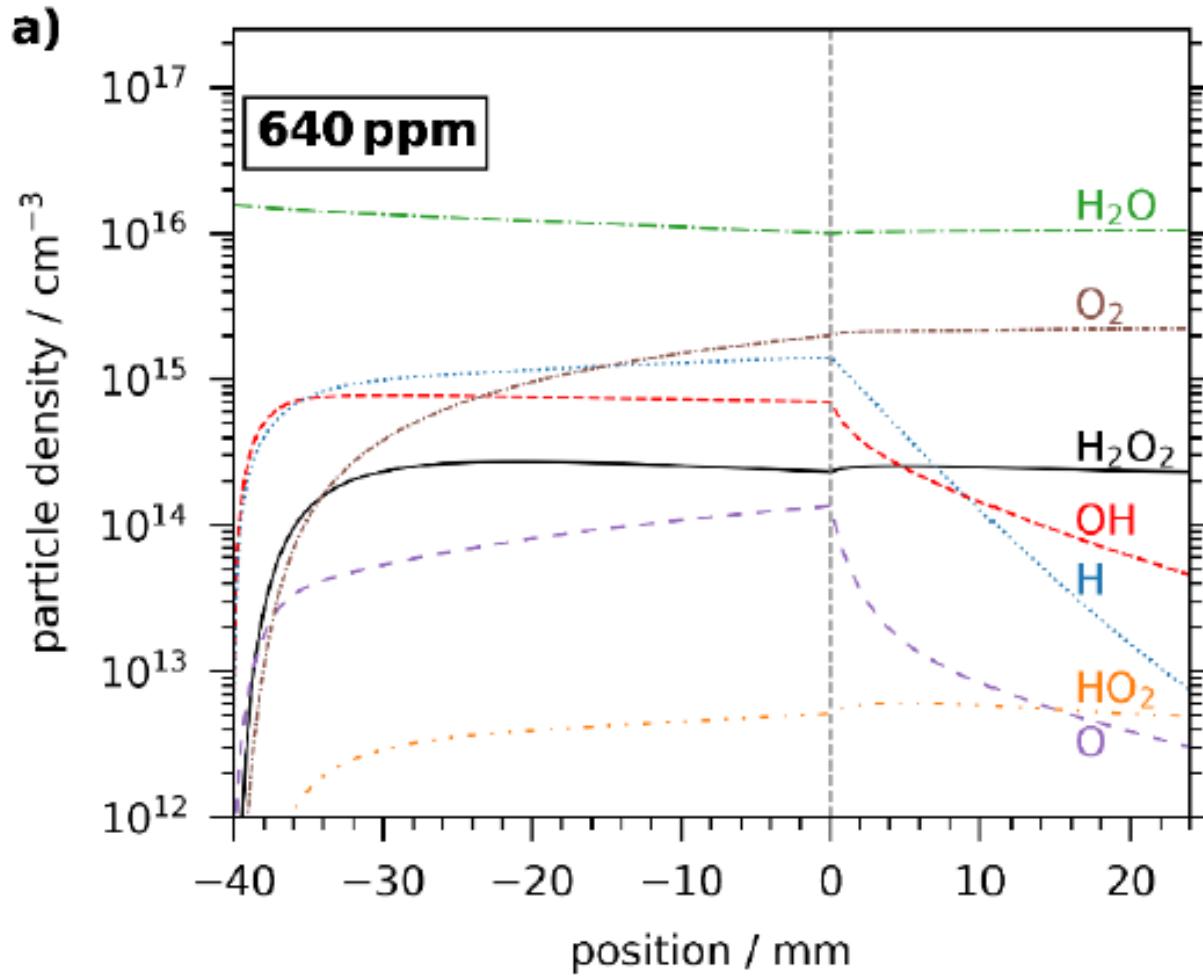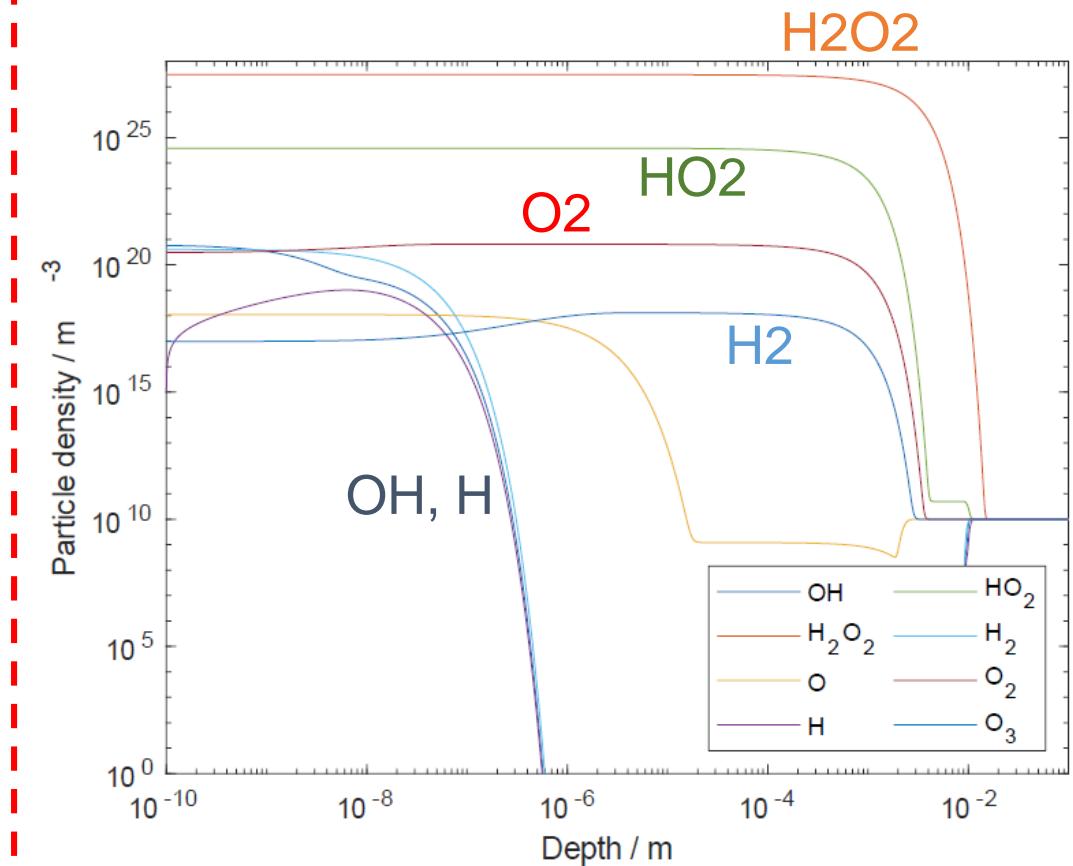| Species	Calibration
H_2O	H_2O
H_2O_2	Ar
OH	-
O	-
O_2	Ar
H	-
H_2	H_2
HO_2	Ar

Plasma driven biocatalysis (group Golda, Gibson @ RUB)

Plasma effluent modeling with 100s of reactands and several 100s of reactions

Agreement only within a factor of 10

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Plasma driven biocatalysis (group Gibson @ RUB)

In the gas phase

In the liquid phase

Chemistry in Plasma Treated Liquids | A. von Keudell et al.

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Conclusion

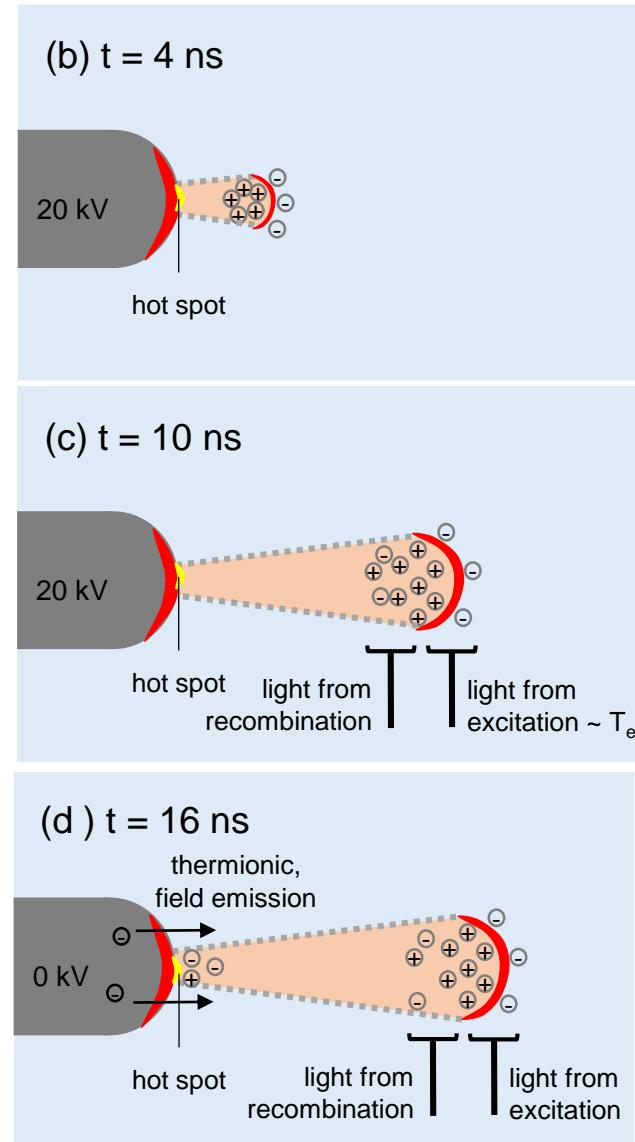plasmas in liquids for life science applications

- Plasma-in-liquids are very efficient, avoiding RONS and H2O2 decay. Physics is extremely complex

- Plasma above the liquid suffer from transfer (Henry constant). More applications.

- Plasmas act as a on-demand source for H2O2

- Design of the perfect plasma source for bio application is crucial, right 'dose" of reactive species
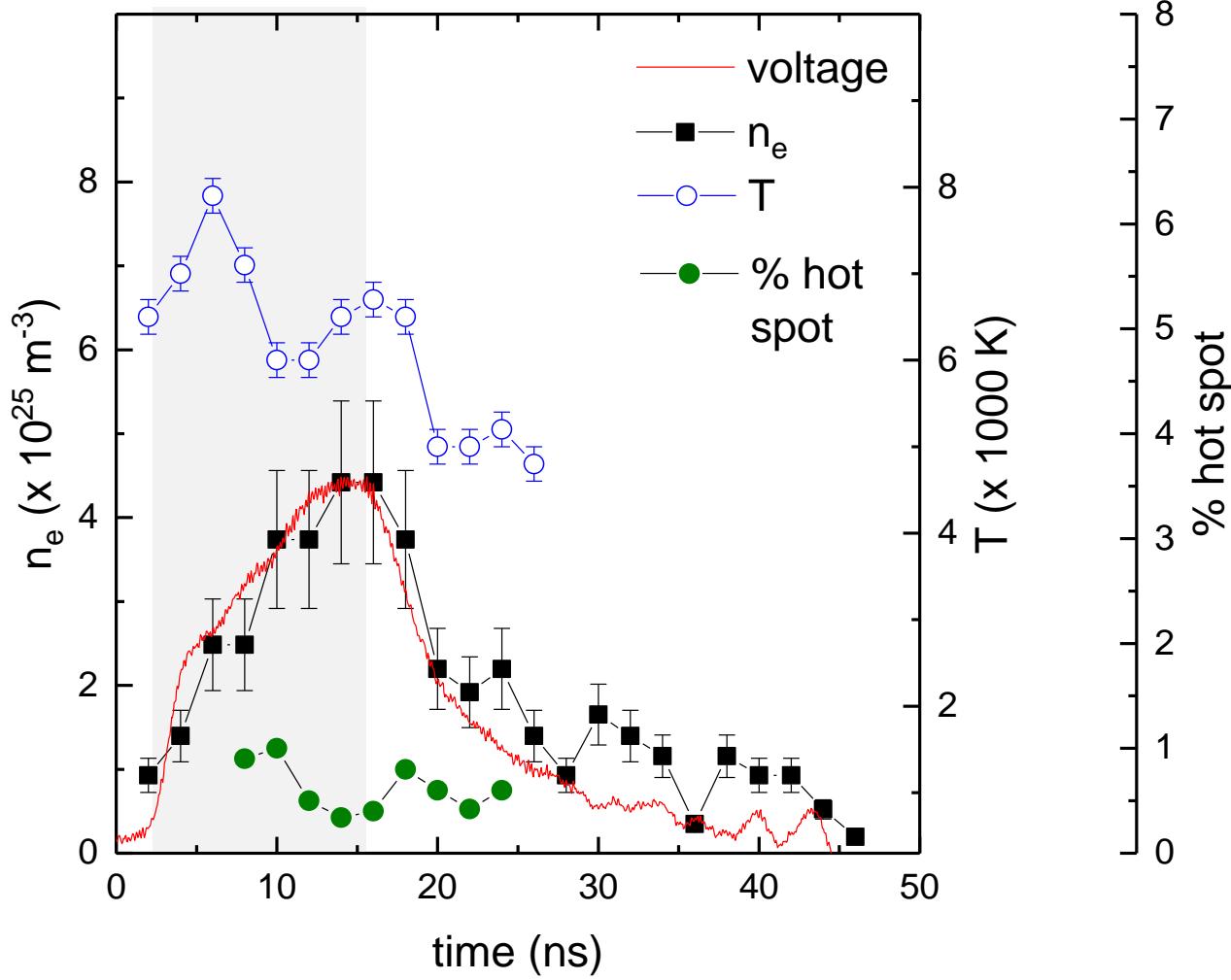
Backup Slides

Chemistry in Plasma Treated Liquids | A. von Keudell et al.

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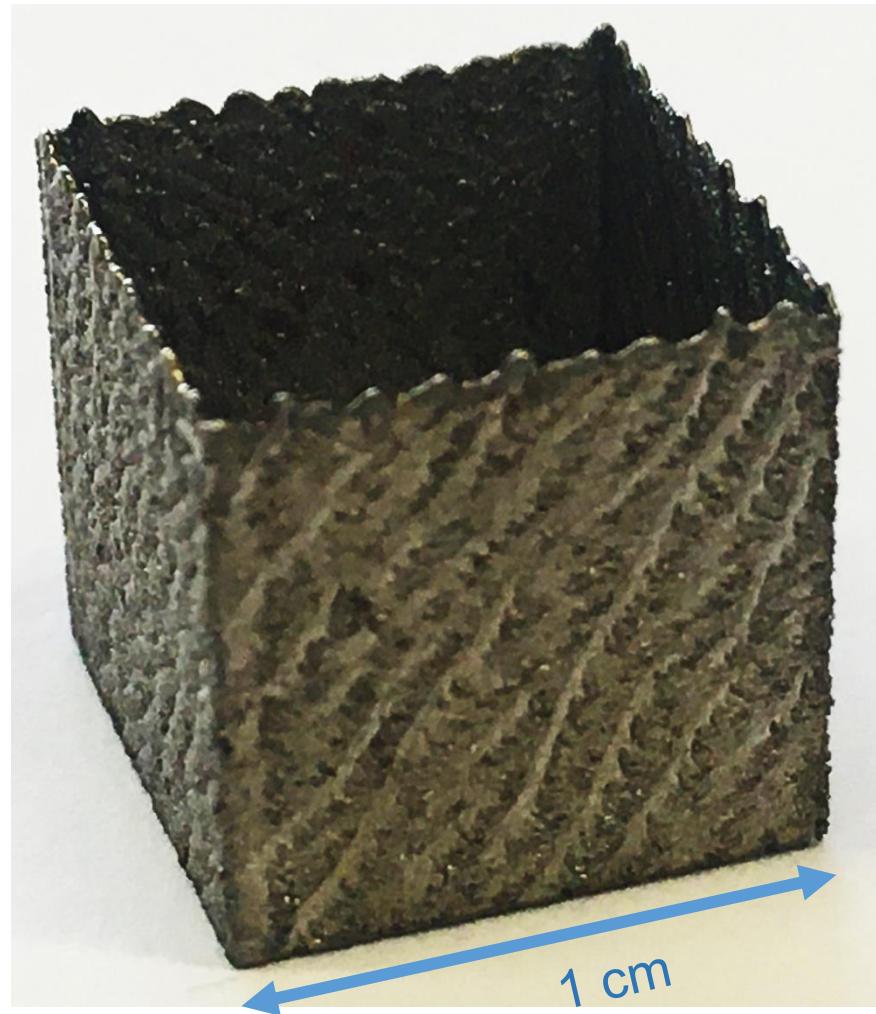
1 cm

Line emission – H alpha from ionization region of Hydrogen Balmer Series

Temperature variation

(b) t = 4 ns

20 kV

hot spot

(c) t = 10 ns

20 kV

hot spot · light from recombination · light from excitation ~ T_e
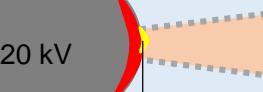
(d) t = 16 ns

thermionic, field emission

0 kV

hot spot · light from recombination · light from excitation
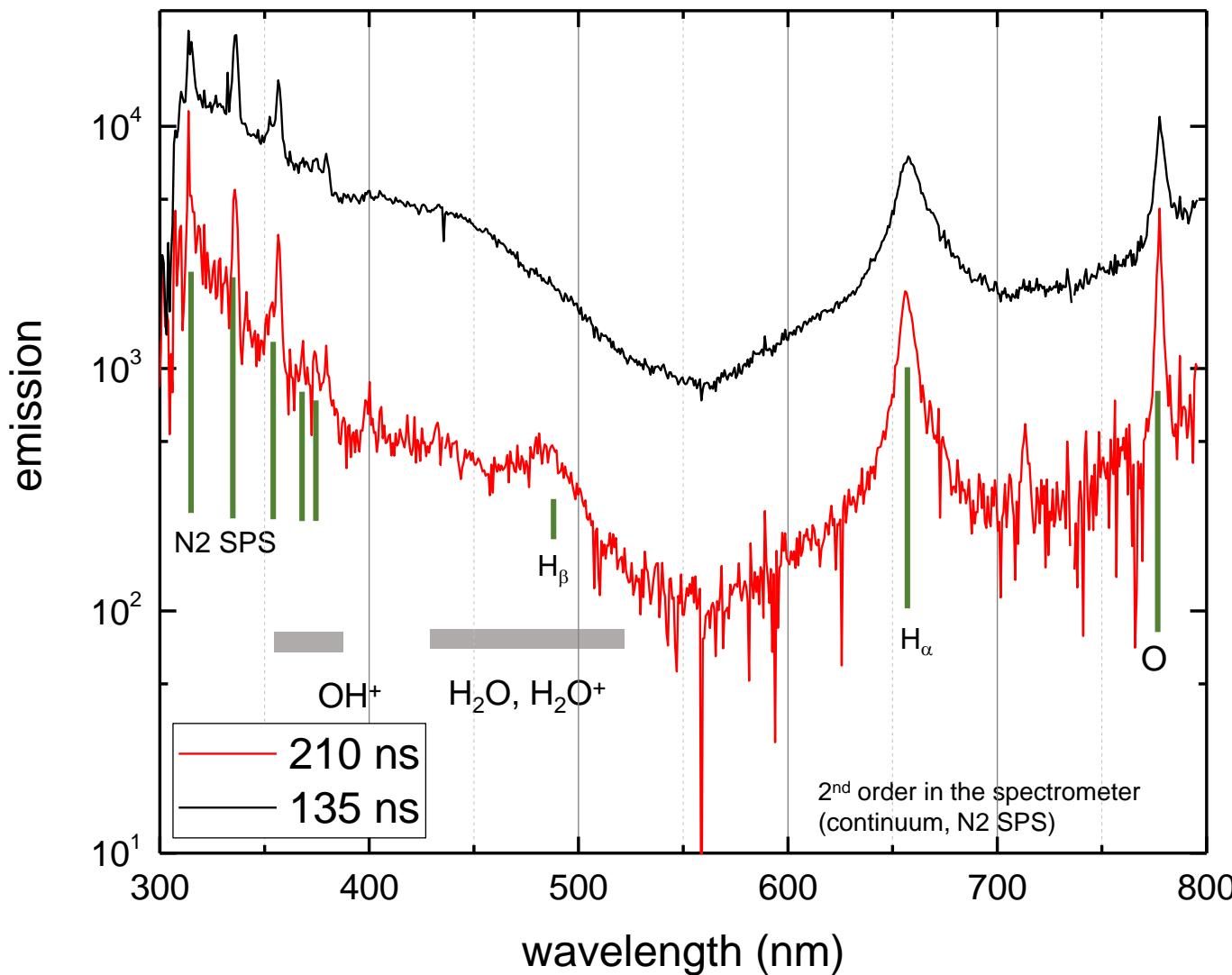
H alpha from ionization region dominates when electrons are being accelerated

- Strong gradients in the beginning
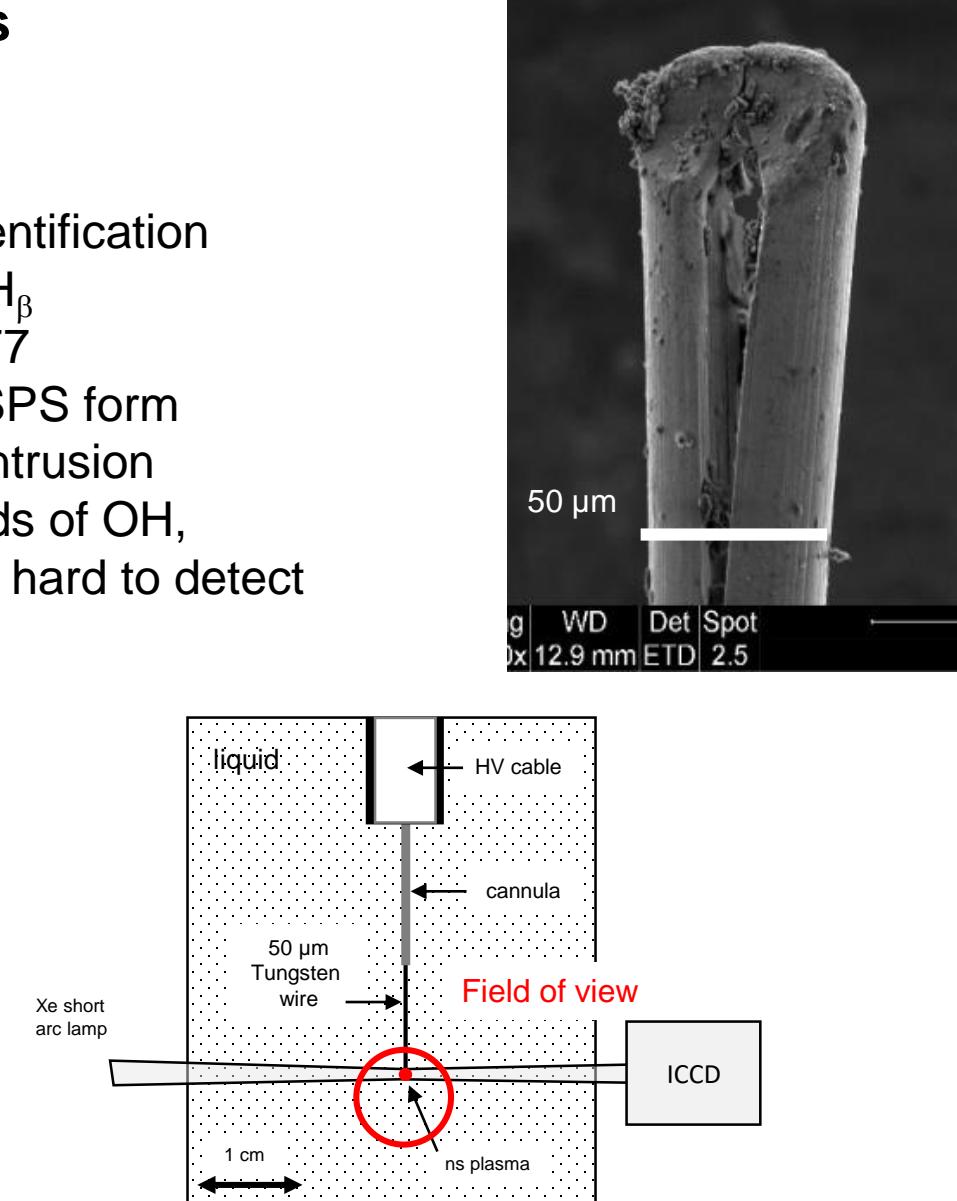- Field emission at the end of the pulse

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Line identification
- H_α, H_β
- O 777
- N2 SPS form
  N2 intrusion
- Bands of OH,
  H2O hard to detect

Plot labels: emission vs wavelength (nm)

N2 SPS
H_β
H_α
O
OH$^+$
H_2O, H_2O^+

210 ns
135 ns

2nd order in the spectrometer
(continuum, N2 SPS)

Diagram labels: liquid, HV cable, cannula, 50 µm Tungsten wire, Xe short arc lamp, Field of view, ICCD, ns plasma, 1 cm

SEM labels: 50 µm, WD 12.9 mm, Det ETD, Spot 2.5

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Temperatures from N2 SPS as thermometer for the later stages

For 20 kV Experiment

T_{vib} ~ 3250 K @ 135 ns
T_{rot} ~ 650 K

T_{vib} ~ 2500 K @ 210 ns
T_{rot} ~ 400 K
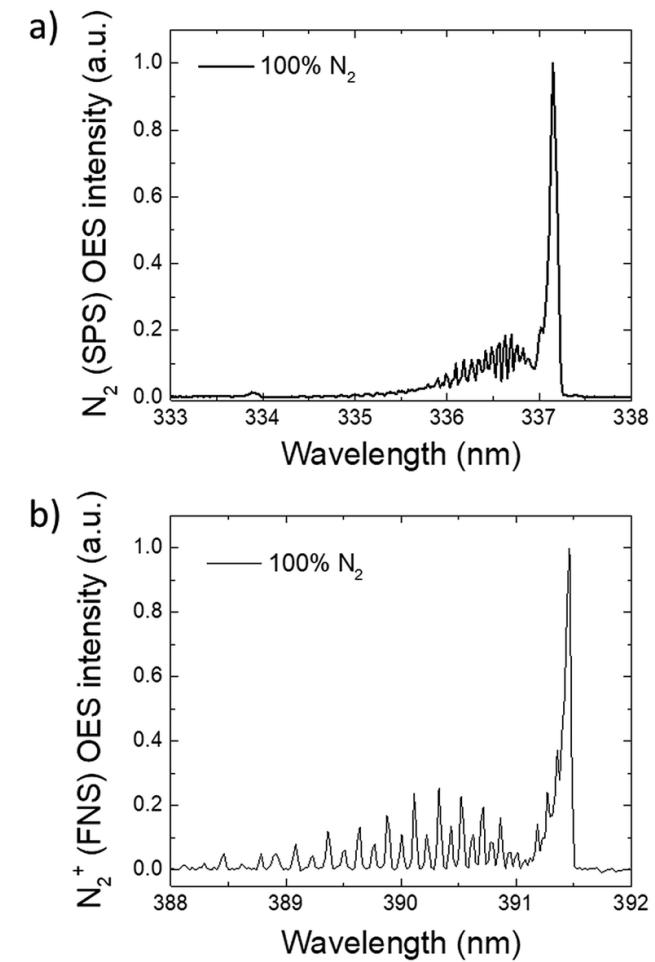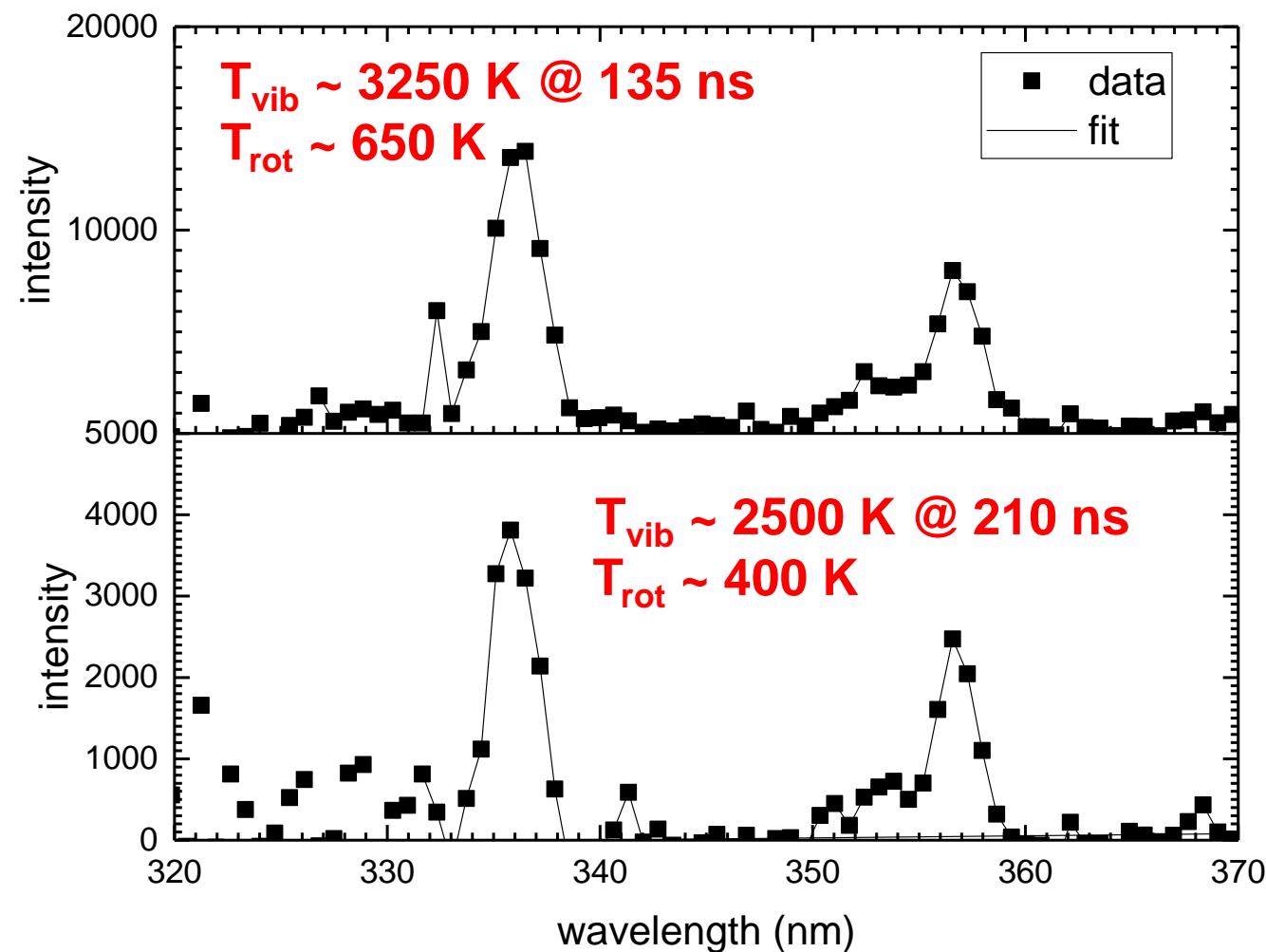
From Girard et al. PCCP 20, 2198 (2018)

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Temperatures from spectroscopies

Chemistry in Plasma Treated Liquids | A. von Keudell et al.

T from cavitation theory

Cooling during expansion depends on VV, VT, VR relaxation times.
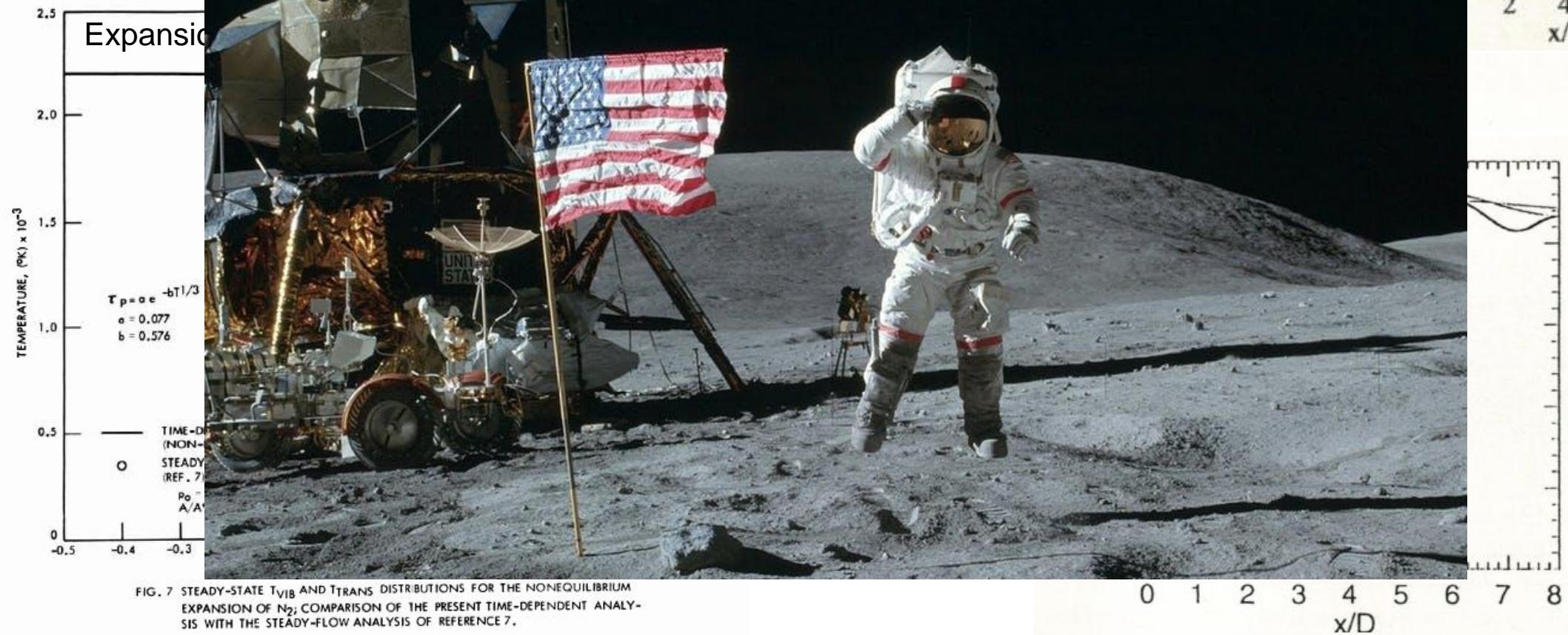
Usually T_{rot} decouples from T_{vib}
In chemical non-equilibrium expanding flows

$\gamma = 1.1$
(20 degrees of freedom)

$\gamma = 1.33$
(H2O, normal)

$\gamma = 1.7$
(monoatomic gas)

$\gamma = 1.95$
(H2O, supercritical @ 700 K)

■ T from black body radiation
■ T_{vib} from N2 spectra
● T_{rot} from N2 spectra
■ scaling of T from adiabatic expansion
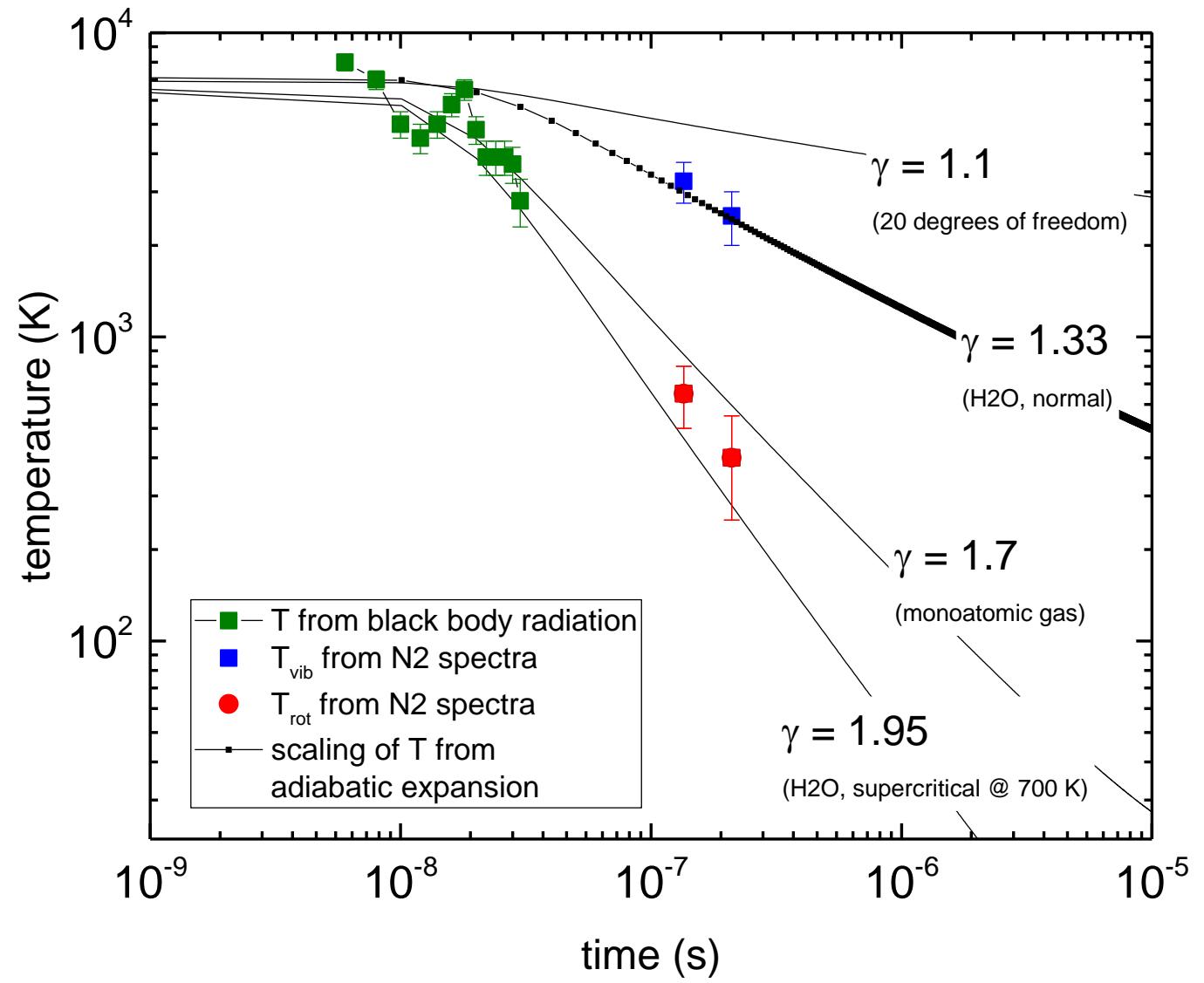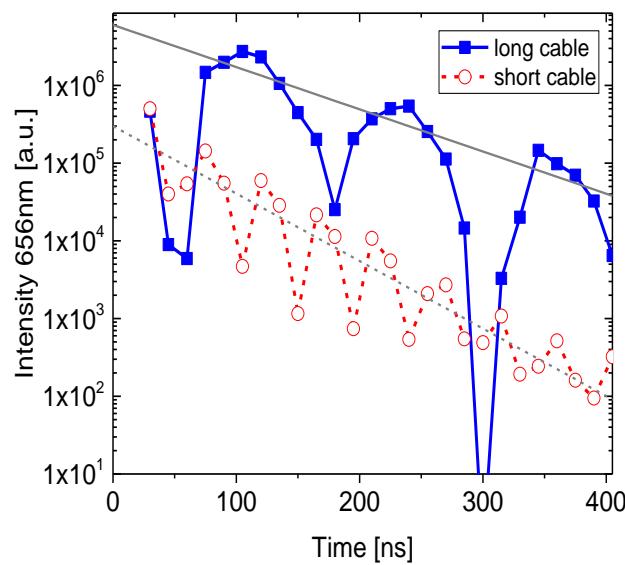
Non-equilibrium in expanding ns plasmas

Rocket Science –
Chemical No
Hypersonic E

FIG. 7 STEADY-STATE T_VIB AND T_TRANS DISTRIBUTIONS FOR THE NONEQUILIBRIUM EXPANSION OF N₂; COMPARISON OF THE PRESENT TIME-DEPENDENT ANALYSIS WITH THE STEADY-FLOW ANALYSIS OF REFERENCE 7.

J. D. Anderson, Report Naval Ordonance Labatory (1969)

M. Nichida, M. Matsumoto, Verlag d. Zeitung f. Naturforschung 0932-0784 (1997)

Solution for R(t) assuming a compressible liquid

$$r\frac{Dh}{Dt} + ru\frac{Du}{Dt} + (c+u)\left(h + \frac{u^2}{2}\right) + rc\frac{\partial h}{\partial r} + rcu\frac{\partial u}{\partial r} = 0$$
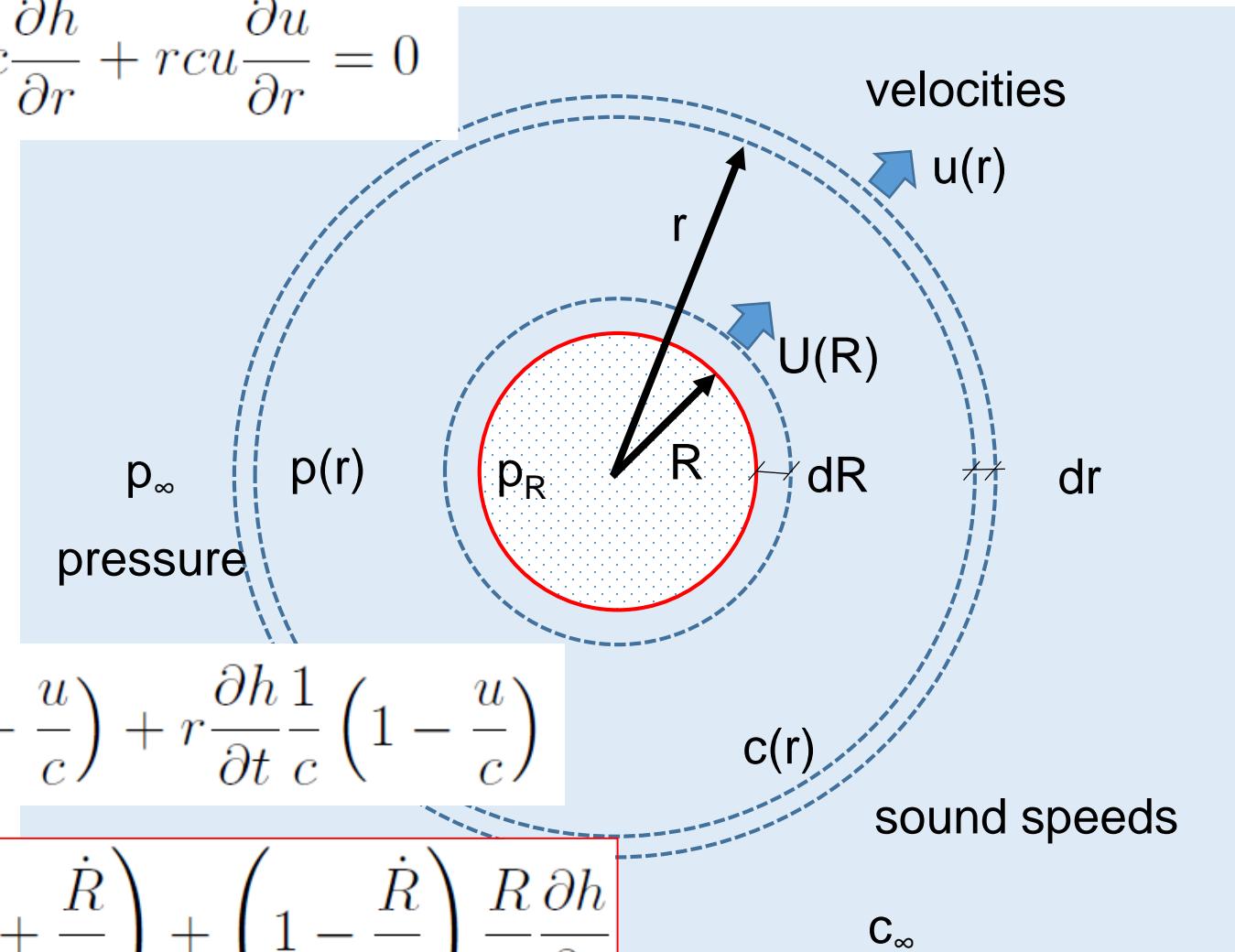
with momentum and mass conservation

$$\frac{Du}{Dt} = -\frac{\partial h}{\partial r}$$

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 u\right) = -\frac{1}{\rho}\frac{d\rho}{dt}$$

$$r\frac{Du}{Dt}\left(1 - \frac{u}{c}\right) + \frac{3}{2}u^2\left(1 - \frac{u}{3c}\right) = h\left(1 + \frac{u}{c}\right) + r\frac{\partial h}{\partial t}\frac{1}{c}\left(1 - \frac{u}{c}\right)$$

$$R\ddot{R}\left(1 - \frac{\dot{R}}{c}\right) + \frac{3}{2}\dot{R}^2\left(1 - \frac{\dot{R}}{3c}\right) = h\left(1 + \frac{\dot{R}}{c}\right) + \left(1 - \frac{\dot{R}}{c}\right)\frac{R}{c}\frac{\partial h}{\partial t}$$

velocities

$u(r)$

$U(R)$

p_∞ $p(r)$ p_R R dR dr

pressure

$c(r)$

sound speeds

c_∞

Solution for R(t) assuming a compressible liquid

momentum balance equation (no Navier Stokes)

$$\frac{\partial}{\partial t}\left(-\vec{\nabla}\phi\right) + (\vec{u}\cdot\vec{\nabla})\vec{u} = -\frac{\nabla p}{\rho}$$

Integrate over r

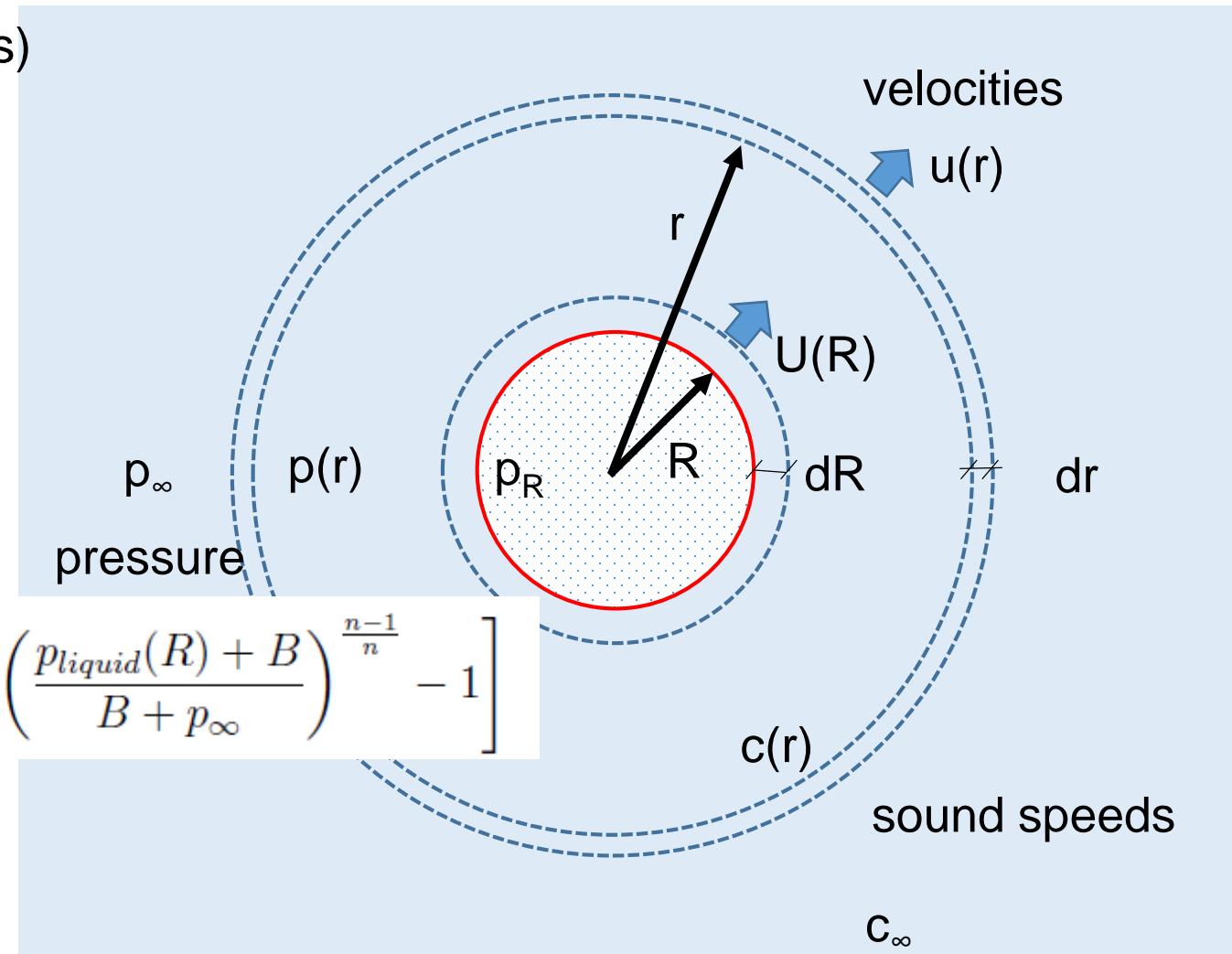$$-\frac{\partial\phi}{\partial t} + \frac{1}{2}\vec{u}^2 = \int_{p_\infty}^{p(r)} -\frac{\mathrm{d}p}{\rho}$$

definition enthalpy

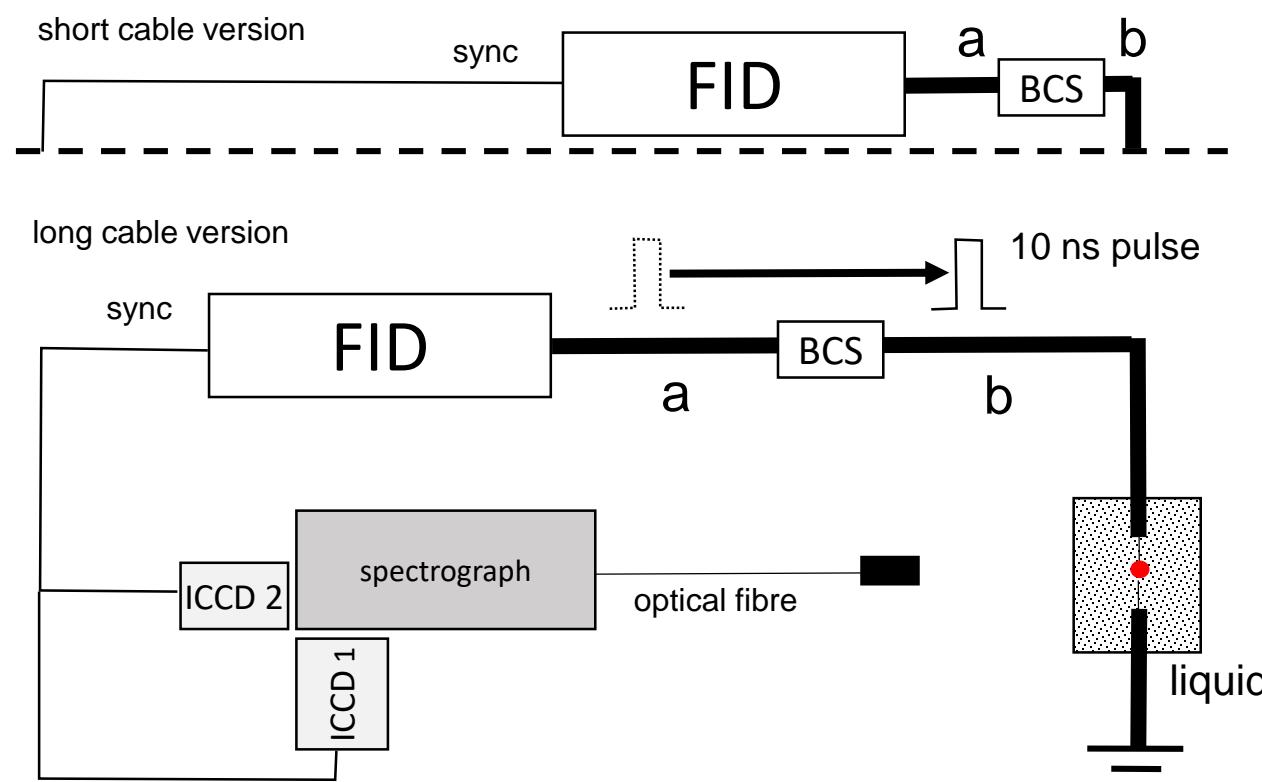$$h = \int_{p_\infty}^{p(r)} -\frac{\mathrm{d}p}{\rho} \qquad h = \frac{n}{n-1}\frac{1}{\rho_0}(B+p_\infty)\left[\left(\frac{p_{liquid}(R)+B}{B+p_\infty}\right)^{\frac{n-1}{n}} - 1\right]$$

results in Bernoulli equation

$$\frac{\partial\phi}{\partial t} = h + \frac{1}{2}\vec{u}^2$$

velocities

$u(r)$

r

$U(R)$

p_∞ $p(r)$ p_R R dR dr

pressure

$c(r)$

sound speeds

c_∞

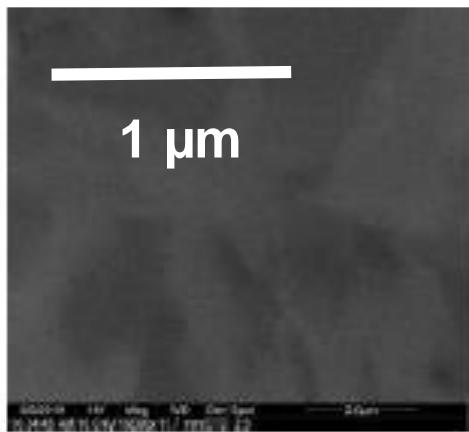# Example 2: Plasma Chemistry in liquids – example H_2O_2 generation

- 10 ns pulses, 14…30 kV, distilled water
- Shadowgraphy 2 ns … 70 ns gate widths
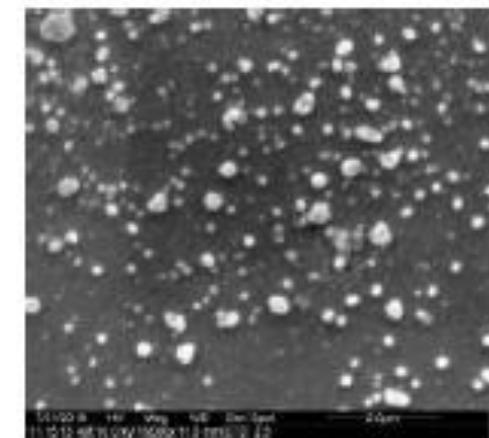- Optical emission spectroscopy with 2ns and 30 ns gate time

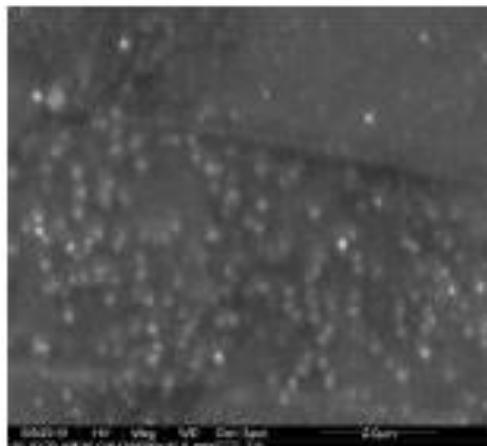# Nanosecond plasma based recovery of CuO nanocubes at copper electrodes
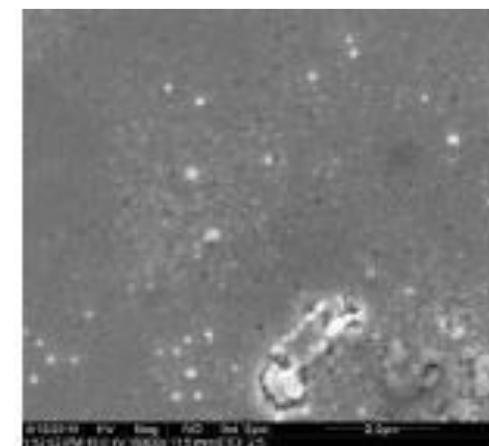
distilled water

dist. Water + 0.0035M KCl
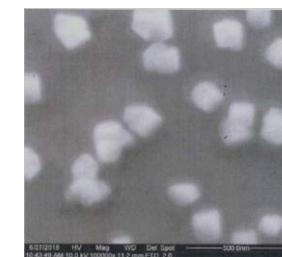
20 kV

1 µm

distilled water

dist. Water + 0.0035M KCl

26 kV

Creation of Cu-nanocubes possible, if

- no direct current to the sample, reduction of the oxide, plasma electrode distance to the sample important

- Cl necessary as nucleation sites

- Competition between oxidation due to H_2O_2, OH and reduction by H, e^-
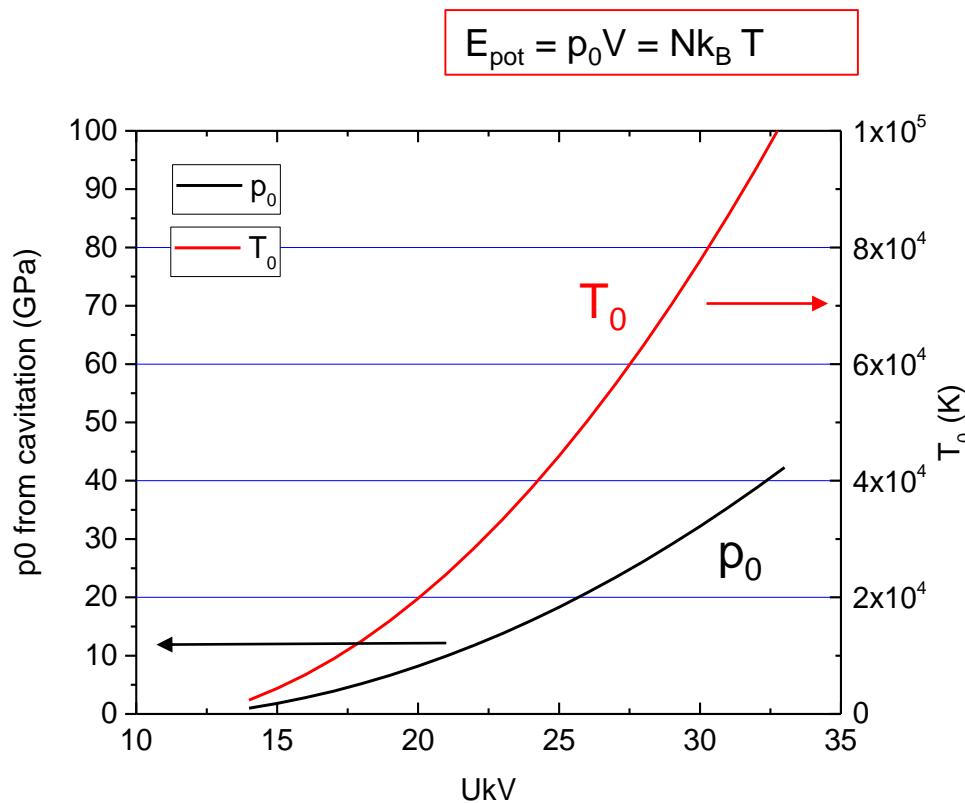
P. Grosse, B. Roldan et al.

Reference plasma based low pressure creation of CuO nanocubes
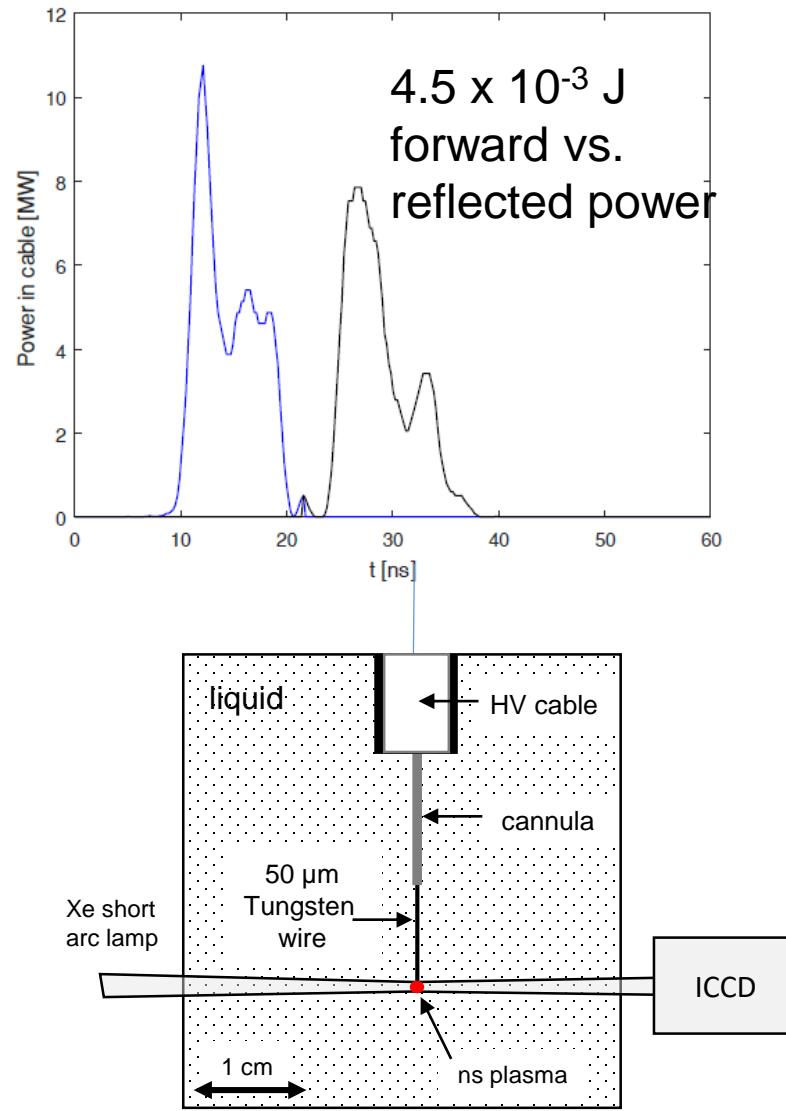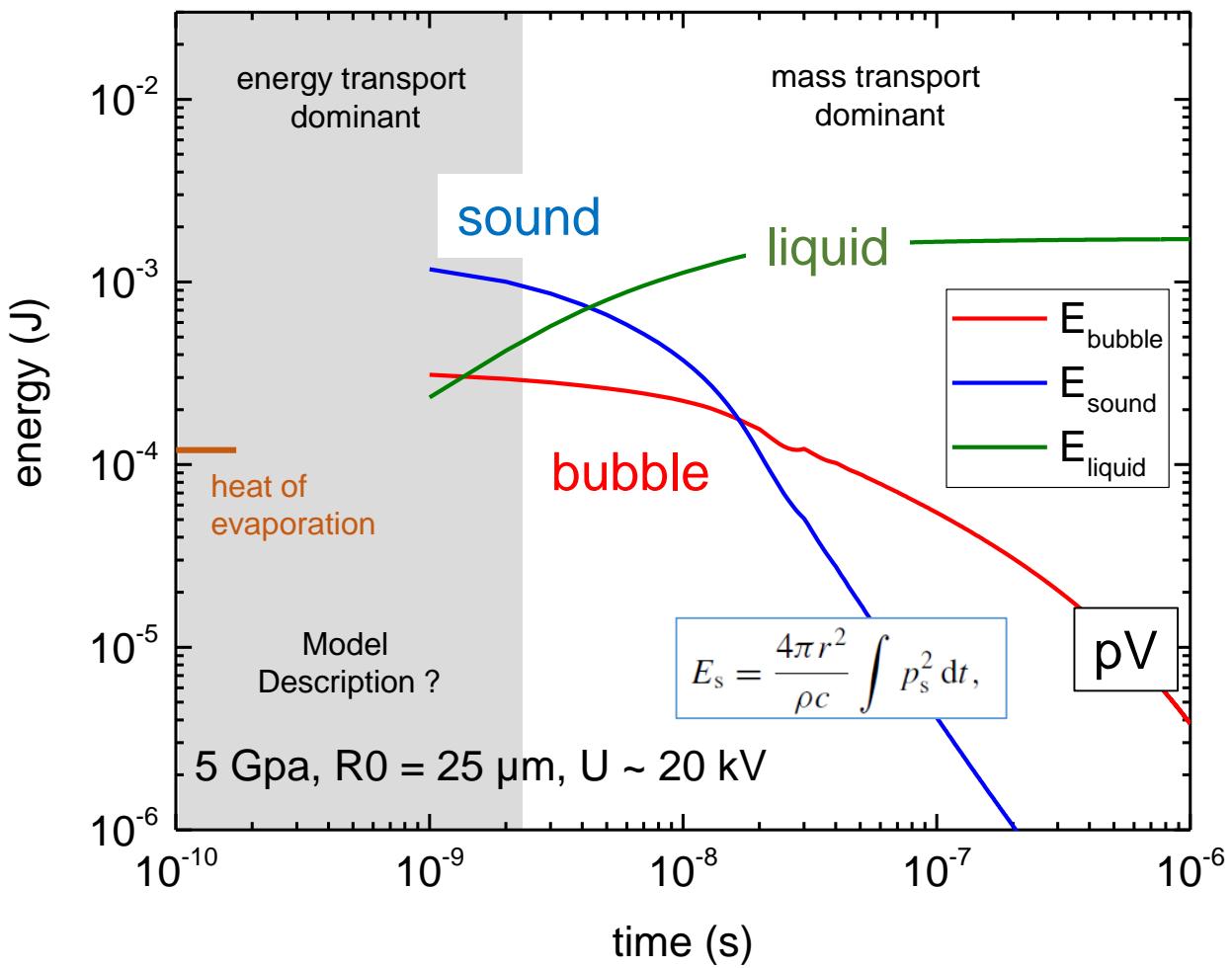
*S. Mededovic, B. Locke
JPD 40, 7734 (2007)
PCPP 32, 875 (2012)

- Taking H_2O chemistry from spark plasma simulation*
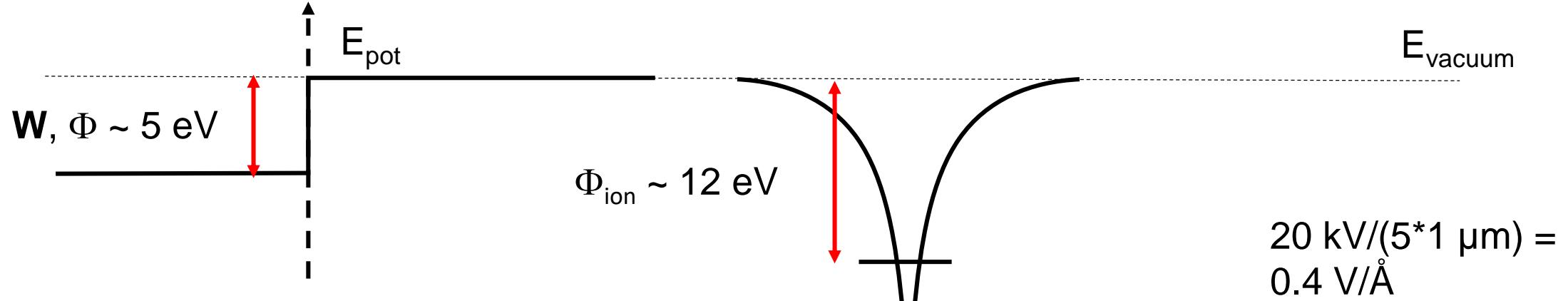- Taking the evolution of the temperature from cavitation theory

$$E_{pot} = p_0 V = N k_B T$$

Reaction		T	rate coefficient
H_2O reactions			
$H_2O + M$	$\rightarrow H + OH + M$	2000-6000 K	$k_{21} = 5.8 \cdot 10^{-9} \exp[-440000(RT)^{-1}]$
O_2 reactions			
$O_2 + M$	$\rightarrow O + O + M$	200-10000 K	$k_{27} = 1.99 \cdot 10^{-10} \exp[-9500(RT)^{-1}]$
OH reactions			
$OH + M$	$\rightarrow H + O + M$	300-2500 K	$k_{22} = 4.09 \cdot 10^{-9} \exp[-416000(RT)^{-1}]$
$OH + OH$	$\rightarrow H_2O + O$	250-300 K	$k_{29} = 1.02 \cdot 10^{-12} (T/298)^{1.4} \exp[1660(RT)^{-1}]$
$O + OH$	$\rightarrow O_2 + H$	250-5000 K	$k_{61} = 4.55 \cdot 10^{-12} (T/298)^{0.4} \cdot \exp[3090(RT)^{-1}]$
$OH + H$	$\rightarrow H_2O$	300-2100 K	$k_{62} = 2.69 \cdot 10^{-10} \exp[-620(RT)^{-1}]$
$H + OH$	$\rightarrow O + H_2$	300-2500 K	$k_{63} = 6.68 \cdot 10^{-14} (T/298)^{2.8} \cdot \exp[-16210(RT)^{-1}]$
$H_2O_2 + OH$	$\rightarrow HO_2 + H_2O$	300-2500 K	$k_{64} = 2.91 \cdot 10^{-12} \cdot \exp[-1330(RT)^{-1}]$
$O_2 + OH$	$\rightarrow HO_2 + O$	300-2500 K	$k_{65} = 3.7 \cdot 10^{-11} \cdot \exp[-220000(RT)^{-1}]$
$OH + OH$	$\rightarrow H_2O_2$	300-1500 K	$k_{66} = 1.51 \cdot 10^{-11} (T/298)^{-0.37}$
$OH + OH$	$\rightarrow 2 O + 2H$	300-2500 K	$k_{67} = 4.09 \cdot 10^{-9} \cdot \exp[-416000(RT)^{-1}]$
H_2O_2 reactions			
$H_2O_2 + O$	$\rightarrow HO_2 + OH$	300-2500 K	$k_{68} = 1.42 \cdot 10^{-12} (T/298)^2 \exp[-16631(RT)^{-1}]$
$H_2O_2 + H$	$\rightarrow OH + H_2O$	300-2500 K	$k_{69} = 4.01 \cdot 10^{-11} \exp[-16630(RT)^{-1}]$
$H_2O_2 + H$	$\rightarrow HO_2 + H_2$	300-2500 K	$k_{610} = 8 \cdot 10^{-11} \exp[-33260(RT)^{-1}]$
$H_2O_2 + O_2$	$\rightarrow 2 HO_2$	300-2500 K	$k_{611} = 9 \cdot 10^{-11} \exp[-166000(RT)^{-1}]$
HO_2 reactions			
$HO_2 + OH$	$\rightarrow H_2O + O_2$	300-2000 K	$k_{612} = 4.81 \cdot 10^{-11} \exp[2080(RT)^{-1}]$
$HO_2 + O$	$\rightarrow OH + O_2$	300-2500 K	$k_{613} = 2.91 \cdot 10^{-11} \exp[-1660(RT)^{-1}]$
$HO_2 + H$	$\rightarrow 2 OH$	300-2500 K	$k_{614} = 2.81 \cdot 10^{-10} \exp[-3660(RT)^{-1}]$
$HO_2 + H$	$\rightarrow H_2 + O_2$	300-2500 K	$k_{615} = 1.1 \cdot 10^{-10} \exp[-8900(RT)^{-1}]$
$HO_2 + HO_2$	$\rightarrow H_2O_2 + O_2$	300-2500 K	$k_{616} = 3.01 \cdot 10^{-12}$
$HO_2 + H_2$	$\rightarrow H_2O_2 + H$	300-2500 K	$k_{617} = 5 \cdot 10^{-11} \exp[-109000(RT)^{-1}]$
$HO_2 + M$	$\rightarrow O_2 + H + M$	300-2200 K	$k_{618} = 2.41 \cdot 10^{-8} (T/298)^{-1.18} \exp[-2031000(RT)^{-1}]$
H reactions			
$O + H + M$	$\rightarrow OH + M$	300-2500 K	$k_{619} = 4.36 \cdot 10^{-32} (T/298)^{-1}$
$H + H + M$	$\rightarrow M + H_2$	300-2500 K	$k_{620} = 6.04 \cdot 10^{-33} (T/298)^{-1}$
$O_2 + H$	$\rightarrow OH + O$	500-2000 K	$k_{621} = 2.94 \cdot 10^{-10} \exp[-69680(RT)^{-1}]$
$O_2 + H + M$	$\rightarrow HO_2 + M$	200-2200 K	$k_{622} = 1.94 \cdot 10^{-32} (T/298)^{-1}$
H_2 reactions			
$H_2 + M$	$\rightarrow H + H + M$	2500-8000 K	$k_{25} = 1.5 \cdot 10^{-9} \exp[-402000(RT)^{-1}]$
$OH + H_2$	$\rightarrow H_2O + H$	200-2400 K	$k_{623} = 2.97 \cdot 10^{-12} (T/298)^{1.21} \exp[-19710(RT)^{-1}]$
$O + H_2$	$\rightarrow OH + H$	300-2500 K	$k_{624} = 3.44 \cdot 10^{-13} (T/298)^{2.67} \exp[-26270(RT)^{-1}]$
O reactions			
$O + O + M$	$\rightarrow O_2 + M$	200-4000 K	$k_{625} = 5.21 \cdot 10^{-35} \exp[7480(RT)^{-1}]$
$O + H_2O$	$\rightarrow OH + OH$	300-2000 K	$k_{626} = 6.68 \cdot 10^{-13} (T/298)^{2.60} \exp[-63520(RT)^{-1}]$

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Dissipated energy during plasma ignition within the first 10 ns – comparison to experiments

4.5 x 10^{-3} J forward vs. reflected power

In ns plasmas at very high initial pressure, most of the energy is transferred to the sound wave

$$E_s = \frac{4\pi r^2}{\rho c} \int p_s^2 \, \mathrm{d}t,$$

5 Gpa, R0 = 25 µm, U ~ 20 kV

Field emission effects

E_{pot}

E_{vacuum}

W, $\Phi \sim 5$ eV

$\Phi_{ion} \sim 12$ eV

20 kV/(5*1 μm) = 0.4 V/Å

H₂O

Field effects at surfaces

E_{pot}

- 20 kV

E_{pot}

+ 20 kV

E_{pot}

+ 20 kV

W
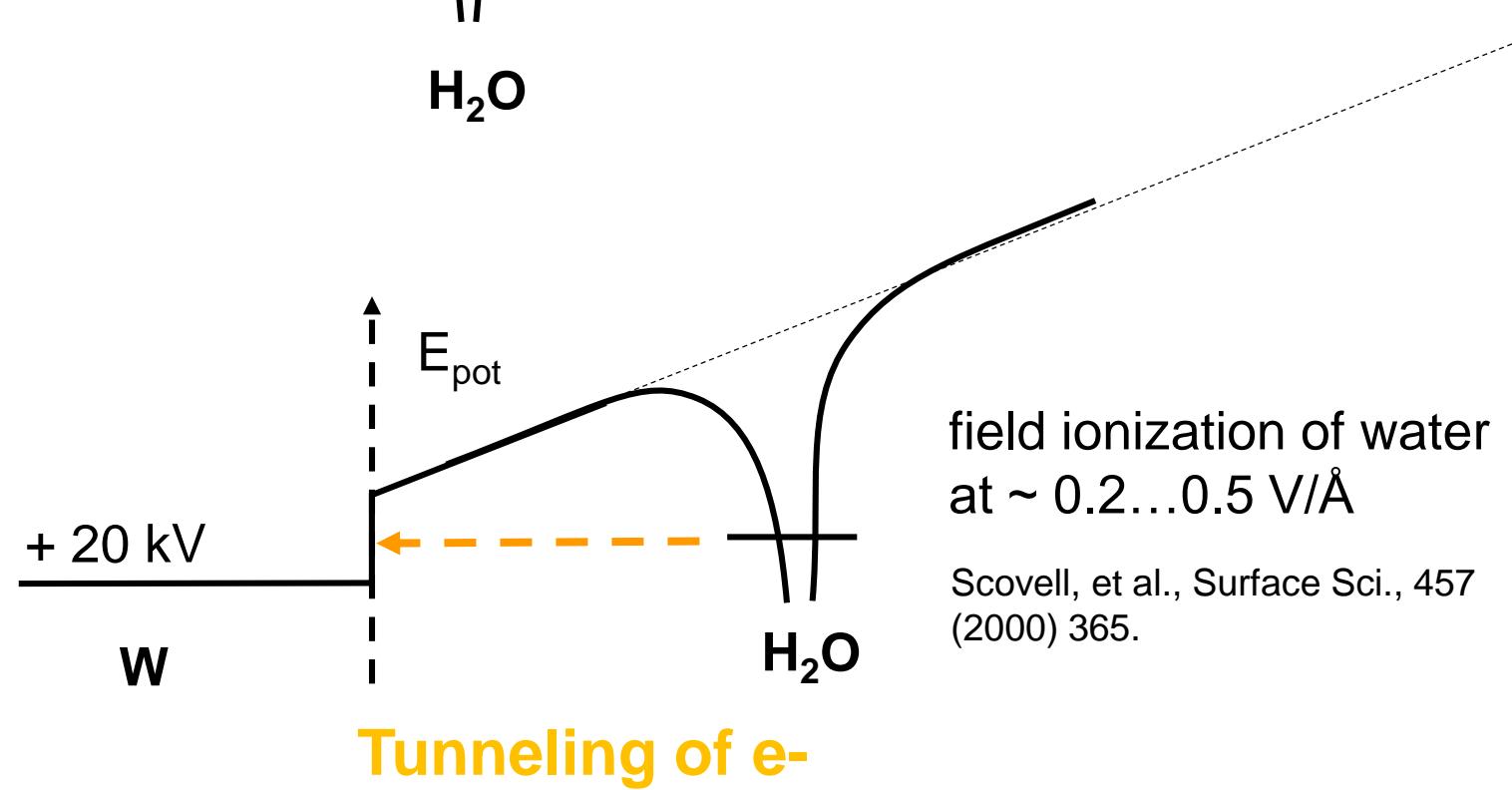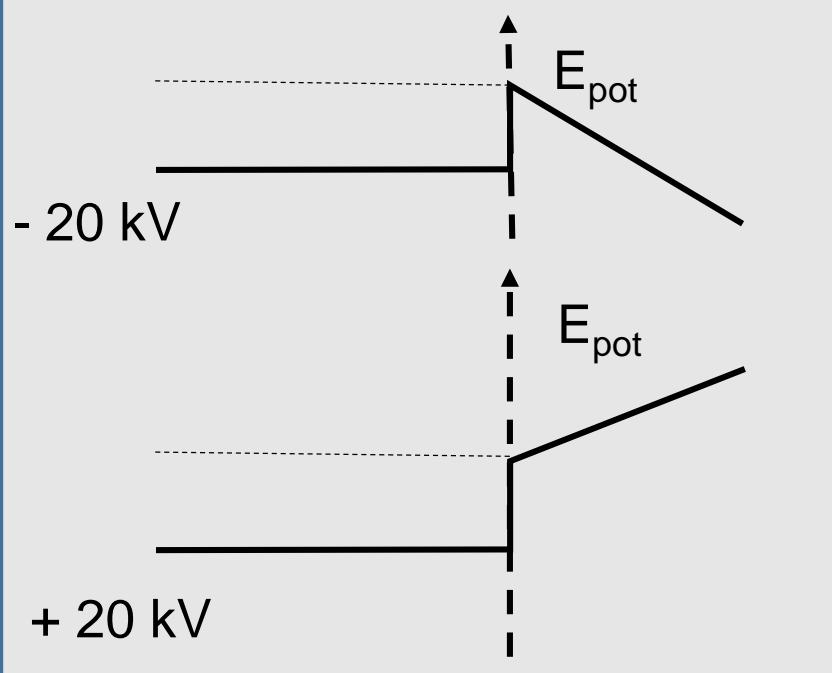
field ionization of water at ~ 0.2…0.5 V/Å

Scovell, et al., Surface Sci., 457 (2000) 365.

H₂O

Tunneling of e-

Streamer velocities in distilled water
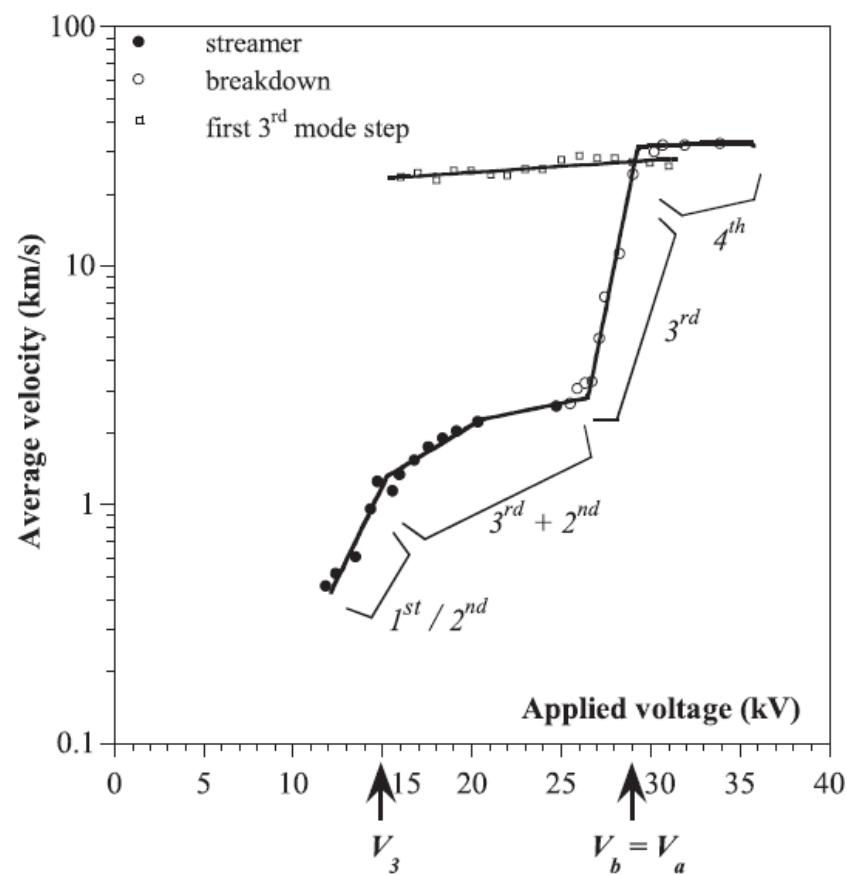
Figure 15. Average streamer propagation velocity v_{av} versus voltage in distilled water [52]. $d = 3$ cm, $r_p = 1$ μm.

Lesaint et al. JPD 49 144001 (2016)
Starikovsky et al. PSST 20, 24003 (2011)

A: 1st mode
$v_{av} = 100$ m/s
6 kV / 6 mm

B: 2nd mode
$v_{av} = 2$ km/s
30 kV / 6 mm

C: 2nd mode
$v_{av} = 2$ km/s
160 kV / 10 cm

D: 3rd + 2nd modes
$v_{av} = 10$ km/s
304 kV / 10 cm

E: 4th mode
$v_{av} = 100$ km/s
424 kV / 10 cm
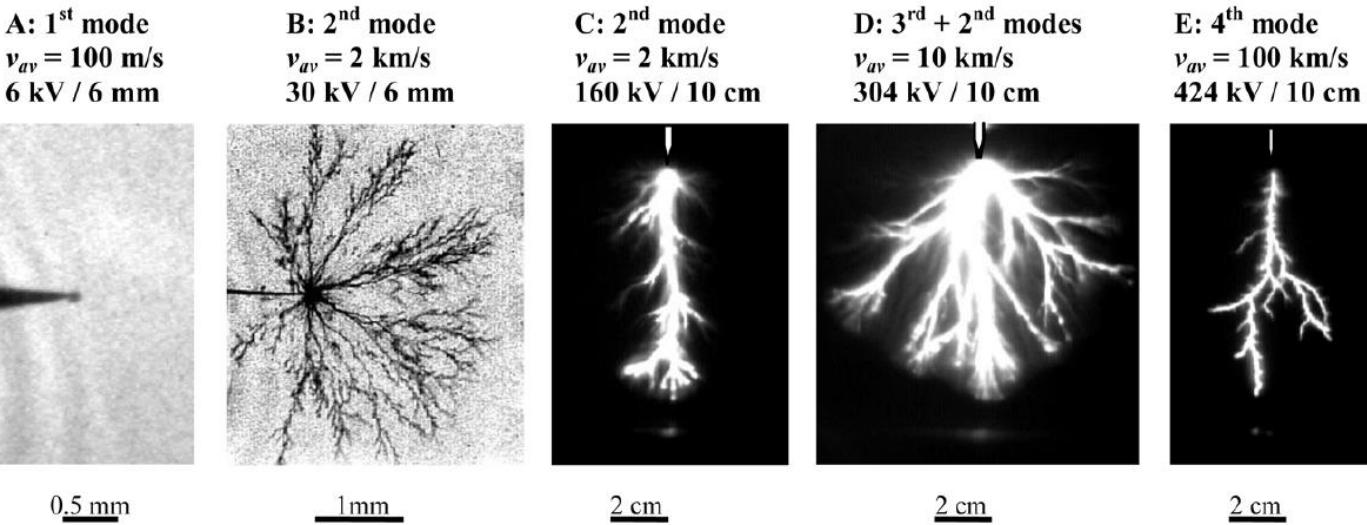
Propagation velocity of streamer in liquids (long pulses)
3 km/s … 100 km/s in 10 ns Δx = 3 µm … 0.1 mm
Propagation velocity of streamer in liquids (short pulses)
1000…5000 km/s in 10 ns Δx = 1 mm … 5 mm
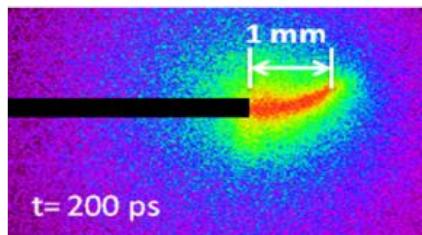
Comparison Streamer
in air ~ 1000 km/s

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Plasma pulse from field ionization to field emisison (gate time 2 ns, 22 kV)

0ns   4ns   8ns   12ns   14ns   18ns   22ns   26ns

0.5 mm

I — during the pulse field ionization

Example voltage pulse 20kV (8.65m cable)

II — after the pulse field emission

Start of the pulse water is polarized **Field ionization**

e⁻

More directed discharge in field emission phase

Voltage stops, **Field emission** electron flow reverses attracted to positive streamer head

e⁻

3 µm

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Current and Voltage signals for 10 ns 20 kV pulses using the 8.65 m cable

Chemistry in Plasma Treated Liquids | A. von Keudell et al.
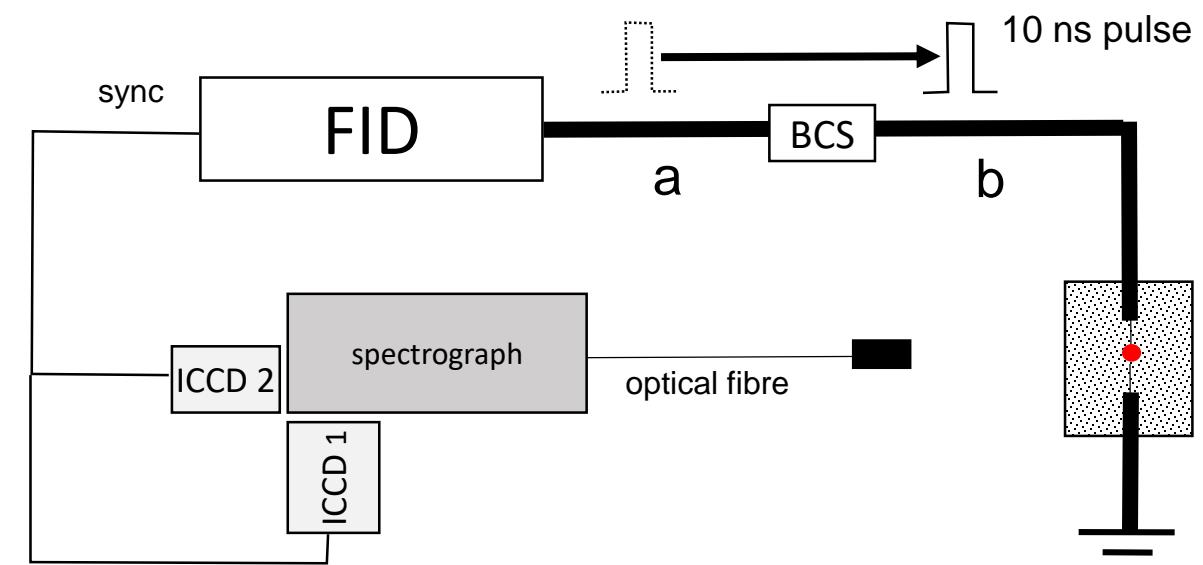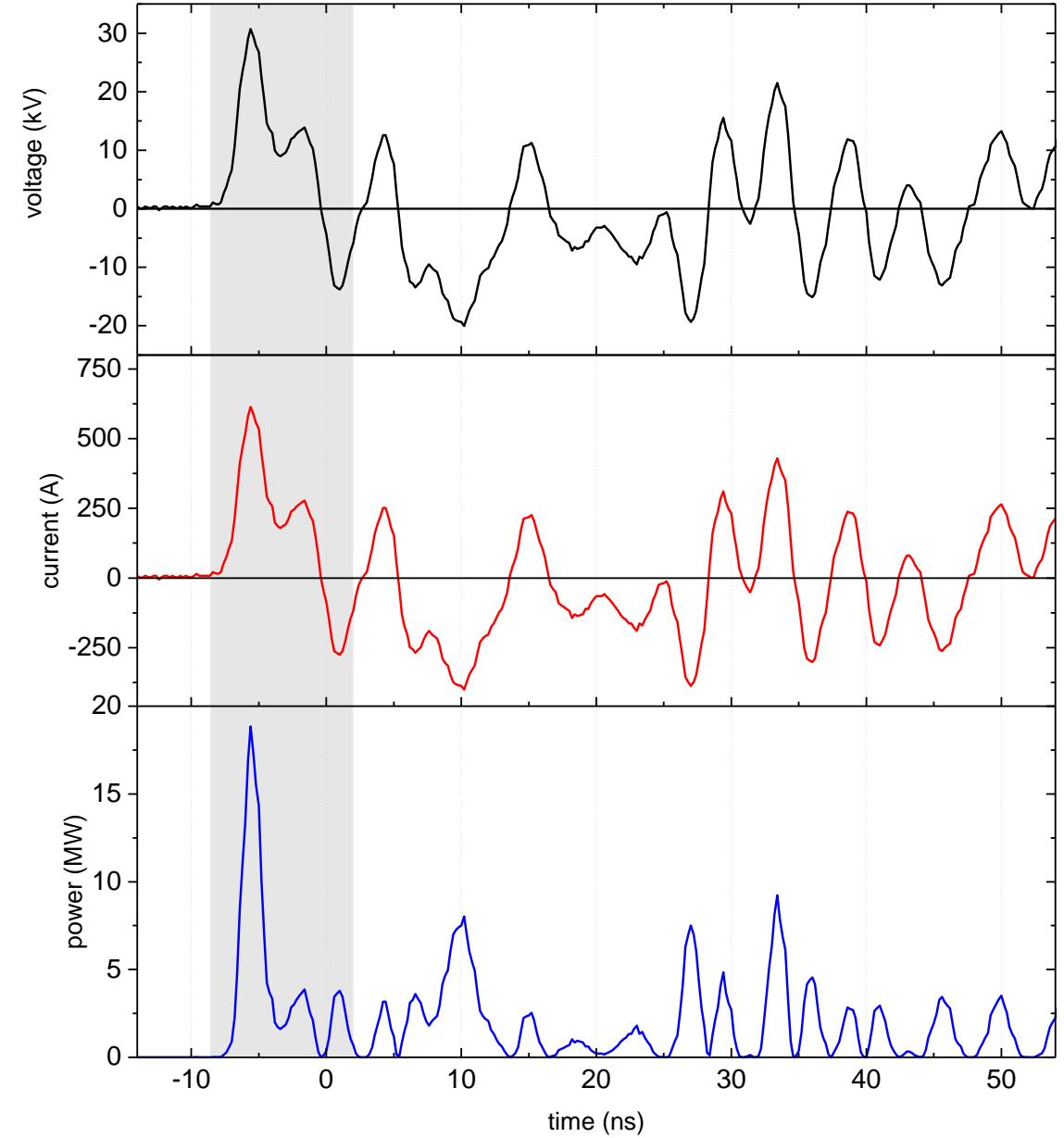
Tungsten vs. Titanium* tip (500 µm tip radius vs. 50 µm tip radius)

ns pulse 10 ns

Spark 5..10 µs   3 J 1.5×10^7 J/m²
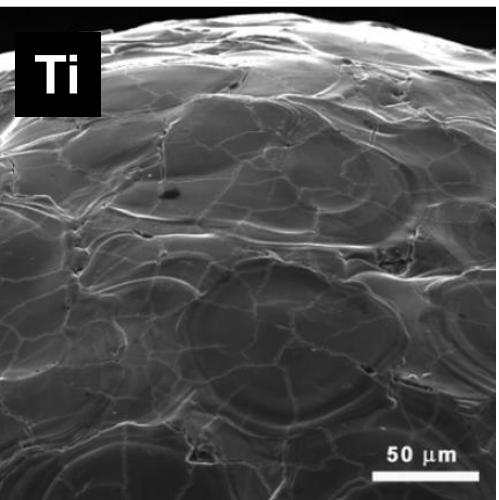
0.03 J 1.5×10^7 J/m²
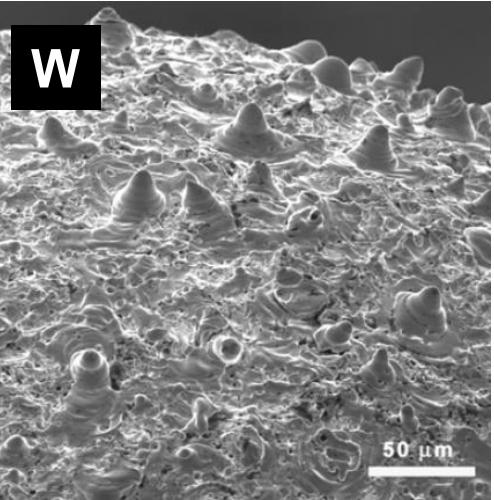
- similar energy per m² dissipated
- Sequence of melting and solidification

thermal conductivity @ 1000 ºC melting temp.
- Ti – 22 W/m K, 2000 K
- W – 115 W/m K, 3700 K
- Pt – 82 W/m K, 2500 K

- In case of W only small melting tips (for Pt, T, larger molten areas)

- similar to cathode spot in lamps
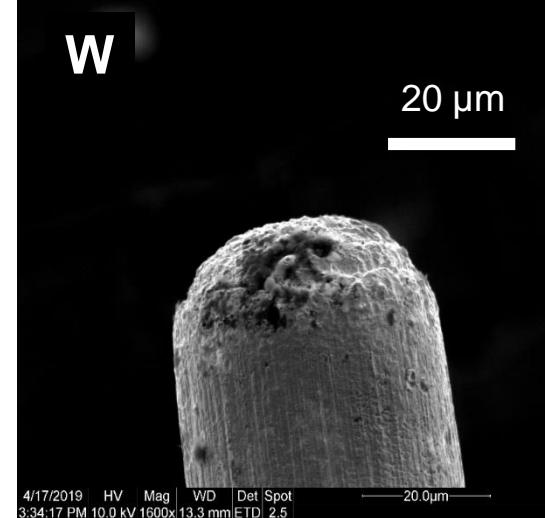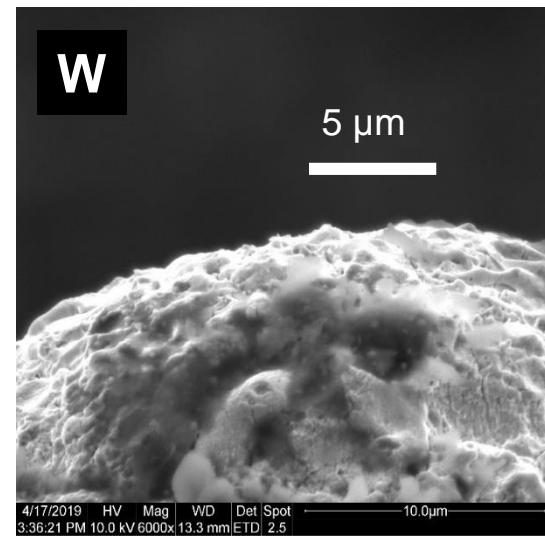
*P. Lukes et al. PSST 20, 3401 (2011)

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Sequence of the propagating discharge

Propagation velocity of streamer in liquids
3 … 1000 km/s
in 10 ns
Δx = ~ mm

I
Start of the pulse water is polarized **Field ionization**

II
Streamer Propagates, electrons are collected from channel voltage drops

III
Voltage stops, **Field emission** electron flow reverses attracted to positive streamer head

IV
thermal emission leads to change of polarity
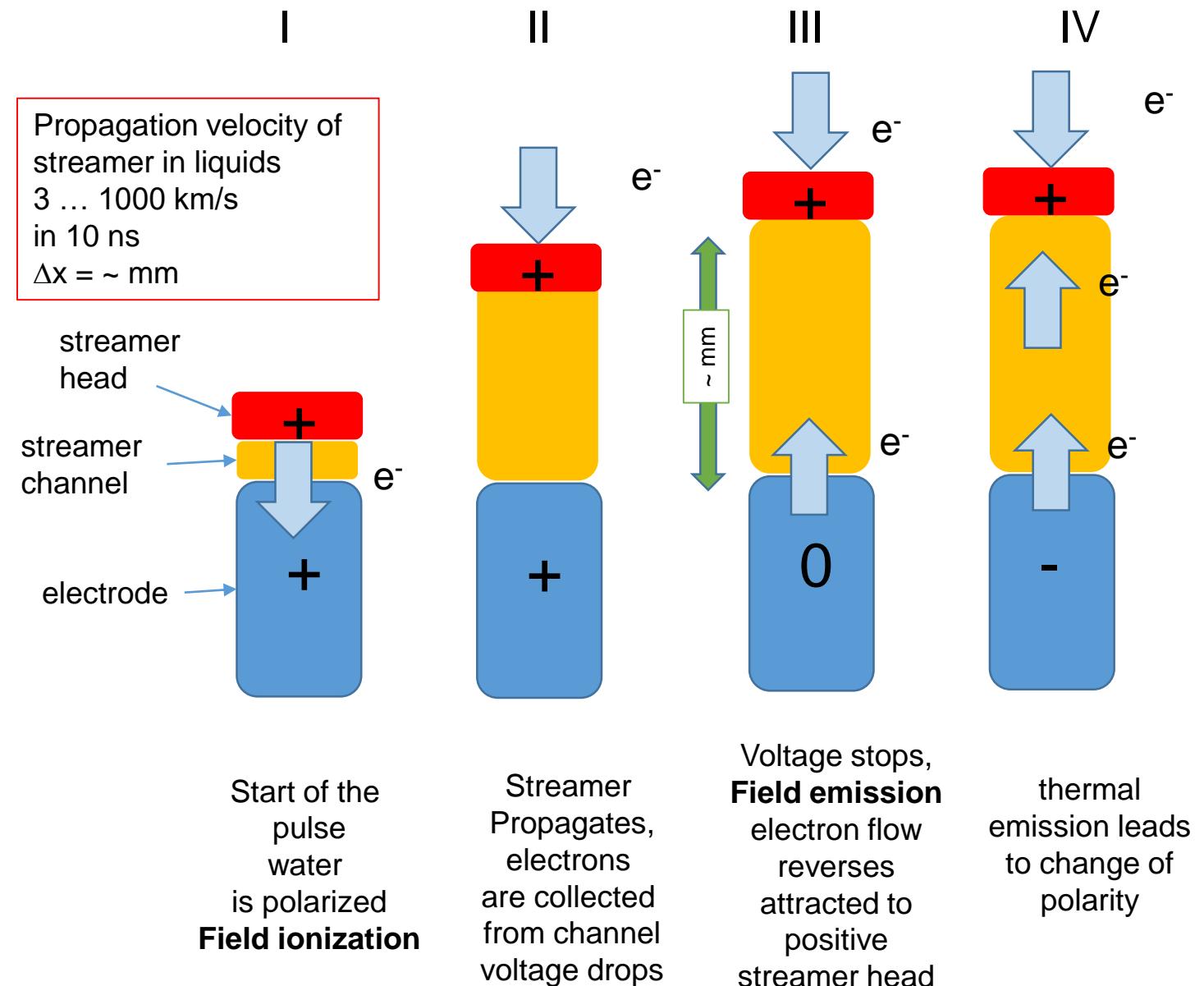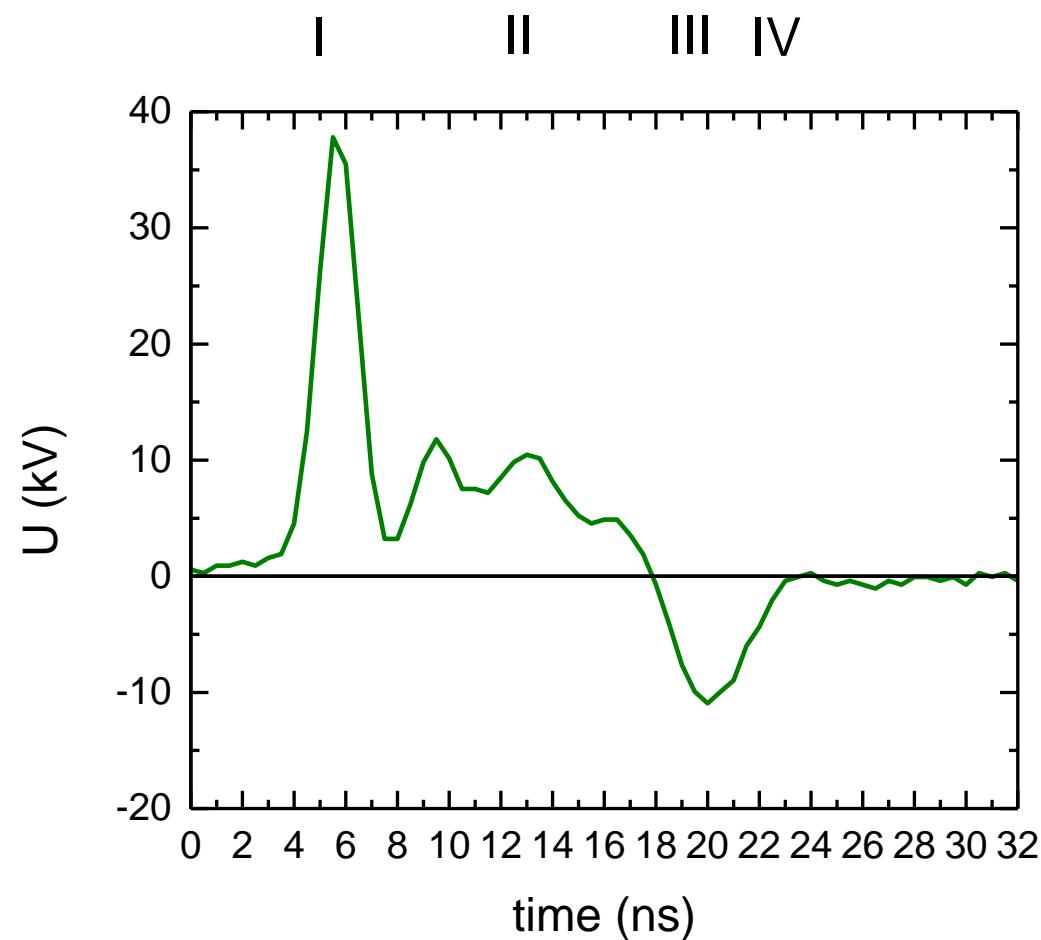
Comparison to cathode spots at high pressure lamps

@500 A on a 2 µm radius spot
= magnetic field pressure of 1 Gpa

Pinch effects at W tips

(d) $i_{arc} = 15.0$ A

5 µm
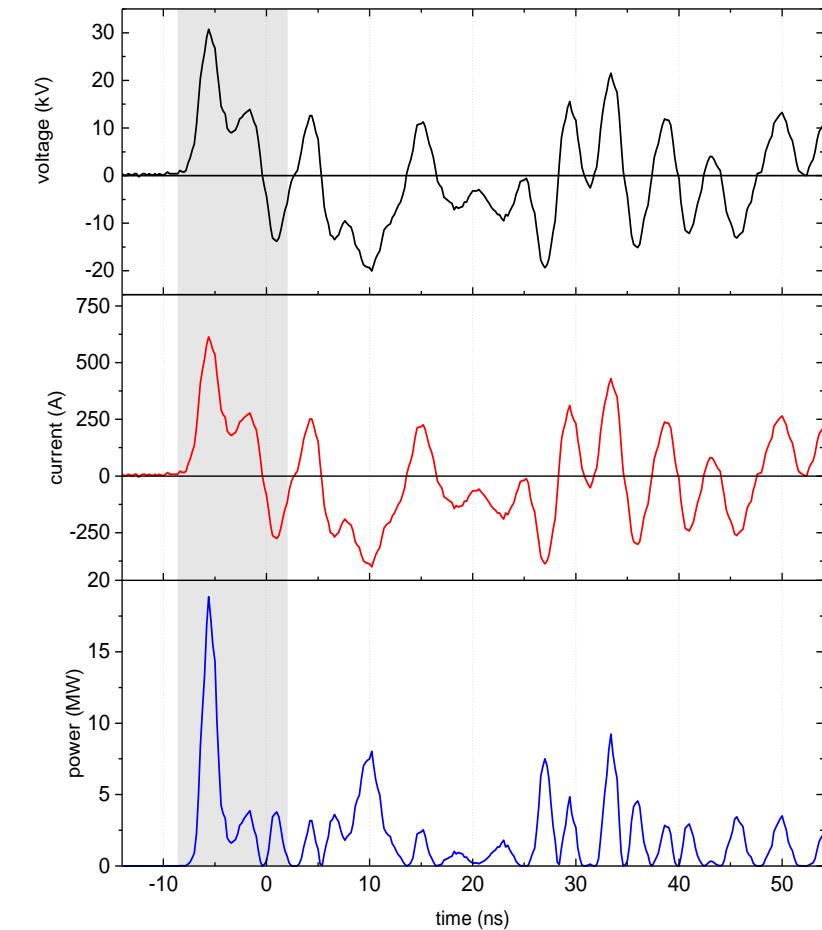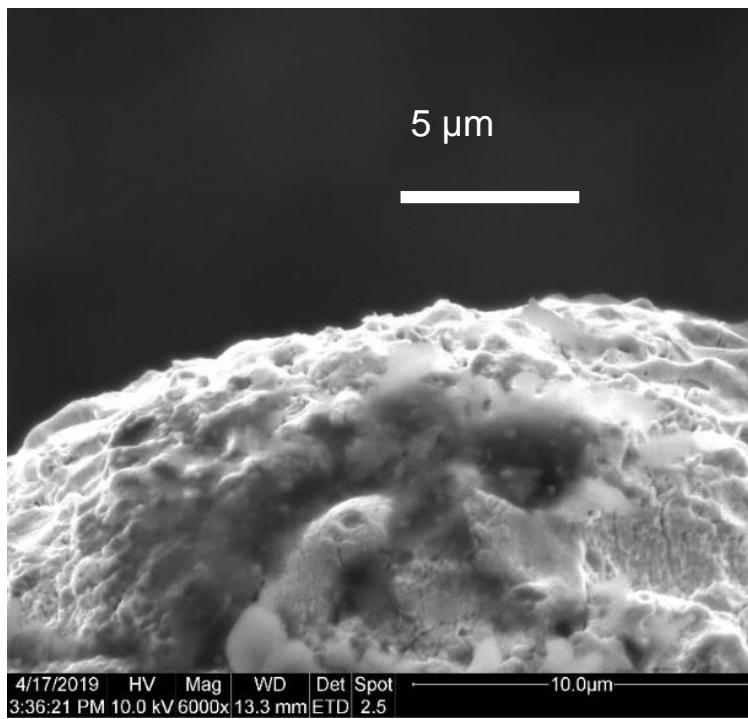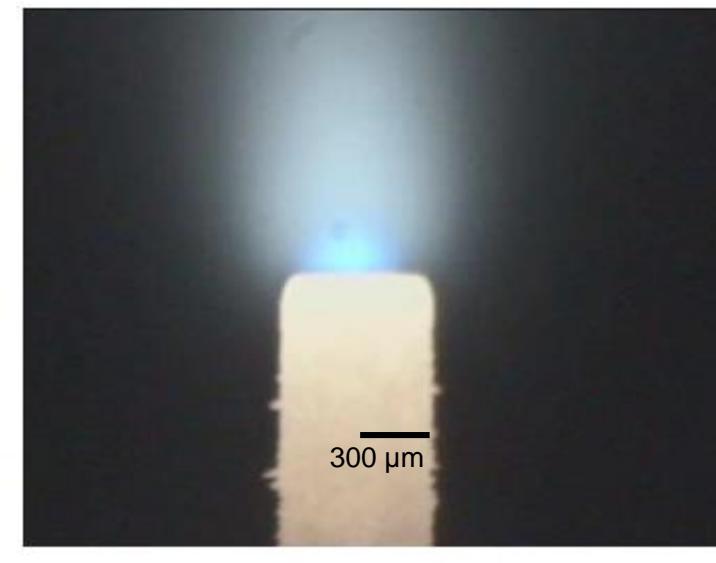
A. Bergner et al. PSST 23, 054005 (2014)

Temperatures from emission spectra of the plasma

Spectrum (first 50 ns, time resolution 2 ns)

- Recombination
- H_2, H_2O recomb. continuum
- OH, OH^+, H_2O, H_2O^+ bands
- Black body radiation (W)
- H_α
- $O_{(777nm)}$

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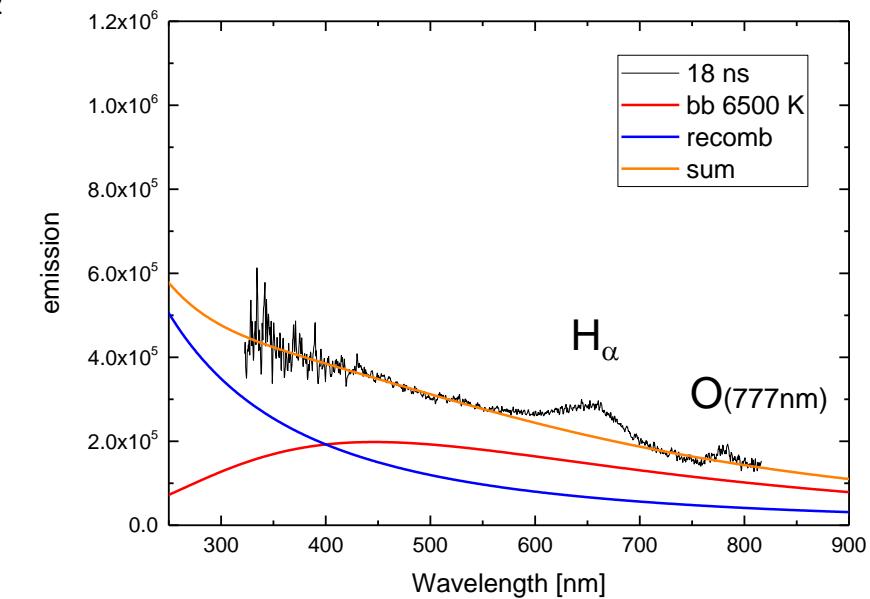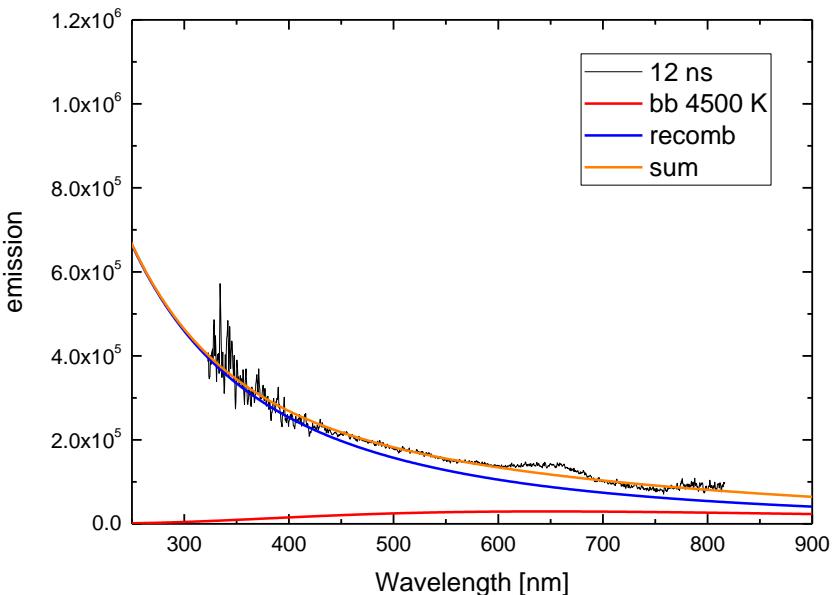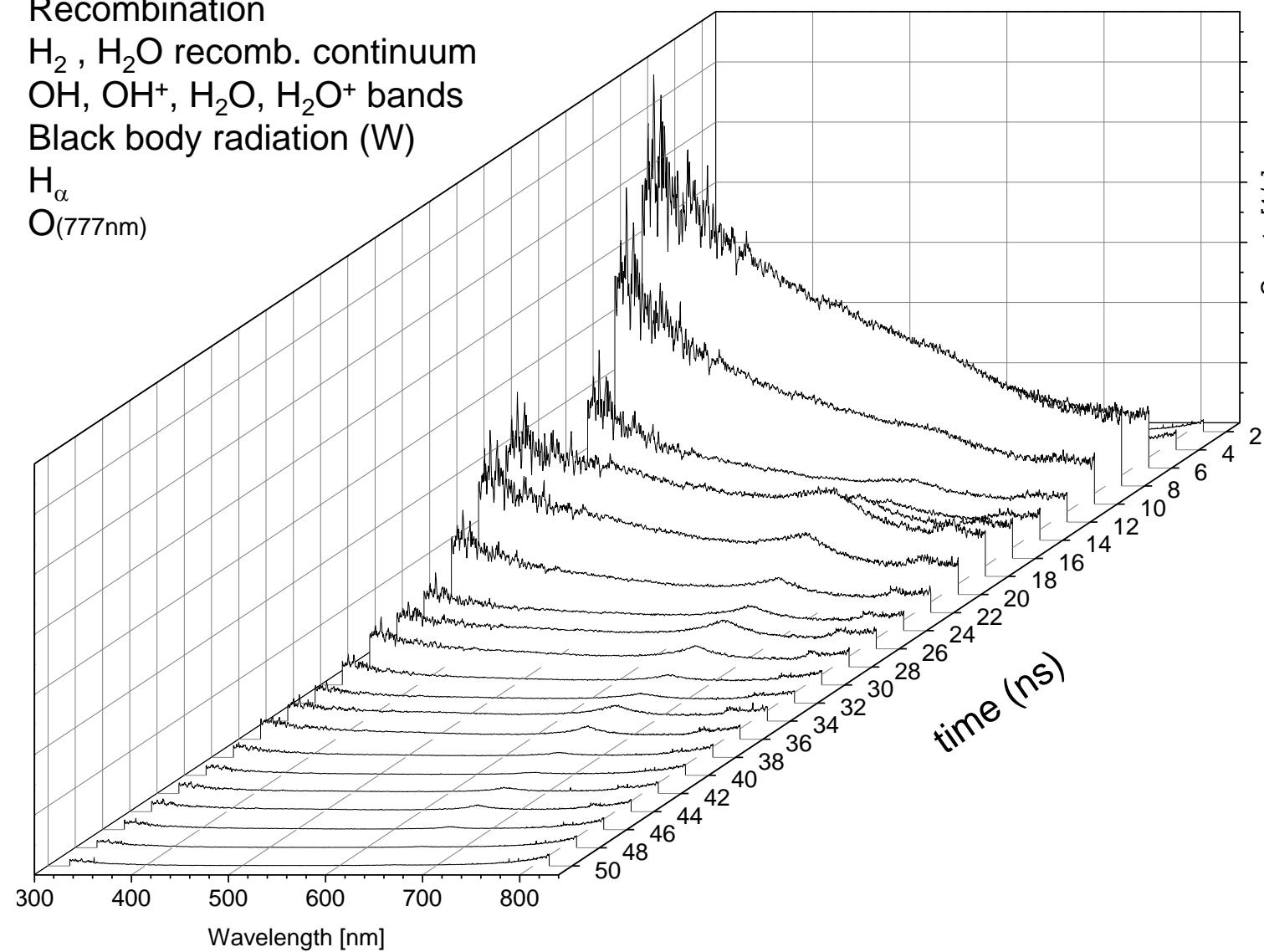
Temperatures from emission spectra of the plasma

- Power absorption at the beginning of the pulse and due to reversal of the voltage
- Black body radiation, followed by $1/\lambda^x$ spectrum.

$$T_0 < 8000 \text{ K @ 0 ns}$$

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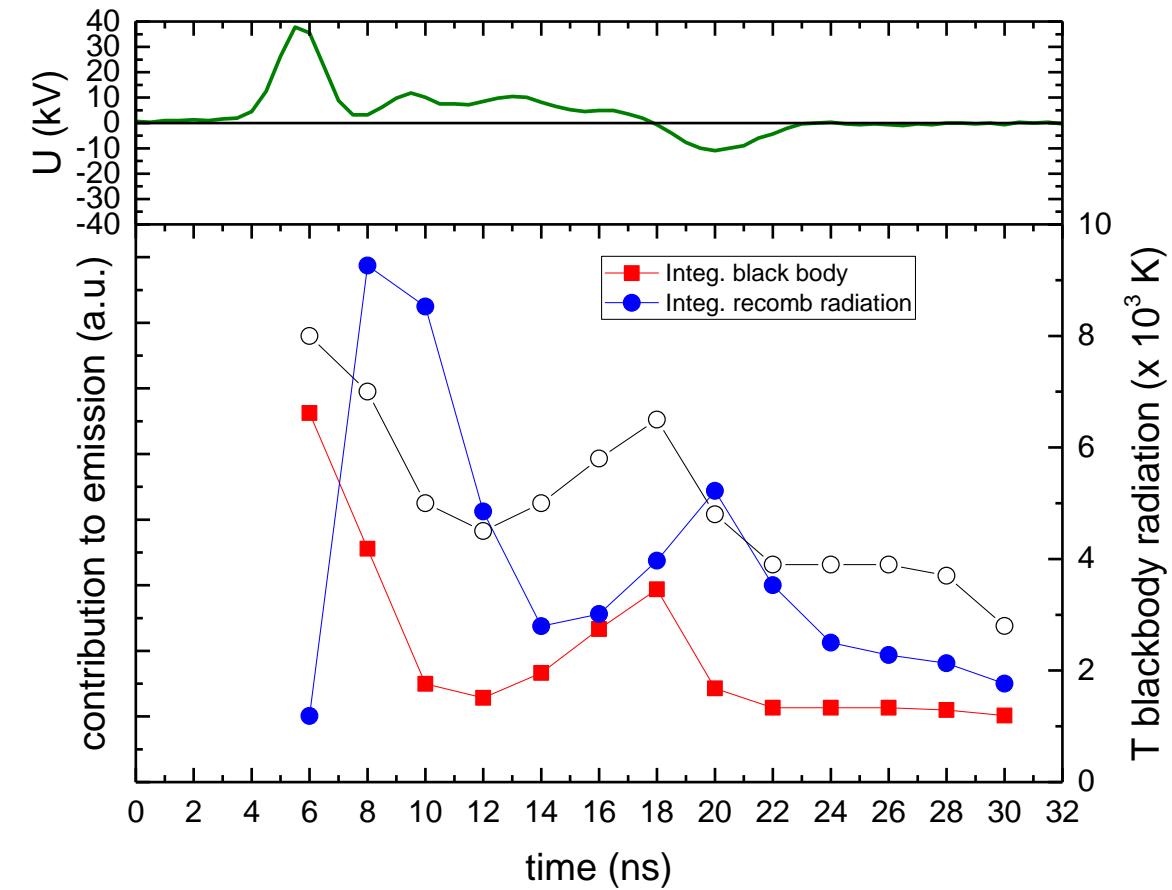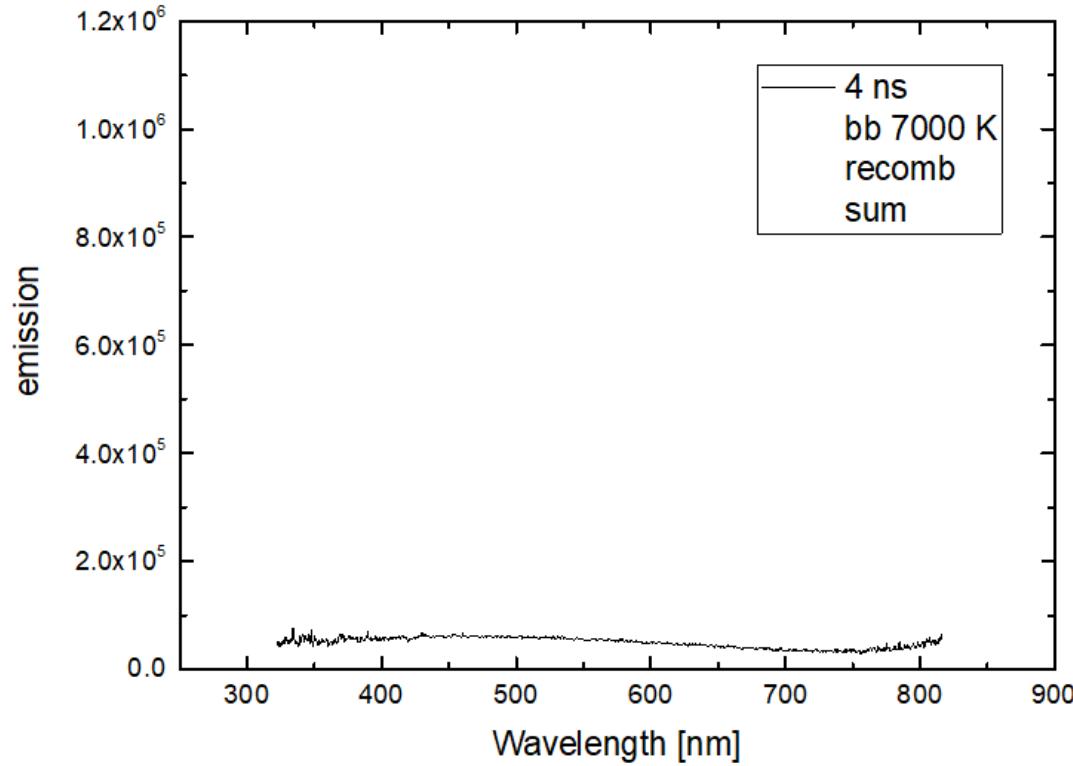
Tungsten tip

- Long term operation possible

- W as high melting temperature 3700 K

- W therm. conduct. 115 W / m K

- W oxidizes, melting temperature 1800 K

- Crystallites are formed
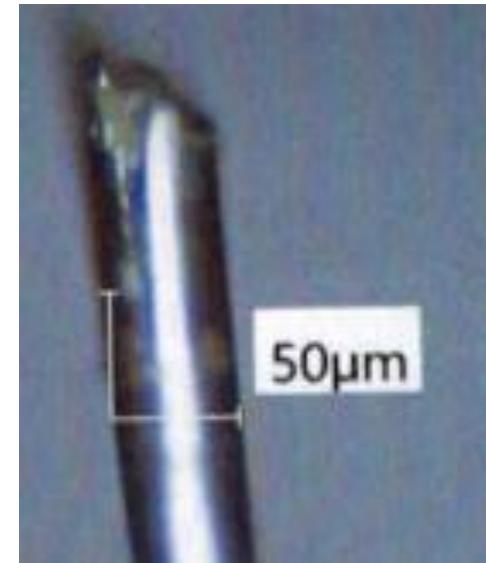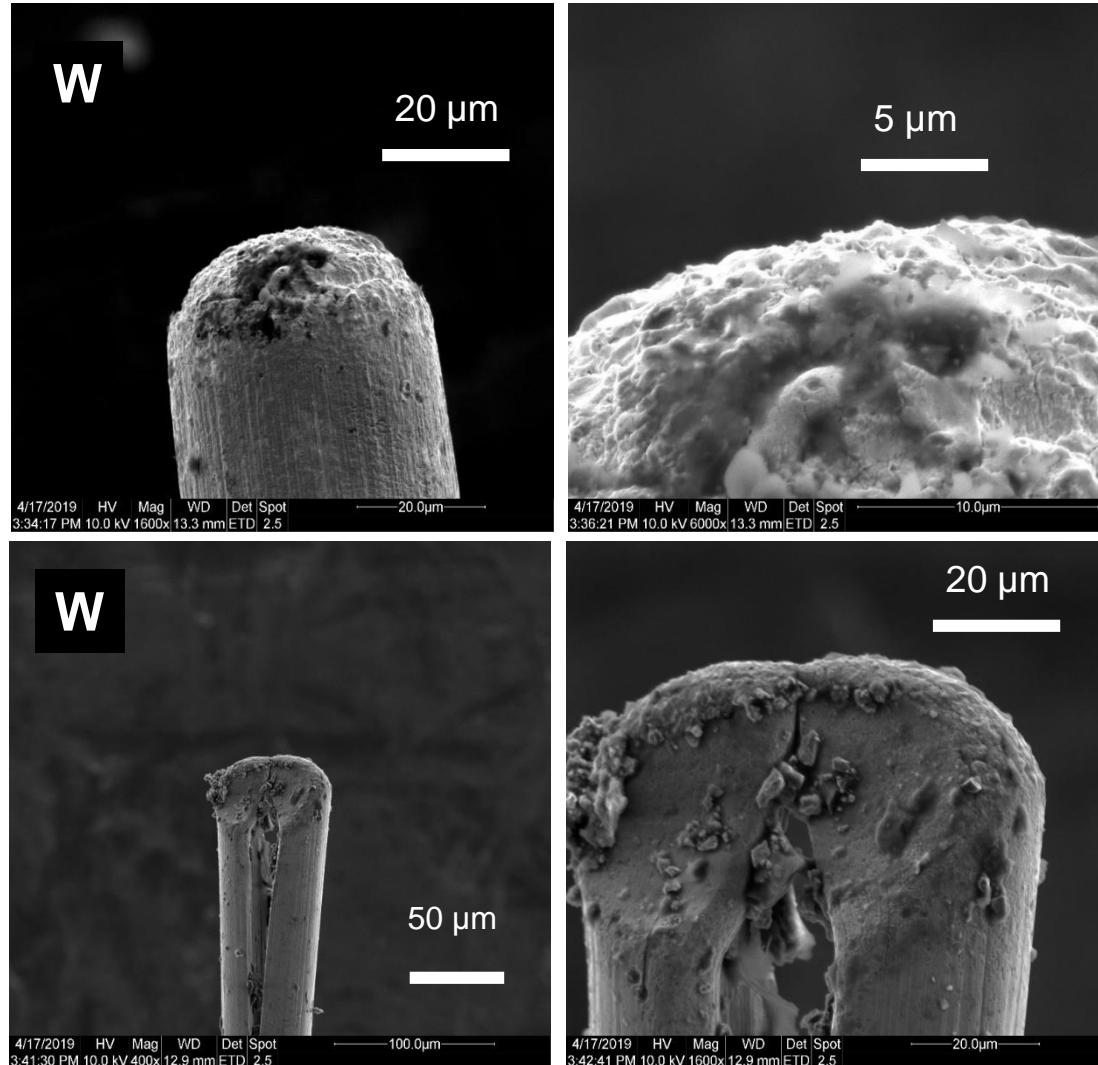
Short term use, < 7 h

long term use, ~ 30 h

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Platinum / Iridium tip (from AFM/SEM microscopes with 5..10 nm tip radius)

- Only short term operation possible

- After 1 h no plasma ignition possible anymore

- Pt melting temperature 2100 K

- Pt thermal conduct. 82 W/ m K

- Ir melting temperature 2700 K

- only Ir oxidizes
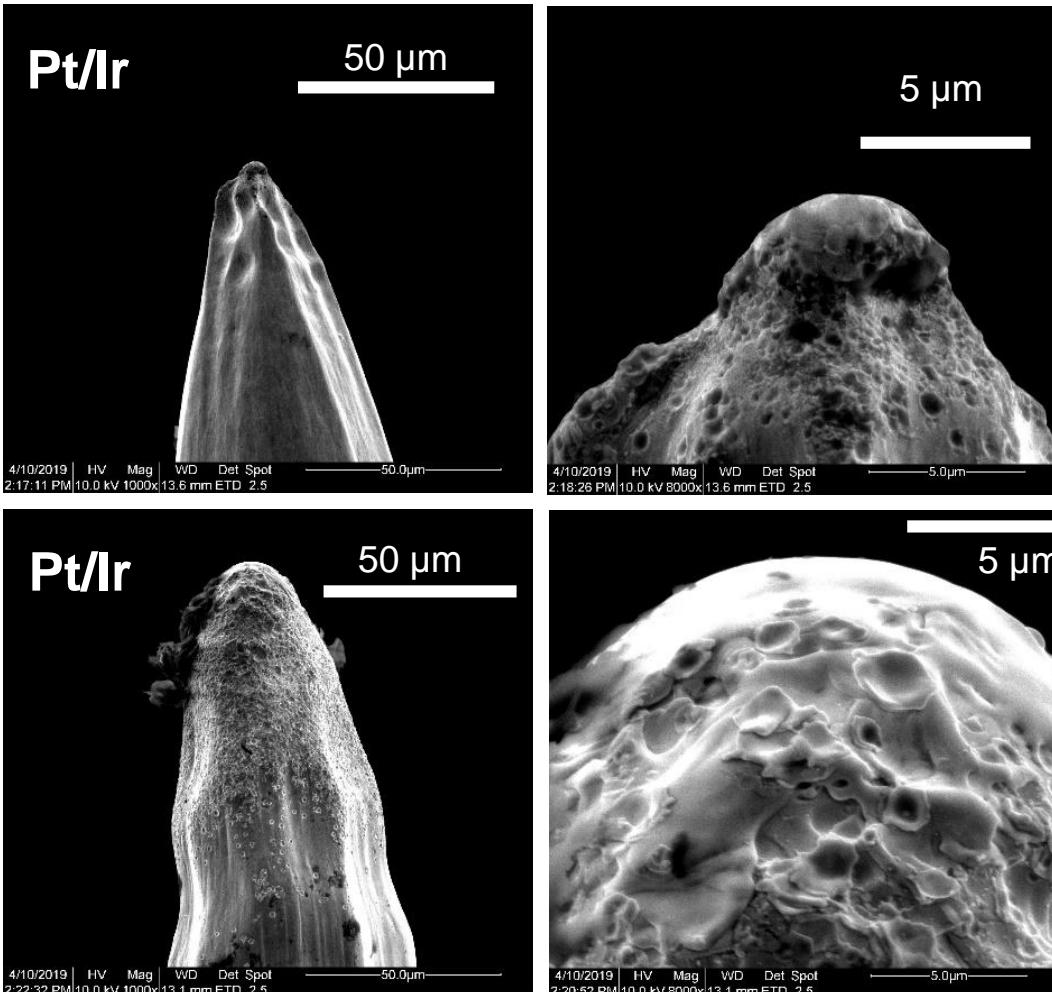
Short term use, 2 min

long term use, ~ 1 h

Dissipated energy during plasma ignition within the first 10 ns – comparison to experiments

4.5 x 10⁻³ J forward vs. reflected power

In ns plasmas at very high initial pressure, most of the energy is transferred to the sound wave

$$E_s = \frac{4\pi r^2}{\rho c} \int p_s^2 \, dt,$$

5 Gpa, R0 = 25 µm, U ~ 20 kV

59   **Chemistry in Plasma Treated Liquids** | A. von Keudell et al.

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200 µm

200 µm

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Chemistry in Plasma Treated Liquids | A. von Keudell et al.

Nature of the 1/λˣ background in emission – cathode spots on the tungsten electrode

Chemistry in Plasma Treated Liquids | A. von Keudell et al.
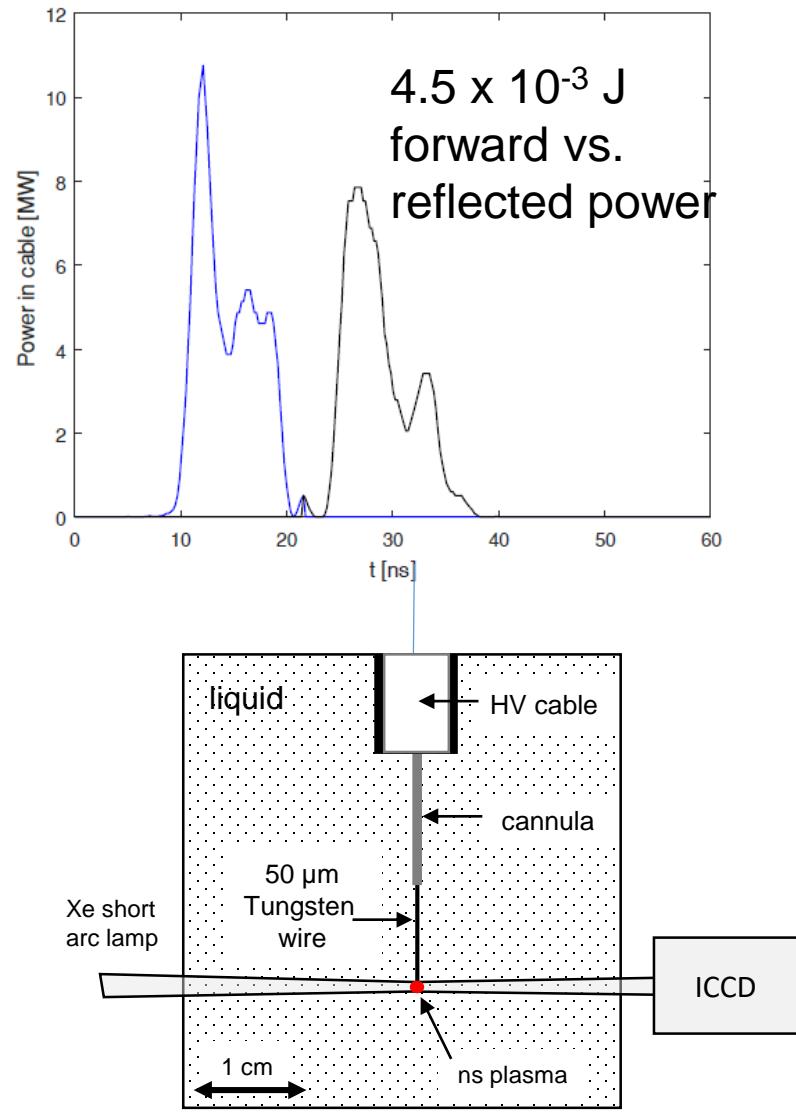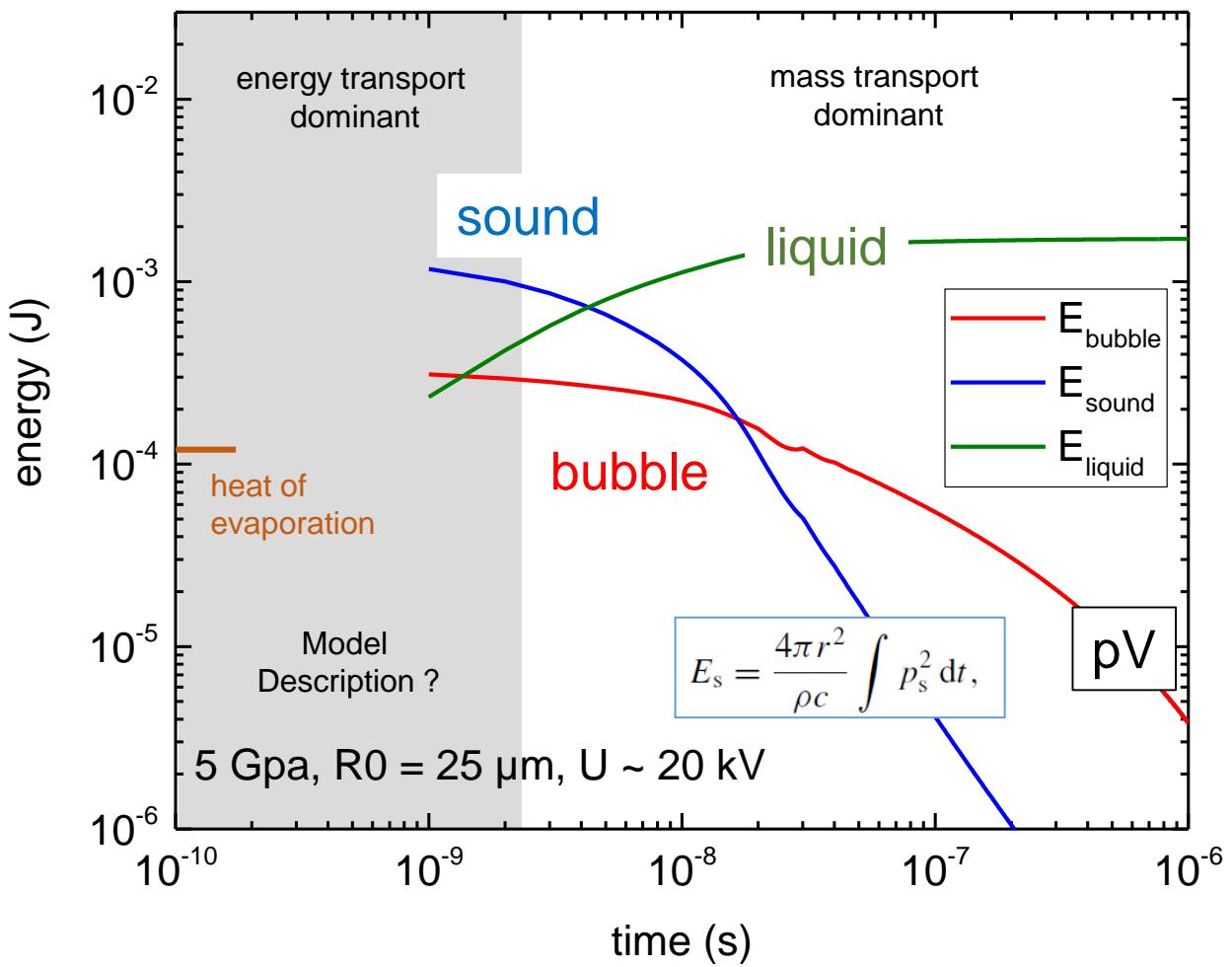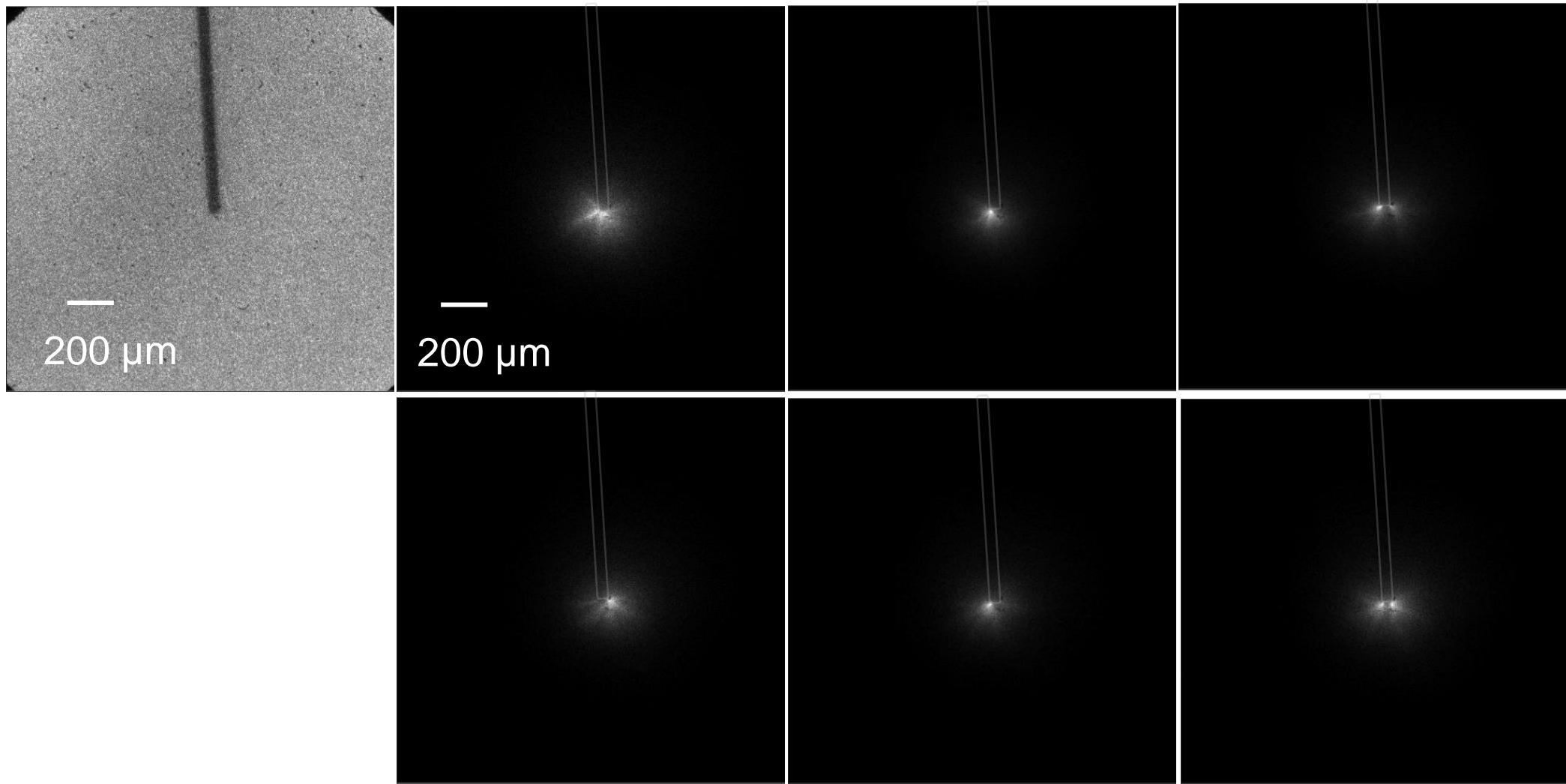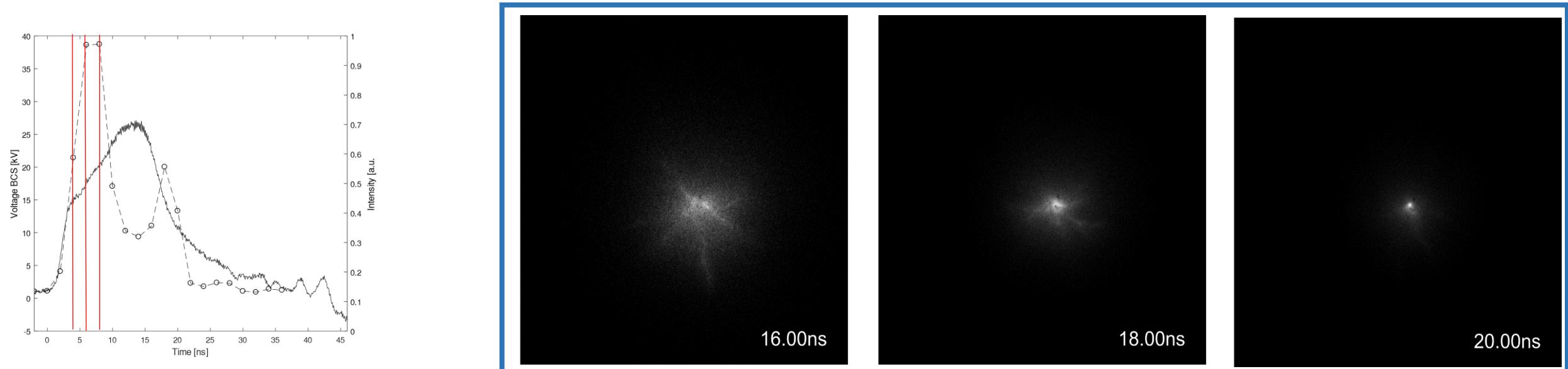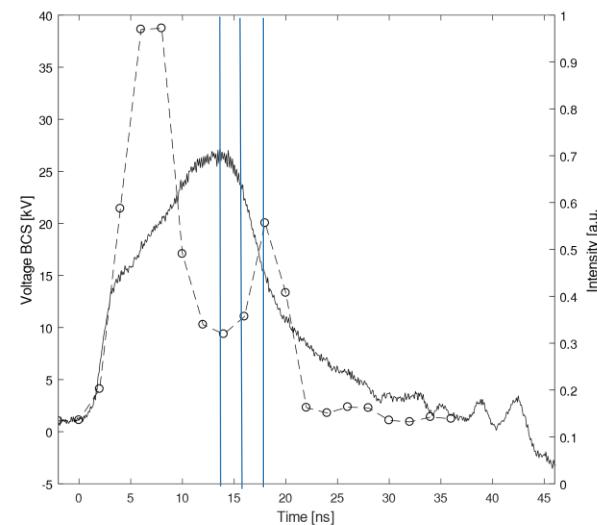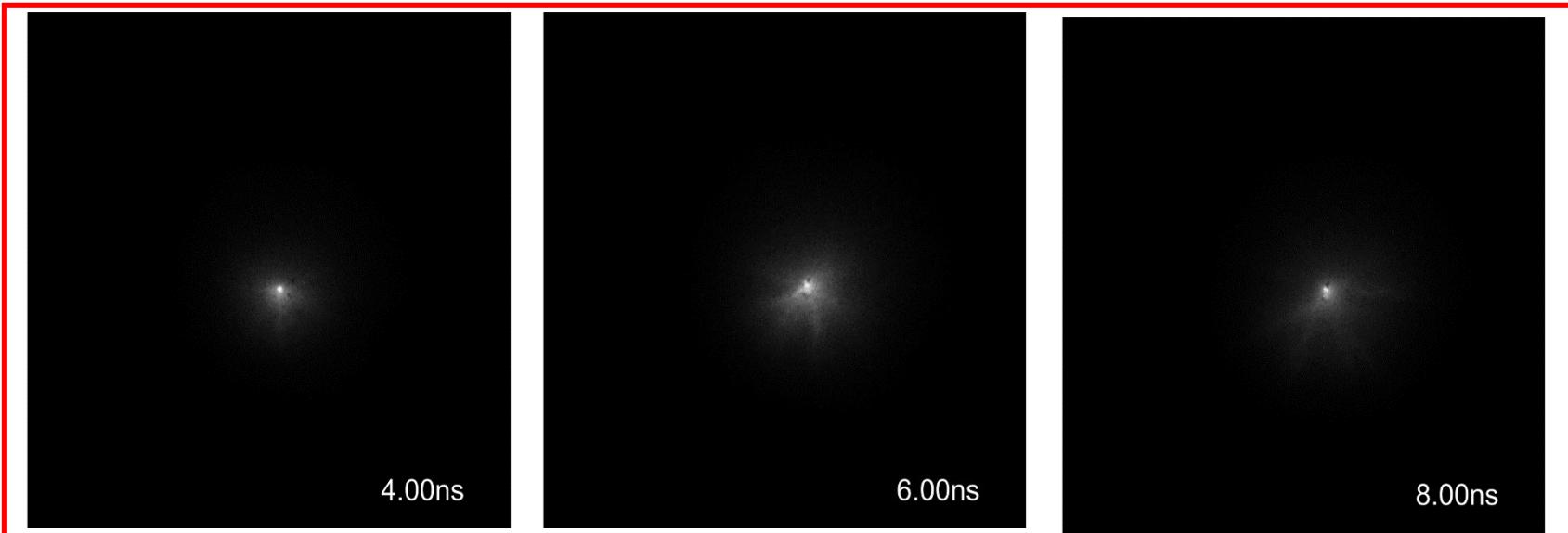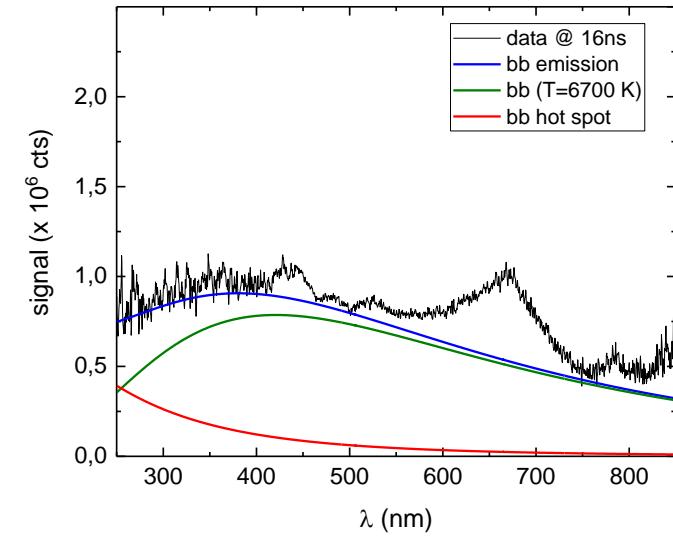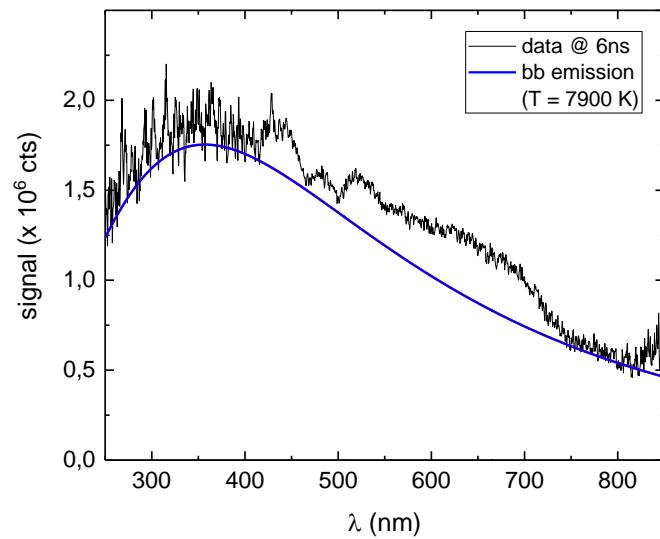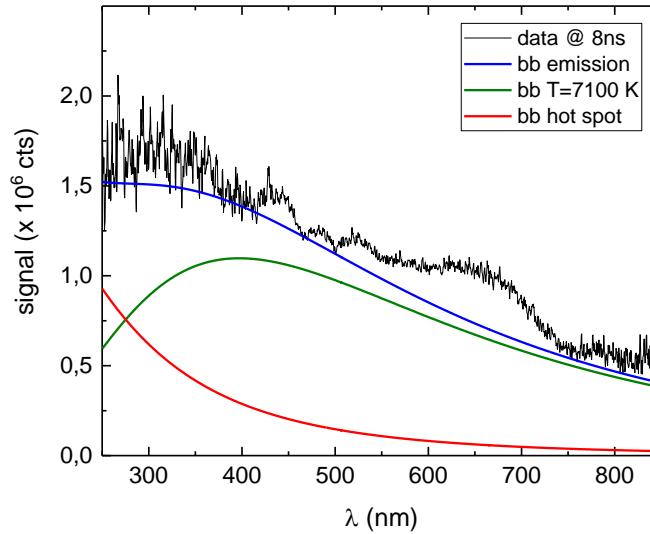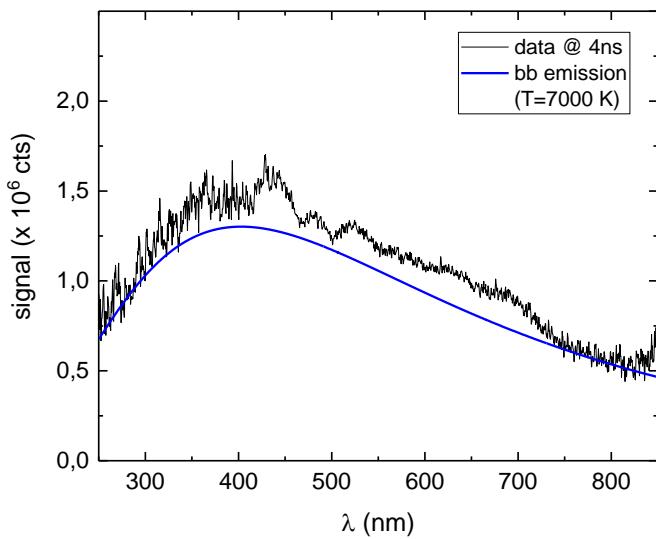
$<p>_{initial}$ scales with the dissipated energy

$$p_0 V_0 / \Delta t = P_{electrical} = U^2 / R$$

for R= 2.5 kOhm

p_0, V_0

r = 25 µm
t = 10ns

T ~ 2000… 70000 K

Ignition plasma

$<p>_{initial}$, $p_{0,gas}$ (GPa)

U_{HV} (kV)

- data
- $p_{initial} \sim U^2$
- $p_{0,gas}$ from cavitation theory

from sound waves

from cavitation model

26 ns
0.5 mm
gate 2ns

28 ns
gate 2ns

44 ns
gate 70ns

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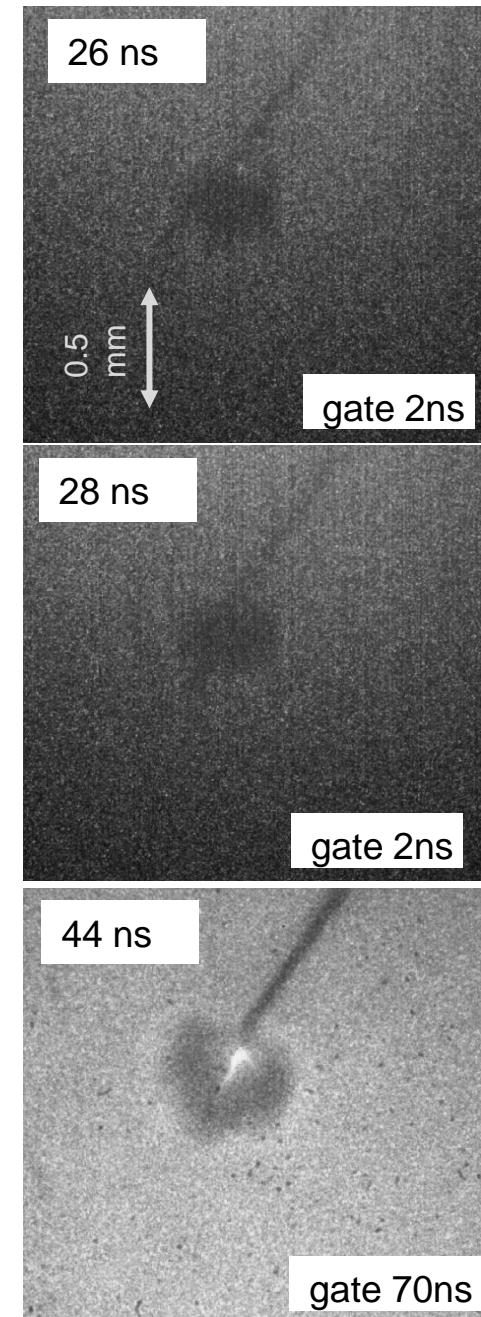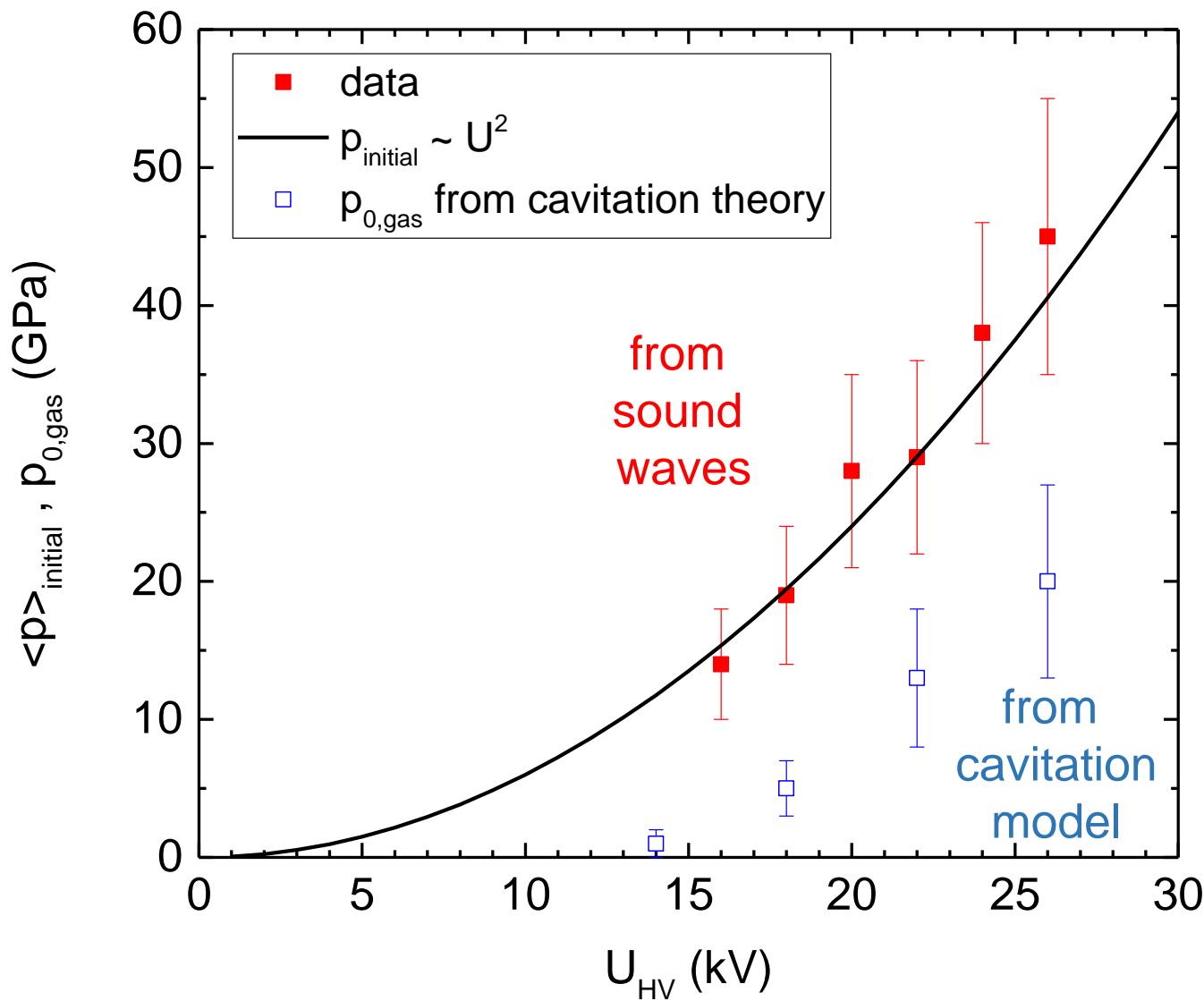
Transition of the water vapor in the bubble through the phase diagram of water

Solution for R(t) assuming a compressible liquid and condensation of vapor species

Balance between
surface flux and
volume loss depending
on R,
β=sticking coeff. = 1

$$\frac{1}{4}nv_{therm}4\pi R^2\beta = \frac{4\pi}{3}R^3 n\frac{1}{\tau}$$

$$\tau = \frac{4R}{3v_{therm}\beta}$$

$$p_0 \rightarrow p_0 \exp\left(-\frac{t}{\tau}\right)$$

$$p(t) \rightarrow p_0 \exp\left(-\frac{t}{\tau}\right)\left(\frac{R_0}{R}\right)^{3\gamma}$$

super critical water

0.5 mm

44 ns

1 mm

1µs

Plasma in a bubble expansion

everything to scale

Ignition sequence

20 bar
5 µm
240 bar

25 bar @ 300 K
5 µm

10 000 bar @ 150000 K

sound wave

r_{max} =600 µm
t=60 µs

r_{min} =5 µm
t=100 µs

gas

collapse

r = 5 µm
t = 1ns

r = 25 µm
t = 10ns

r = 50 µm
t = 100 ns

r = 80 µm
t = 200 ns

r = 100 µm
t = 400 ns

sound wave

Ignition plasma

supercrit. vapor

conden-sation

re-heated

re-heated

re-heated

$n_0=3 \cdot 10^{28}$ m^{-3}
$n_e=3 \cdot 10^{28}$ m^{-3}
$p=10^{11}$ Pa

$n_0=3 \cdot 10^{28}$ m^{-3}
$p=5 \cdot 10^8$ Pa
T = 1200 K

$n_0=2.6 \cdot 10^{27}$ m^{-3}
$n_e=10^{25}$ m^{-3}
$p=2 \cdot 10^7$ Pa
T=550 K

$n_0=1.6 \cdot 10^{27}$ m^{-3}
$n_e=10^{23}$ m^{-3}
$p=10^7$ Pa
T= 450 K

$n_0=2.8 \cdot 10^{26}$ m^{-3}
$p=10^6$ Pa
T= 260 K

$n_0=1.4 \cdot 10^{24}$ m^{-3}
$p=10^3$ Pa
T=50 K

Chemistry in Plasma Treated Liquids | A. von Keudell et al.

How does the plasma Ignites ?

Experiment 22kV, 1Hz, distilled water, t_{gate}=2ns, t_{step}=2ns

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How does the plasma Ignites ?

Experiment 22kV, 1Hz, distilled water, t_{gate}=2ns, t_{step}=2ns

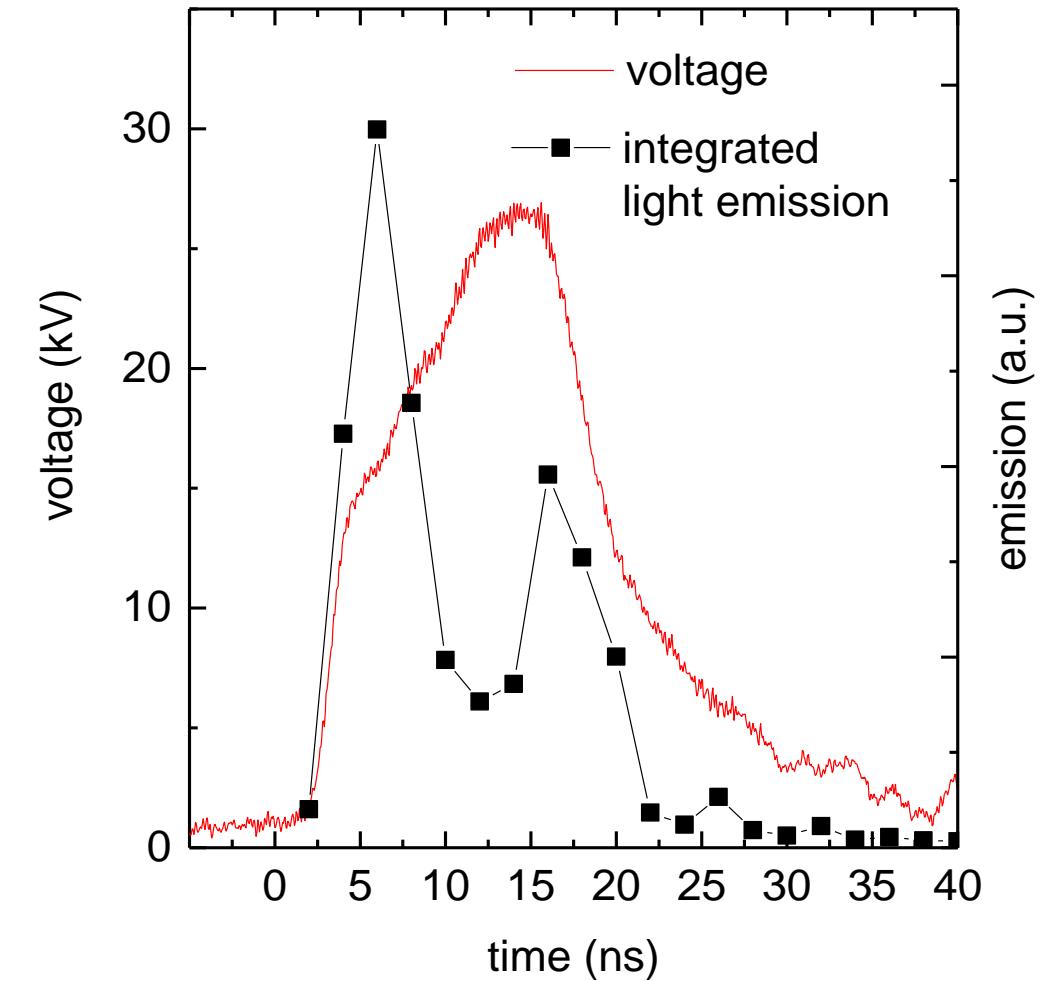**Chemistry in Plasma Treated Liquids** | A. von Keudell et al.
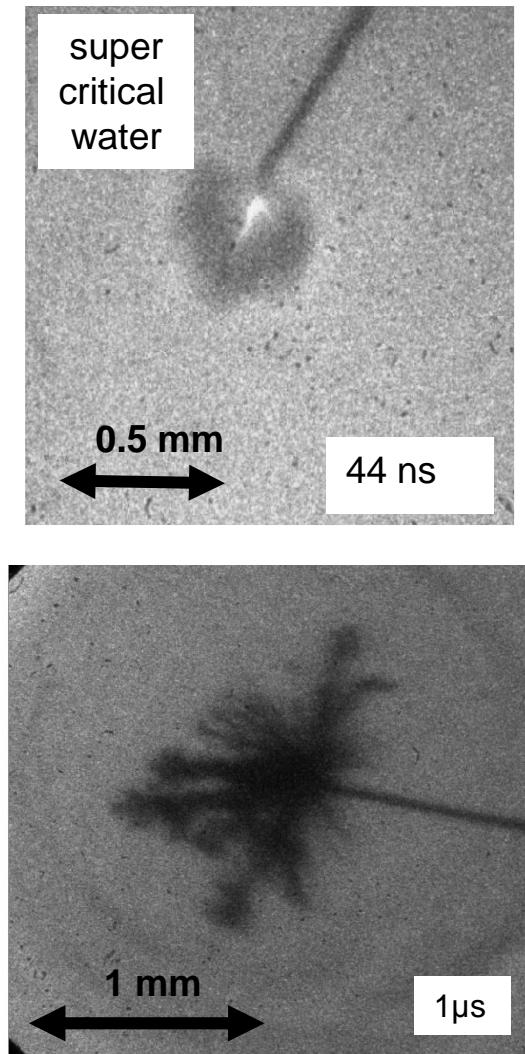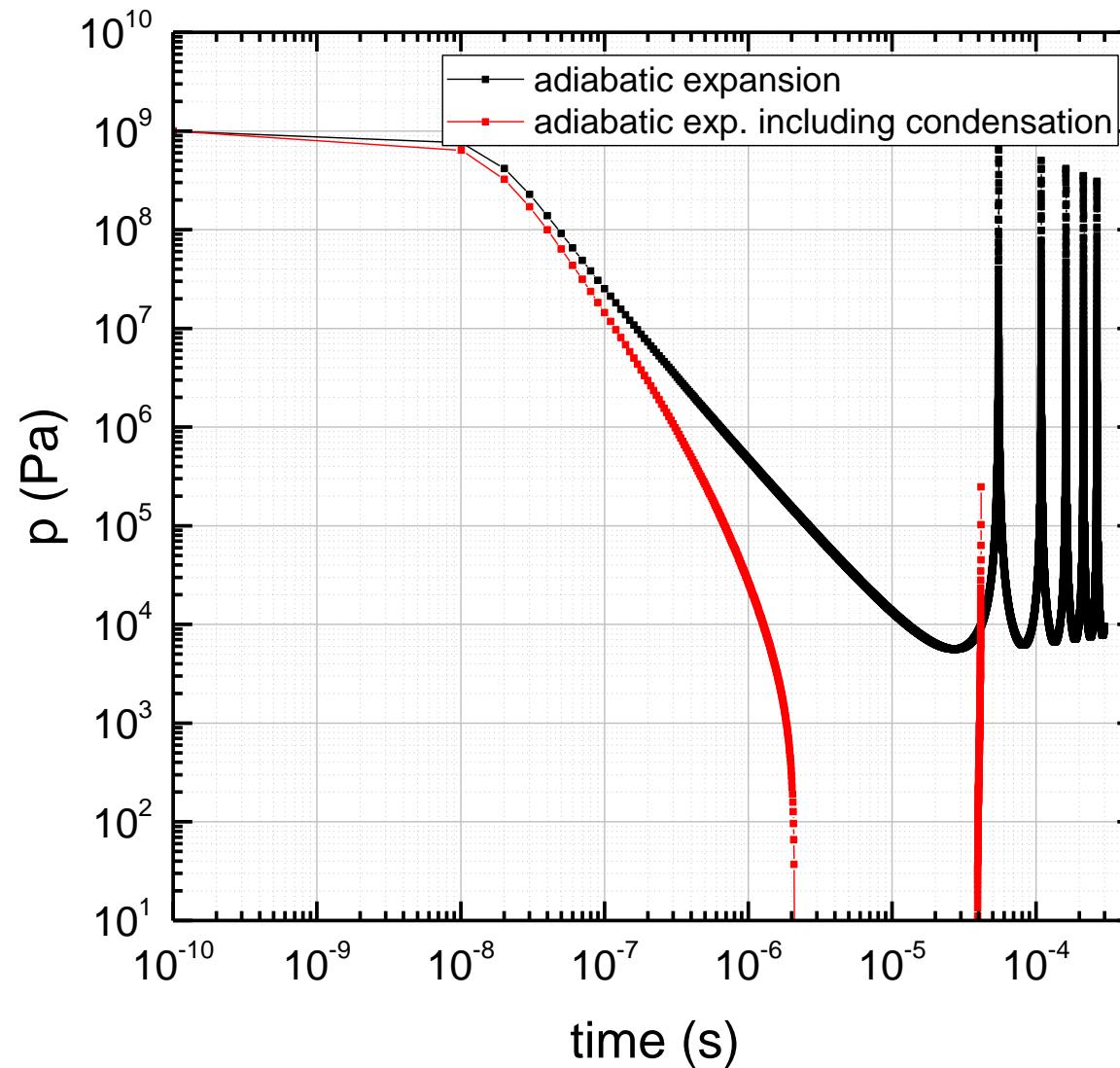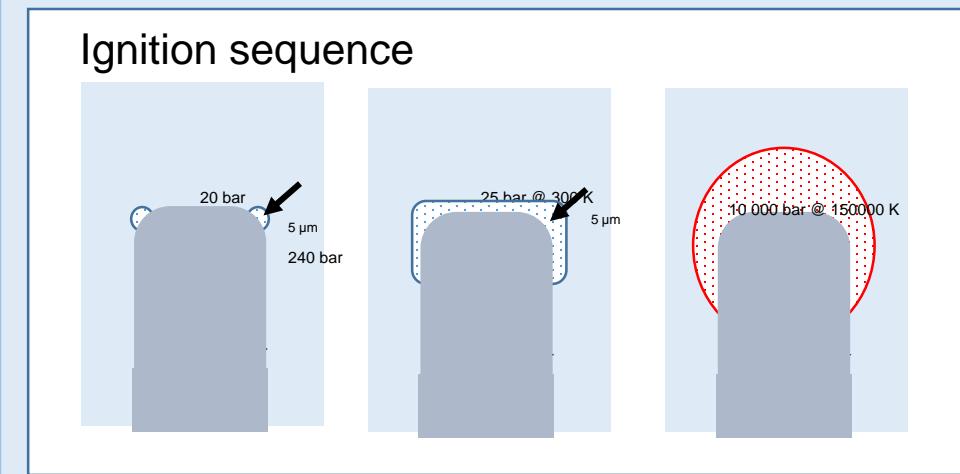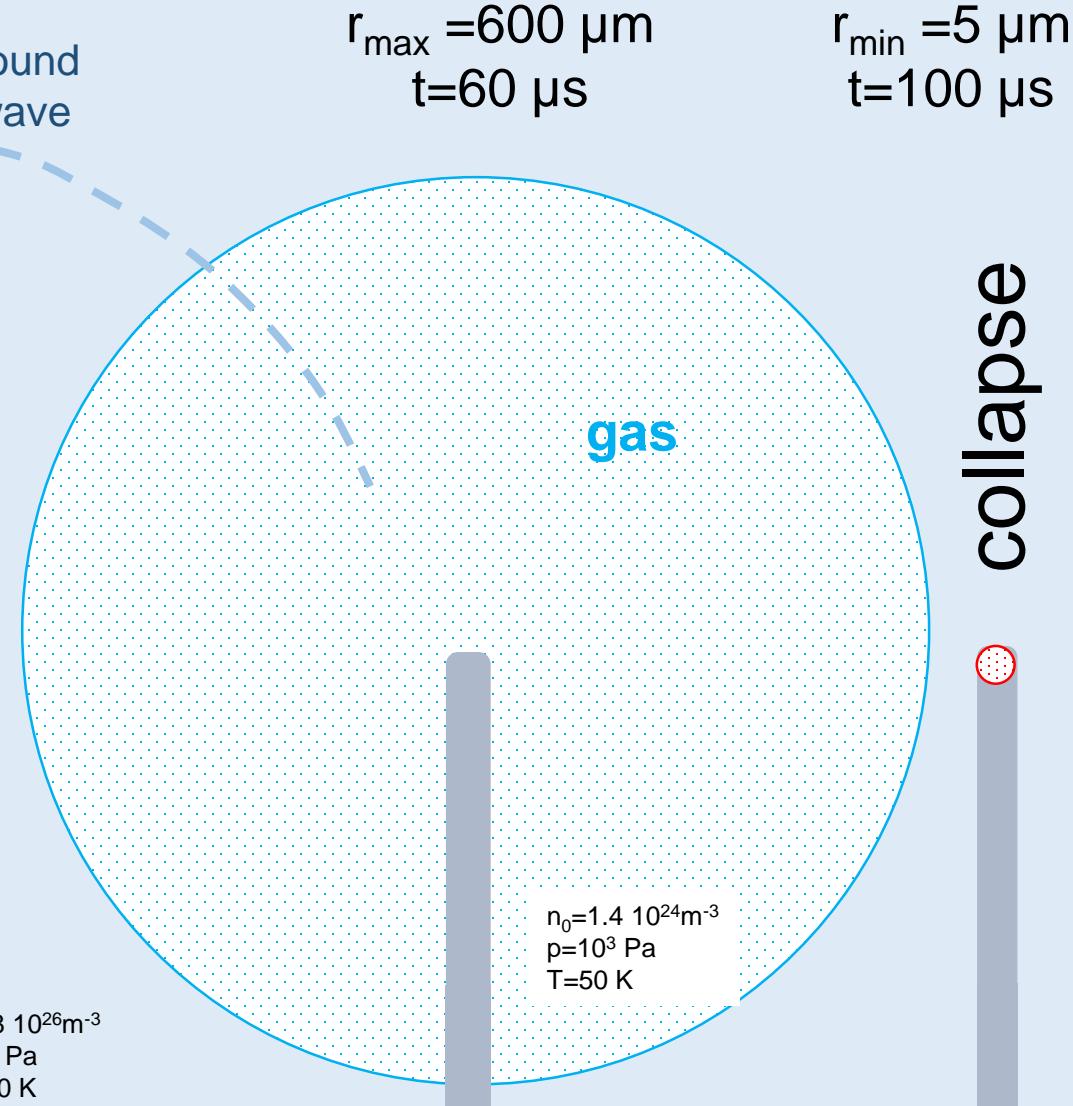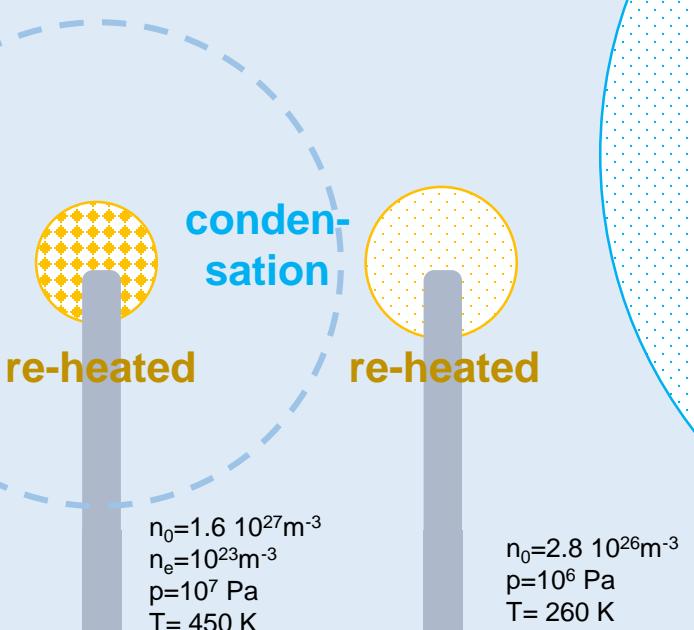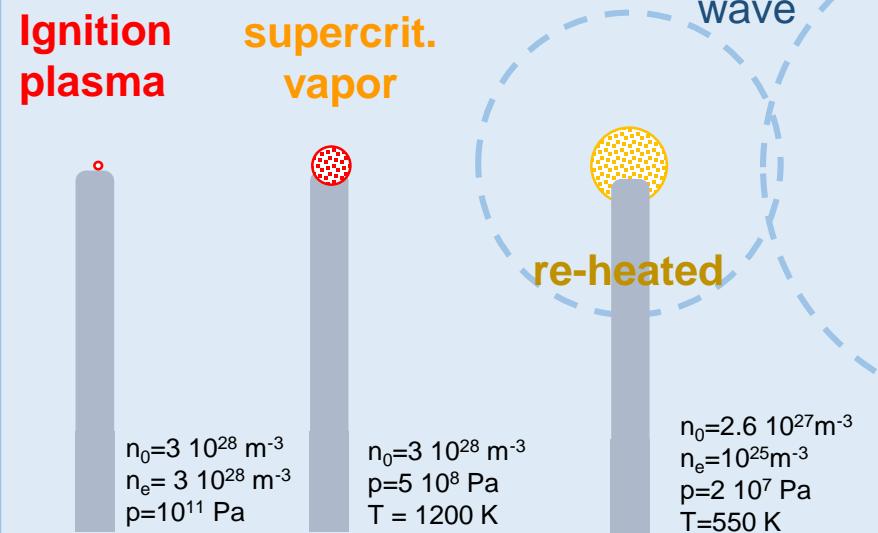
Comparison to Modeling of Streamer Propagation in 80 bar supercritical N2

ns plasma in liquids:
Due to the inertia of the liquid, no bobble formation on ns time scale, so standard ignition in the gas trapped inside a bubble according to Paschen law is impossible

Nanopores (Dobryn et al. JPD 46, 355201 (2013)
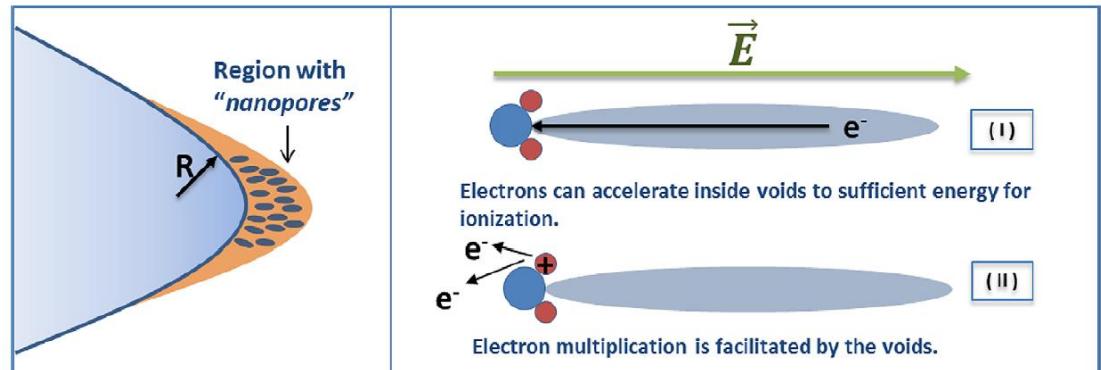
Field emission, field ionization

field emission/ionization of H_2O at ~ 0.3…0.6 V/Å

(a)
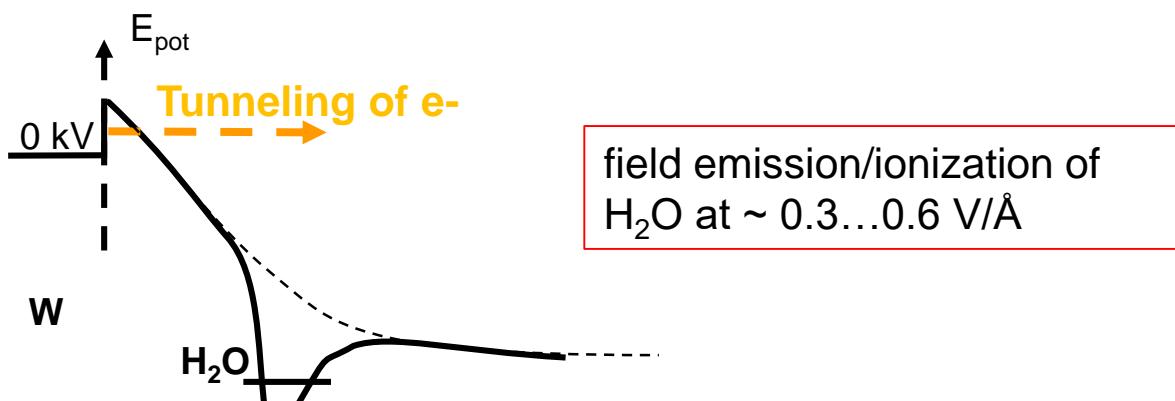
From A. Sun, J. Teunissen, U. Ebert
IEEE Trans. Plas. Sci. 42, 2416 (2014)
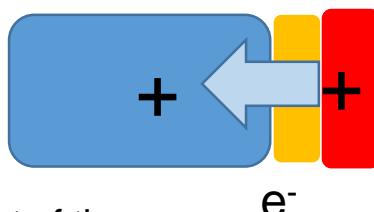
Streamer v ~ 1000 km/s

Field emission effects
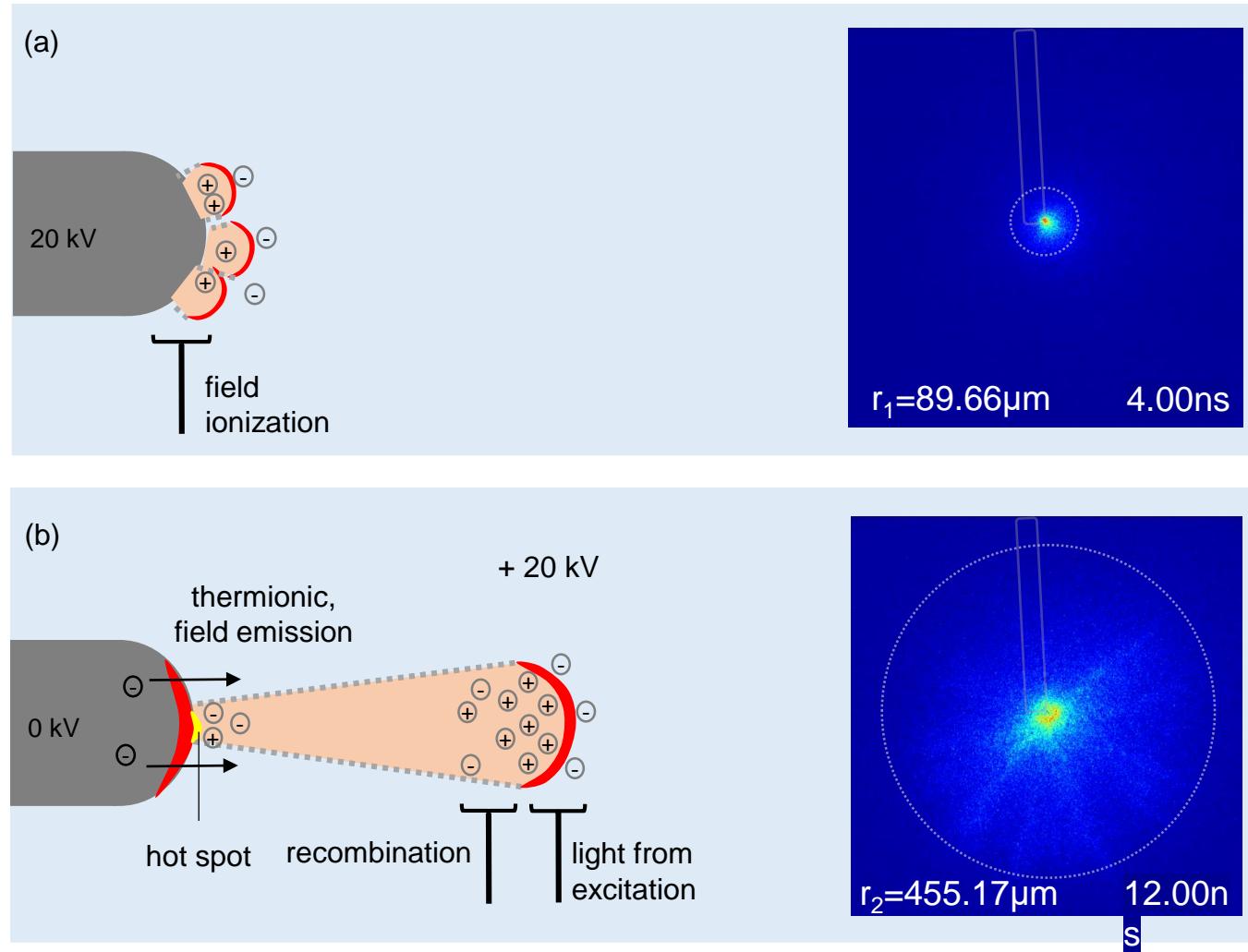
Start of the pulse water is polarized **Field ionization**
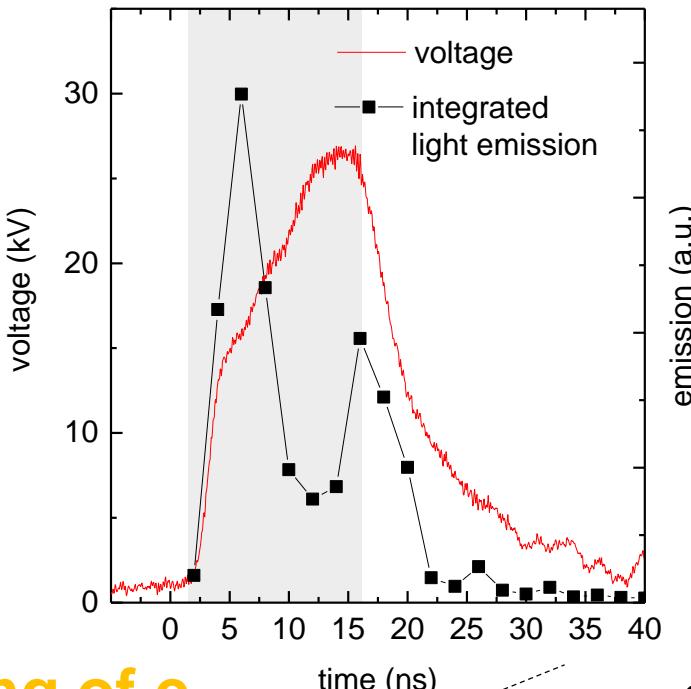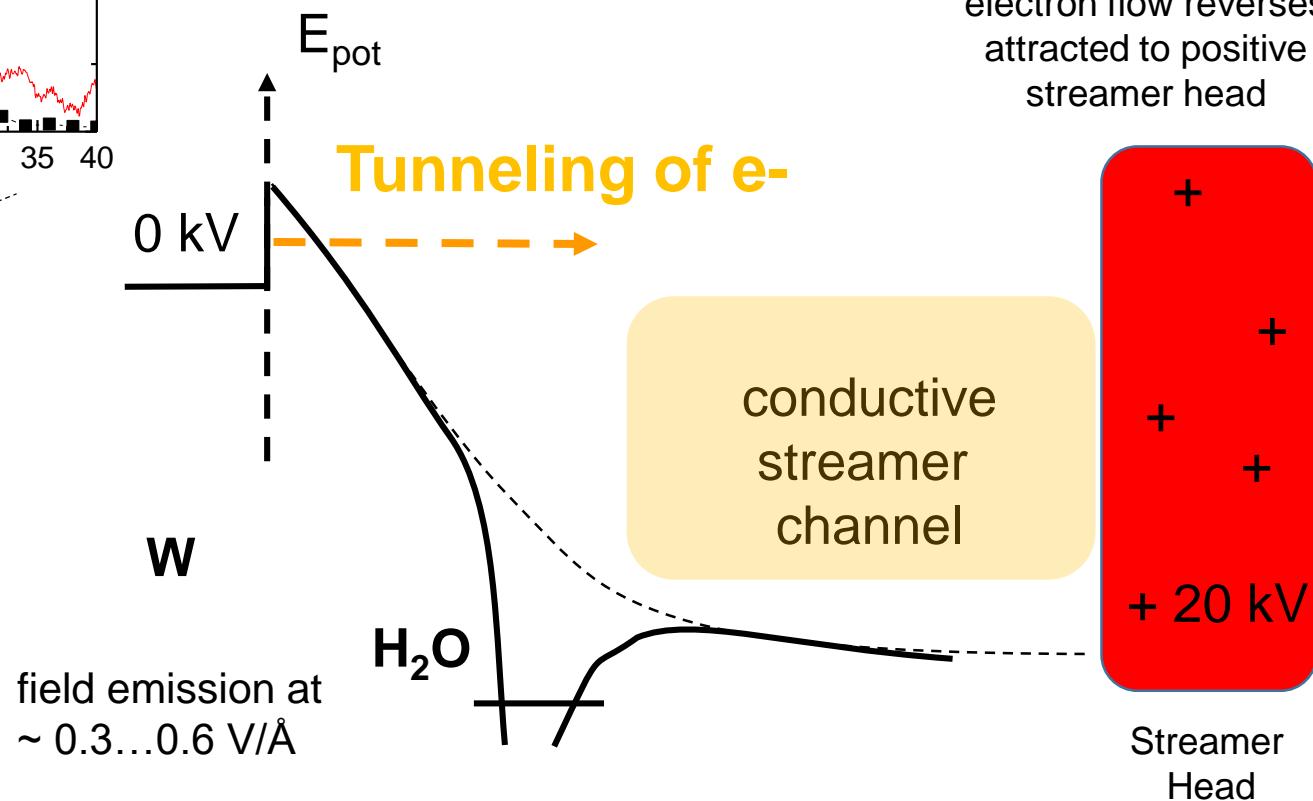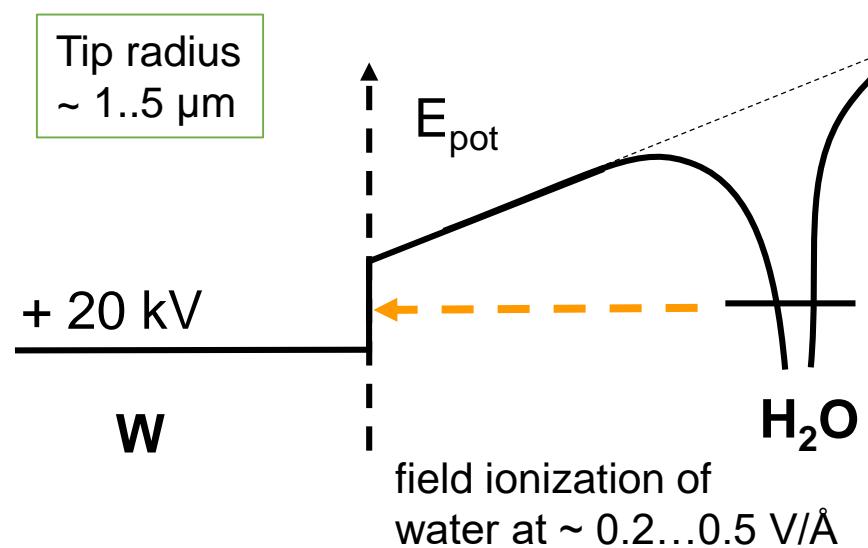
e-

voltage

integrated light emission

voltage (kV)

emission (a.u.)

time (ns)

Voltage stops, **Field emission** electron flow reverses attracted to positive streamer head

0

~ mm

e-

Tunneling of e-

Tip radius ~ 1..5 µm

E_{pot}

+ 20 kV

W

H_2O

field ionization of water at ~ 0.2…0.5 V/Å

E_{pot}

0 kV

Tunneling of e-

W

H_2O

field emission at ~ 0.3…0.6 V/Å

conductive streamer channel

+

+

+

+

+ 20 kV

Streamer Head

How does the plasma Ignites ?

Experiment 22kV, 1Hz, distilled water, t_{gate}=2ns, t_{step}=2ns

Chemistry in Plasma Treated Liquids | A. von Keudell et al.

Tungsten tip vs. Platinum/Iridium tip

- W as high melting temperature 3700 K
- W therm. conduct. 115 W / m K
- W oxidizes, Crystallites are formed

- Pt melting temperature 2100 K
- Pt thermal conduct. 82 W/ m K
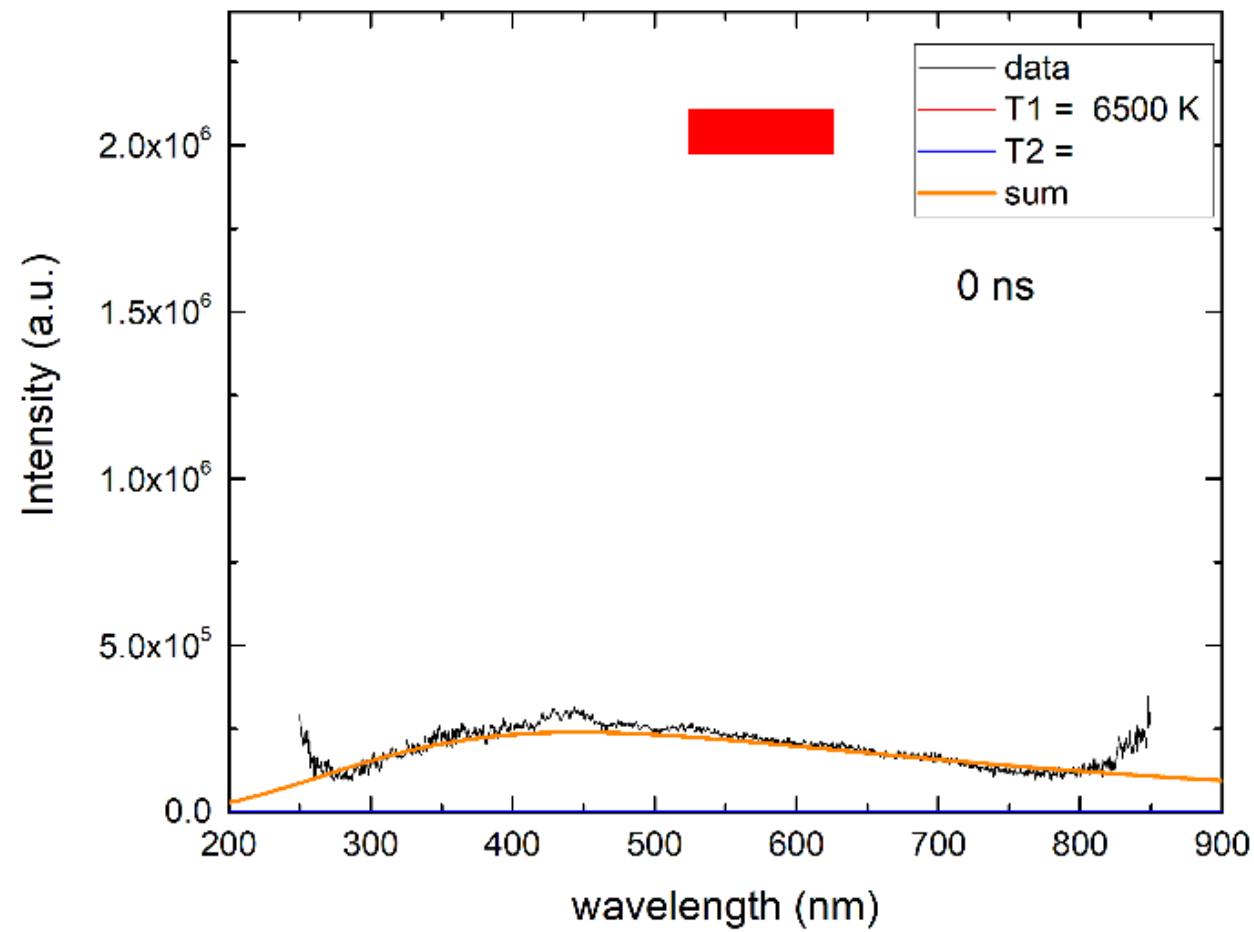- Ir melting temperature 2700 K
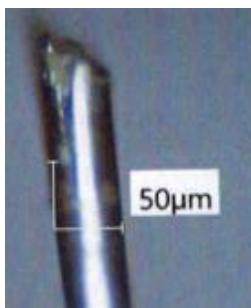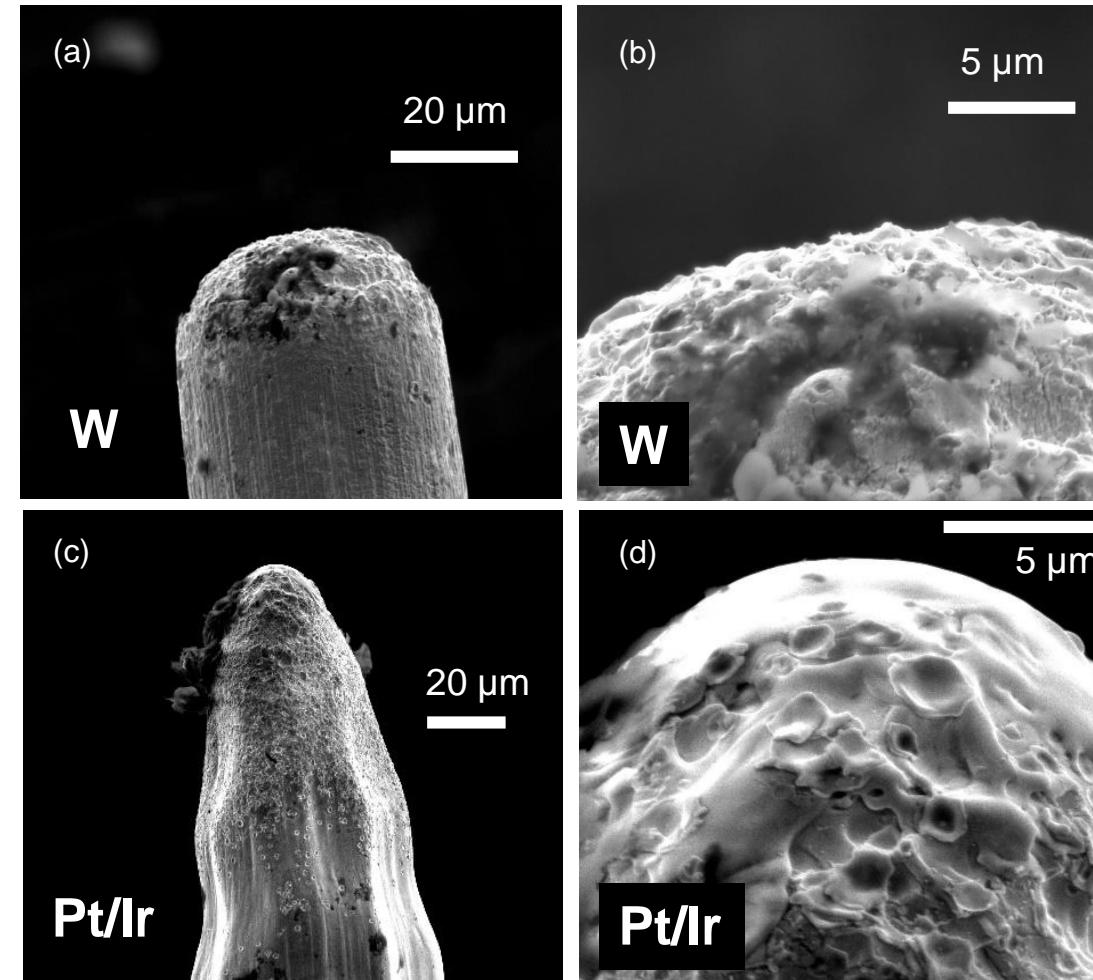
Permanent operation possible

Ignition stops after 1 h of operation

Temperatures from emission spectra of the plasma into the UV

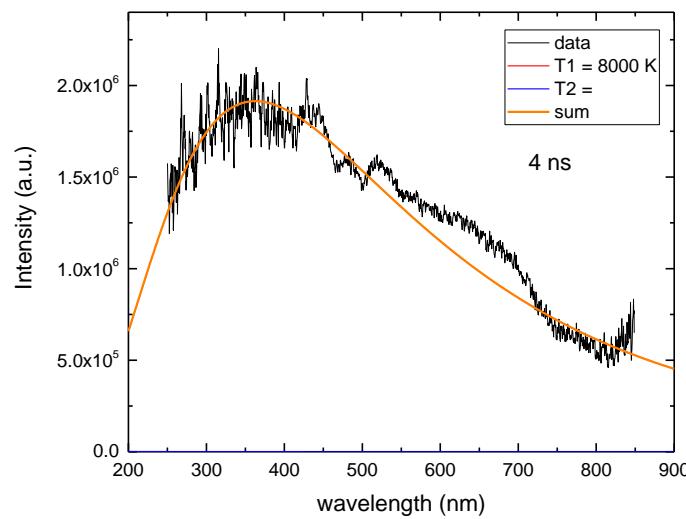Spectrum (first 50 ns, time resolution 2 ns)
- Recombination
- H_2, H_2O recomb. continuum
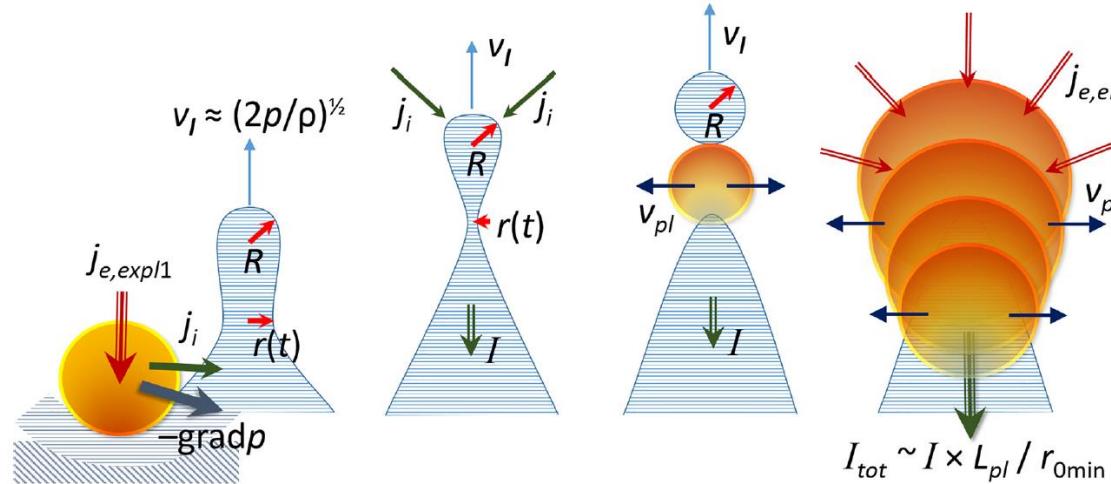- OH, OH^+, H_2O, H_2O^+ bands
- Black body radiation (W)
- H_α
- $O_{(777nm)}$

Chemistry in Plasma Treated Liquids | A. von Keudell et al.

Temperatures from emission spectra of the plasma UV part

Spectrum (first 50 ns, time resolution 2 ns)

- Recombination
- H_2, H_2O recomb. continuum
- OH, OH^+, H_2O, H_2O^+ bands
- Black body radiation (W)
- H_α
- $O_{(777nm)}$

Chemistry in Plasma Treated Liquids | A. von Keudell et al.

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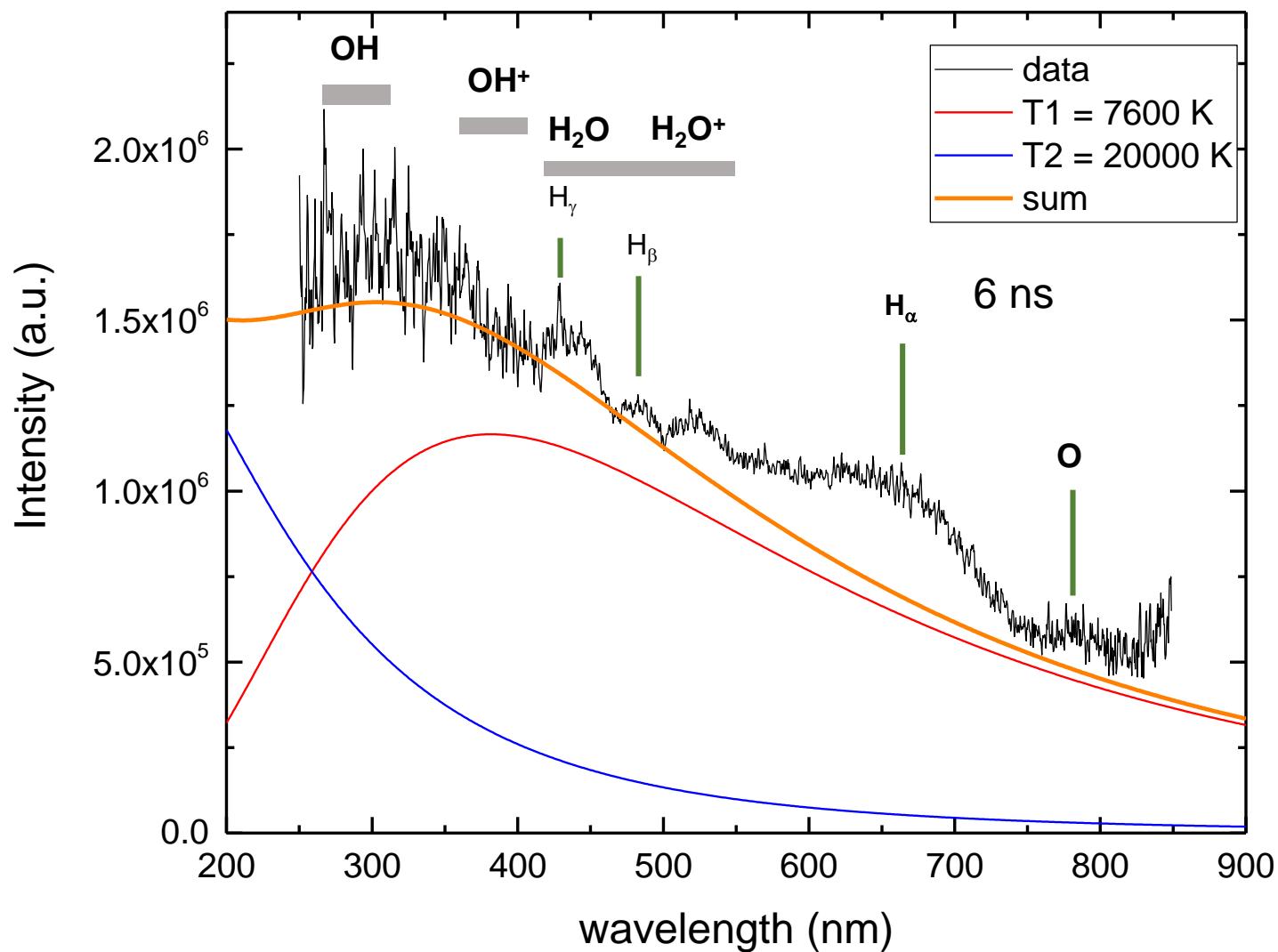
Nature of the 1/λˣ background in emission

Possible sources for $1/\lambda^x$ background
- H_2O, H_2 recombination background (300…500 nm, no part down to 250 nm)
- $1/\lambda^2$ recombination radiation free-free, bound-free
- $1/\lambda^5$ long wavelength part of the emission of a hot cathode spot

Example cathode spot in vacuum arcs T (15000...2000 K)

Cathode spots at W tips

Example cathode spots in arc lamps

$v_l \approx (2p/\rho)^{\frac{1}{2}}$

$I_{tot} \sim I \times L_{pl} / r_{0min}$

initial droplet R=1µm

Coulomb-explosion of the neck leads to metal plasma (10 µm diameter, $n_e \sim 10^{26}$ m⁻³,)

Tsventoukh, Phys. Plasmas 25, 53504 (2018)
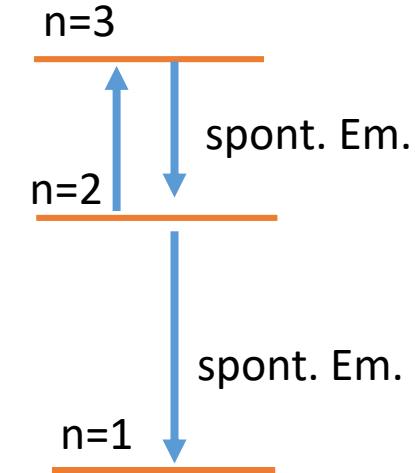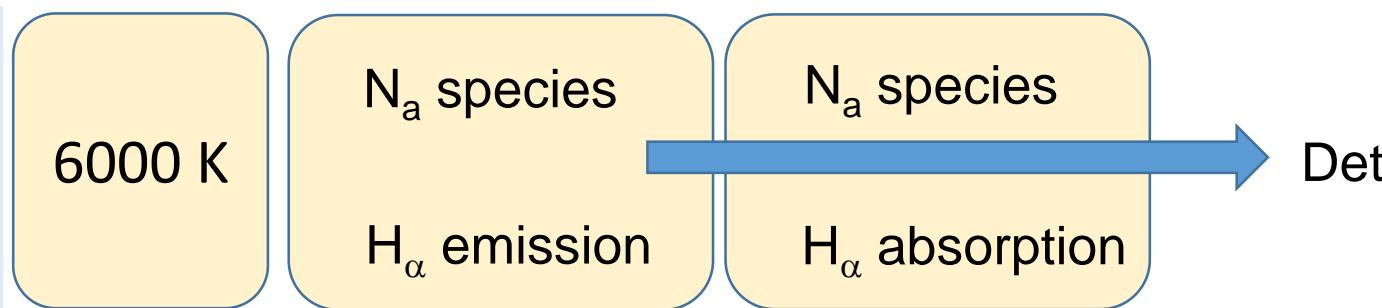
A. Bergner et al. PSST 23, 054005 (2014)

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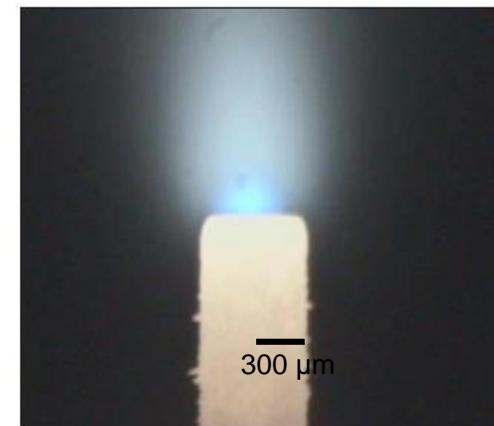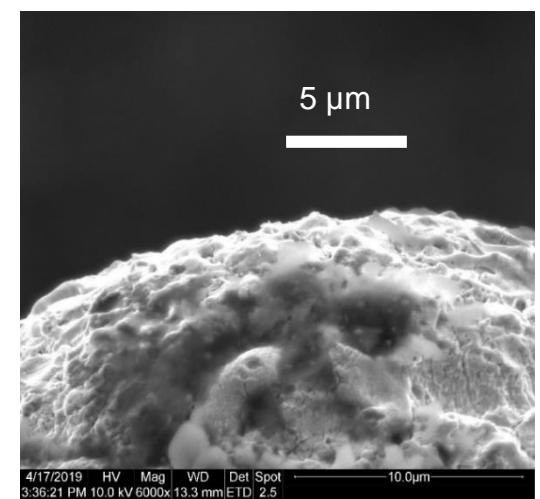
Line emission – Hydrogen Balmer Series

r=455.17µm   12.00ns

hot spot   plasma channel   ionization region

20 kV

tungsten electrode   tungsten tip at boiling temp.   recomb-ination region

data @ 4ns
background (T=7000 K)
data - background

H_γ H_β H_α

signal (cts)

λ (nm)
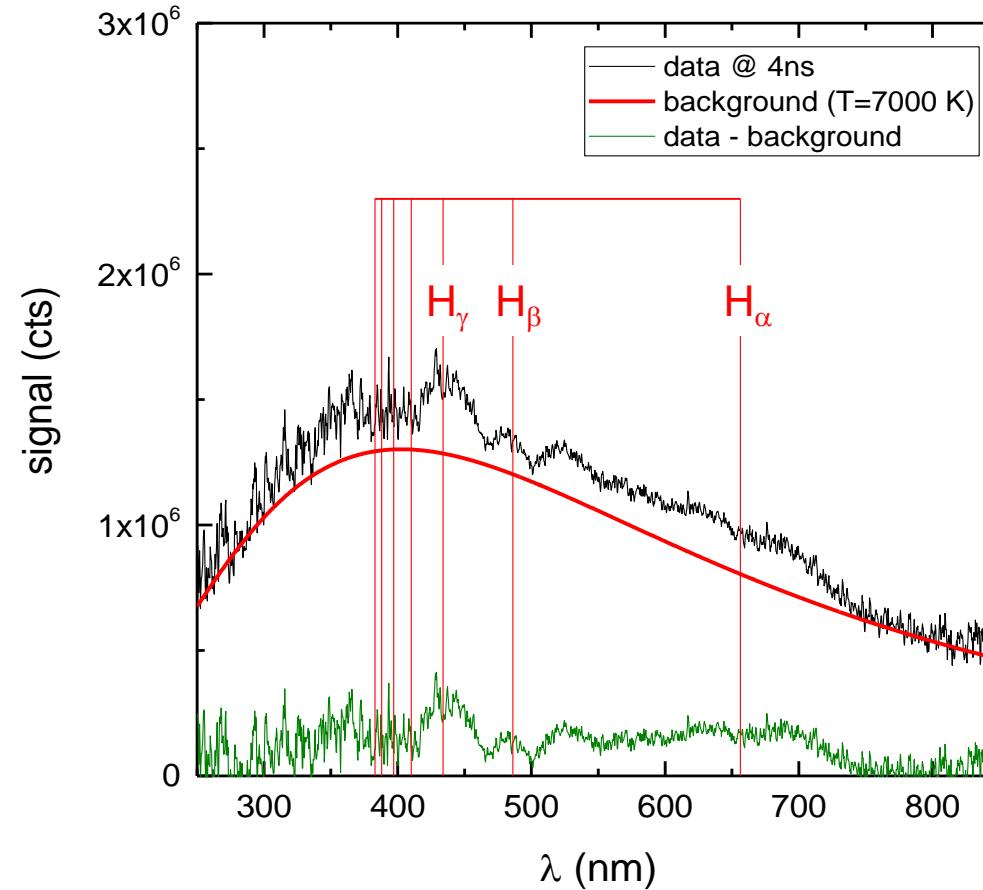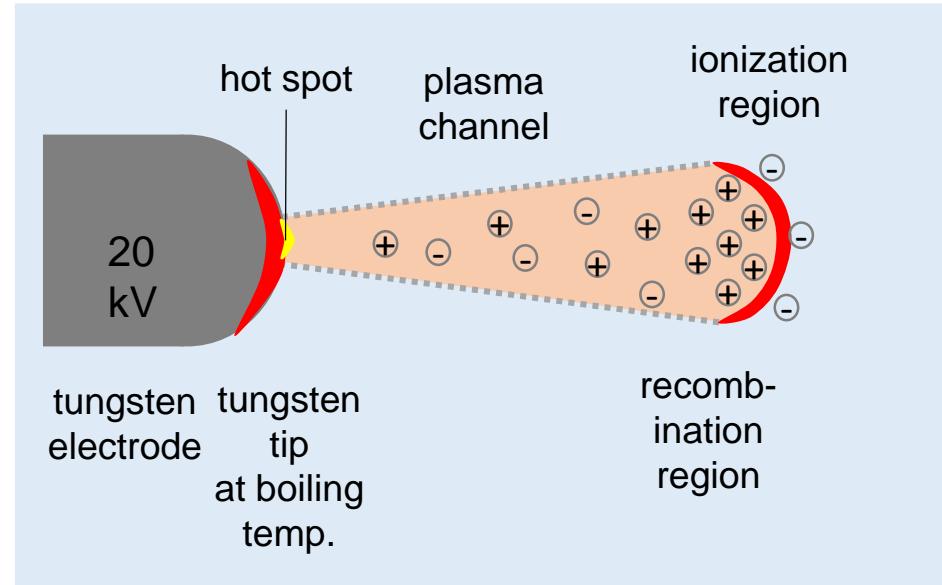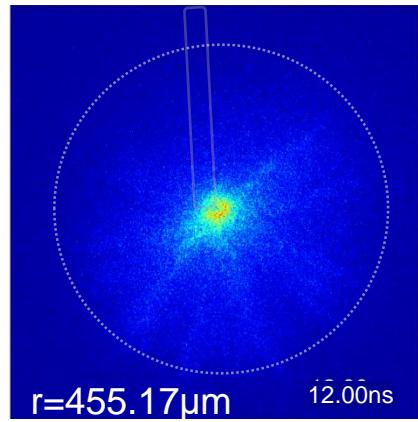
- H Balmer lines clearly visible
- Why is H_γ more pronounced than H_α ?

Line emission – Selfabsorption of Hydrogen Balmer Series

same number
of emitter
and absorber states
Line width
Hg, Hb, Ha
3 nm, 2nm, 10 nm

3,2,10
na = 4e8

same number
of emitter
and absorber states
Line width
Hg, Hb, Ha
3 nm, 2nm, 10 nm

3,2,10
na = 4e14

same number
of emitter
and absorber states
Line width
Hg, Hb, Ha
3 nm, 2nm, 10 nm

3,2,10
na = 4e16

absorption
wavelength (nm)

hot spot
plasma channel
ionization region
20 kV
tungsten electrode
tungsten tip at boiling temp.
recomb-ination region

6000 K

N_a species

H_α emission

N_a species

H_α absorption

Det.

n=3
spont. Em.
n=2
n=1
spont. Em.

Nature of the 1/λˣ background in emission – cathode spots on the tungsten electrode

(a) ionization region

$(n_e = 10^{24}\ m^{-3})$
$\Delta H_\alpha = 5\ nm$
$\Delta H_\beta = 23\ nm$
$\Delta H_\gamma = 28\ nm$
$N_a = 2 \times 10^{13}$

(b) recombination region

$(n_g = 3 \times 10^{27}\ m^{-3},\ T = 7000\ K)$
$\Delta H_\alpha = 6.5\ nm$
$\Delta H_\beta = 3.35\ nm$
$\Delta H_\gamma = 2.6\ nm$
$N_a = 1e16$

Three contributions
- Continuum blackbody ~ 6000 – 7000 K
- H Balmer strong self absorption - recombination region (Hγ dominates)
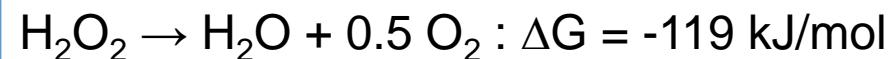- H Balmer small self absorption - ionization region (Hα dominates)

Line emission – Selfabsorption of Hydrogen Balmer Series
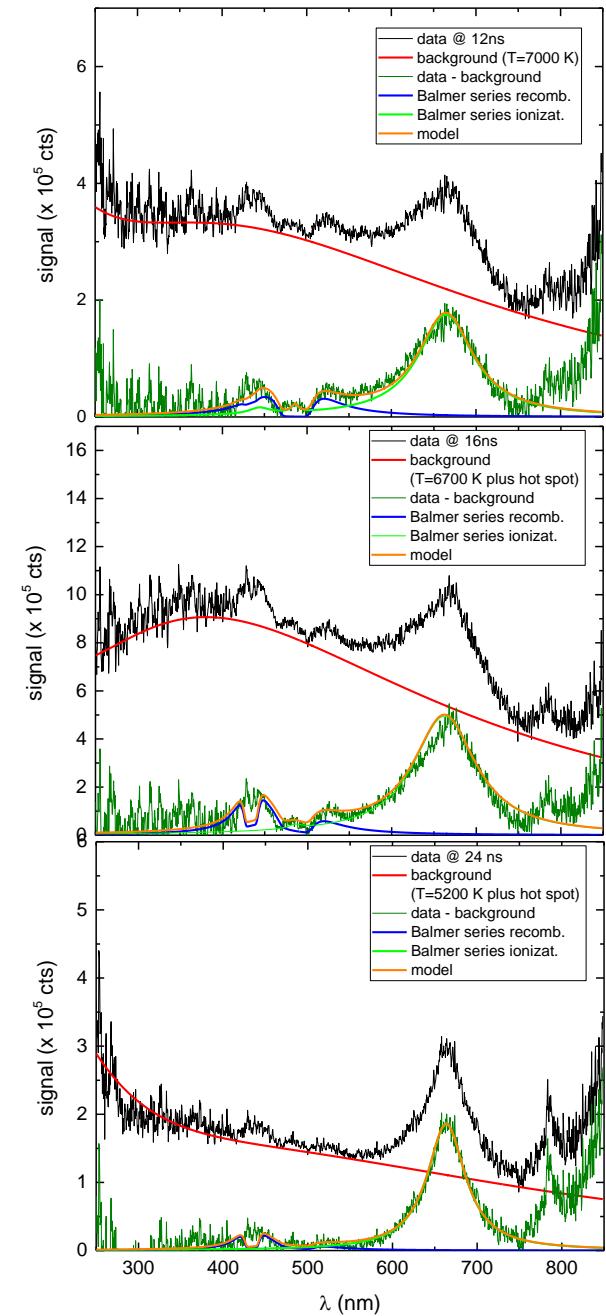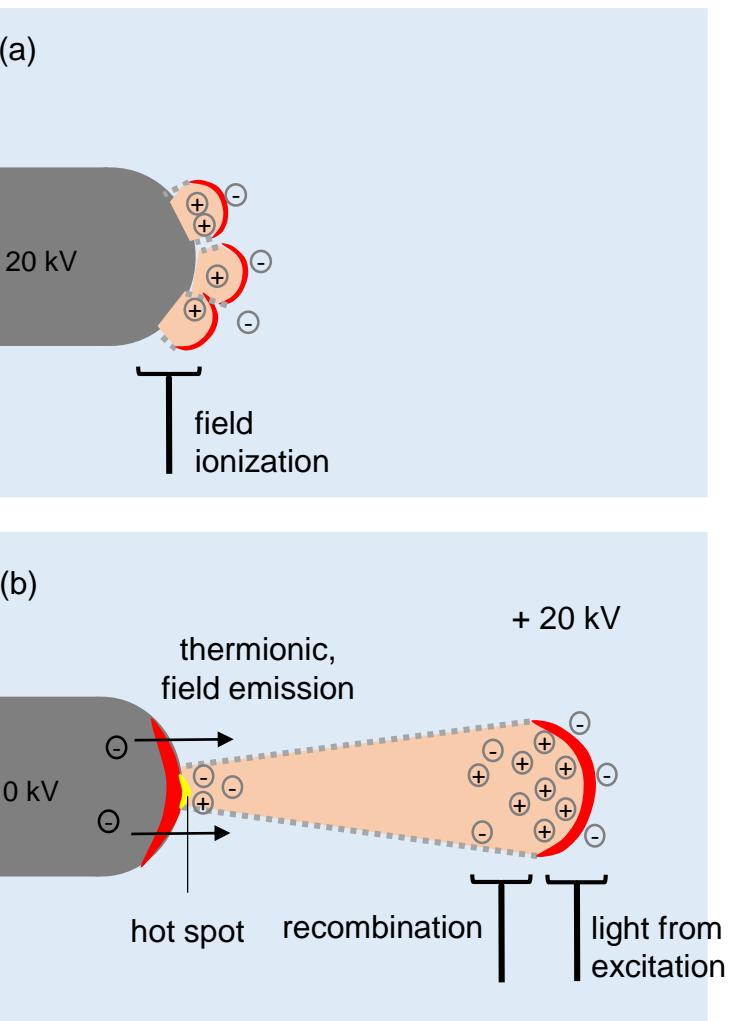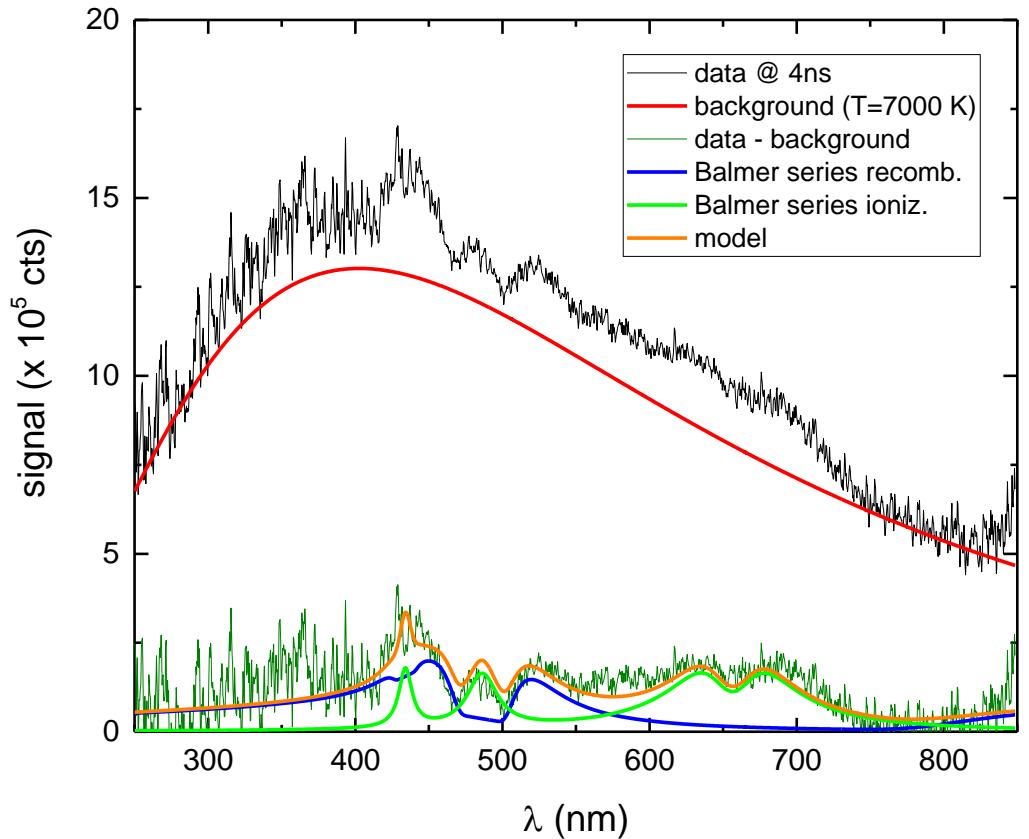
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Efficiency to create H_2O_2 with these plasmas
Modeling the chemistry

- Take T_0 from cavitation
- use chemical equilibrium

$$H_2O_2 \rightarrow H_2O + 0.5\ O_2 : \Delta G = -119\ kJ/mol$$

Oth order reaction (no local H_2O depletion)

$$\frac{dn_{H_2O_2}}{dt} = kn_{H_2O}$$

$$n_{H_2O_2} = \exp\left(-\frac{E_a}{RT}\right)n_{H_2O}\tau + n_{H_2O_2}\big|_0$$

1st order reaction (with local H_2O depletion)

$$\frac{dn_{H_2O_2}}{dt} = -\frac{dn_{H_2O}}{dt} = kn_{H_2O}$$

$$n_{H_2O_2} = n_{H_2O_2}\big|_0 \exp\left[\exp\left(-\frac{E_a}{RT}\right)n_{H_2O}\tau\right]$$
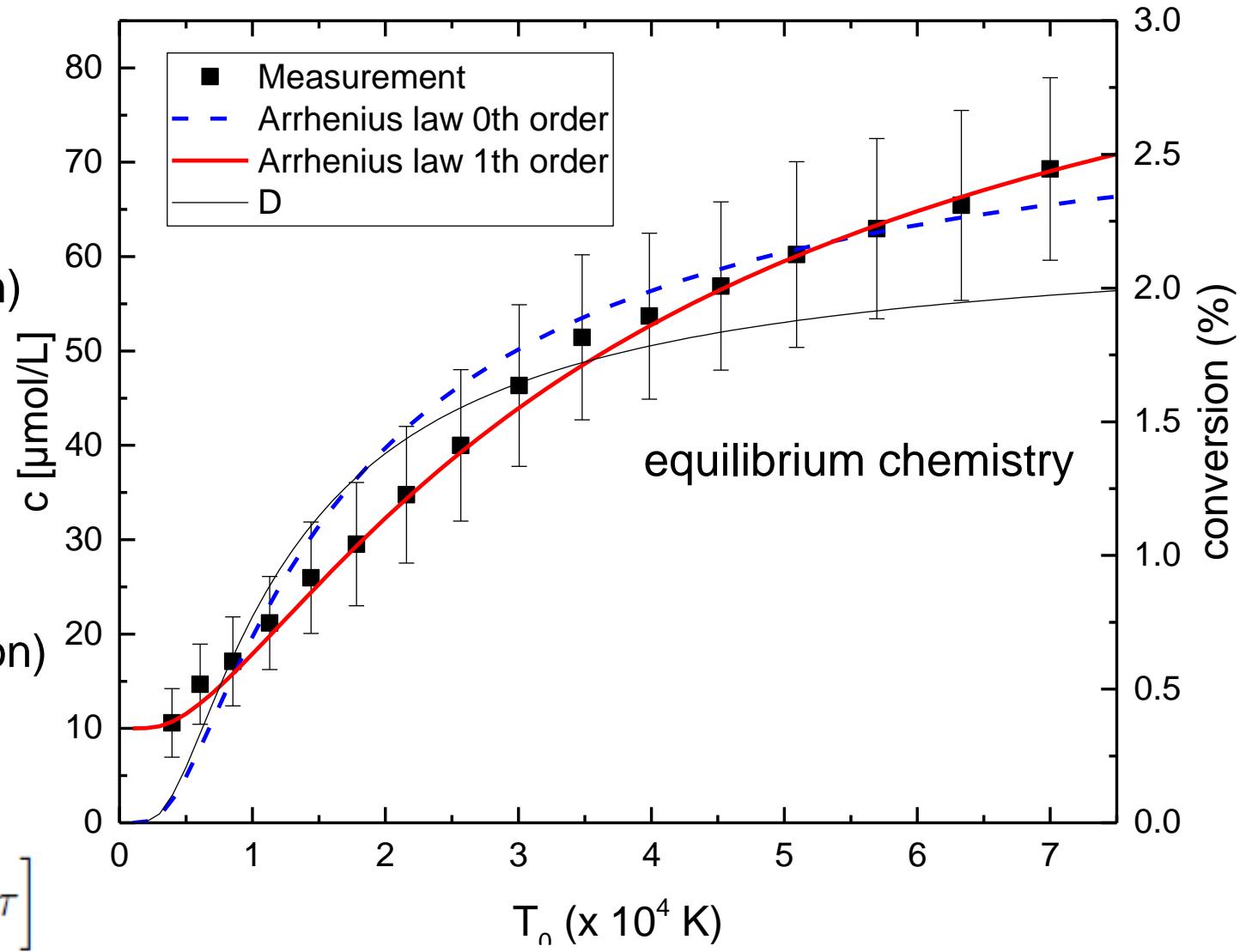
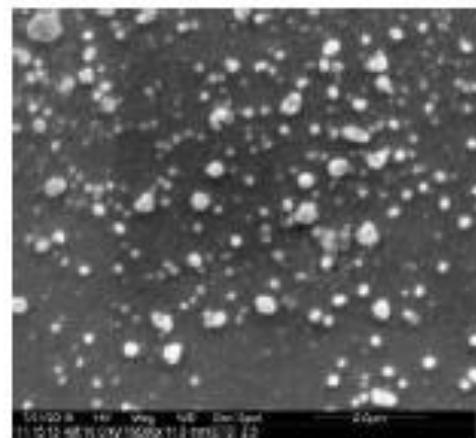equilibrium chemistry

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Nanosecond plasma based recovery of CuO nanocubes at copper electrodes
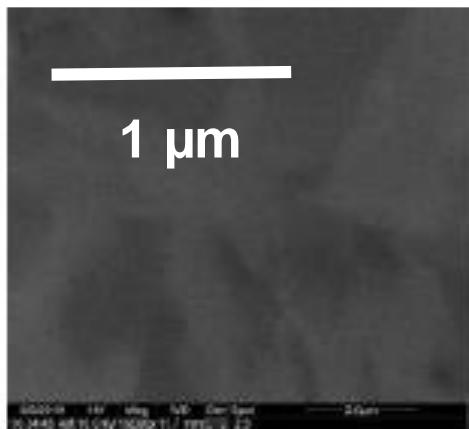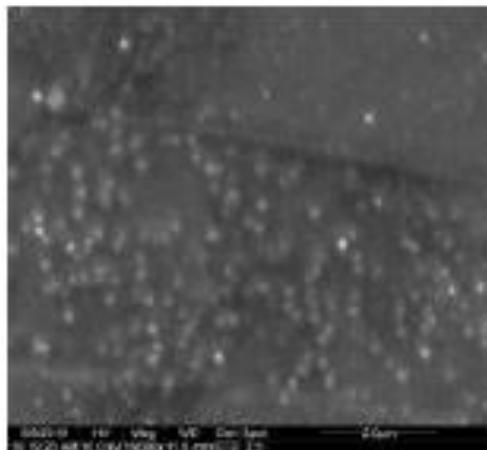
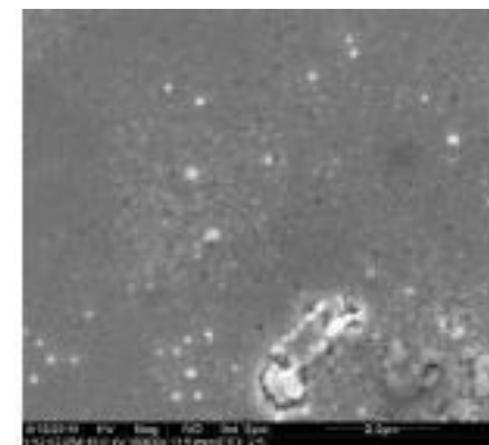distilled water

dist. Water + 0.0035M KCl

Creation of Cu-nanocubes possible, if

20 kV

1 µm

- no direct current to the sample, reduction of the oxide, plasma electrode distance to the sample important

- Competition between oxidation due to H_2O_2, OH and reduction by H, e^-
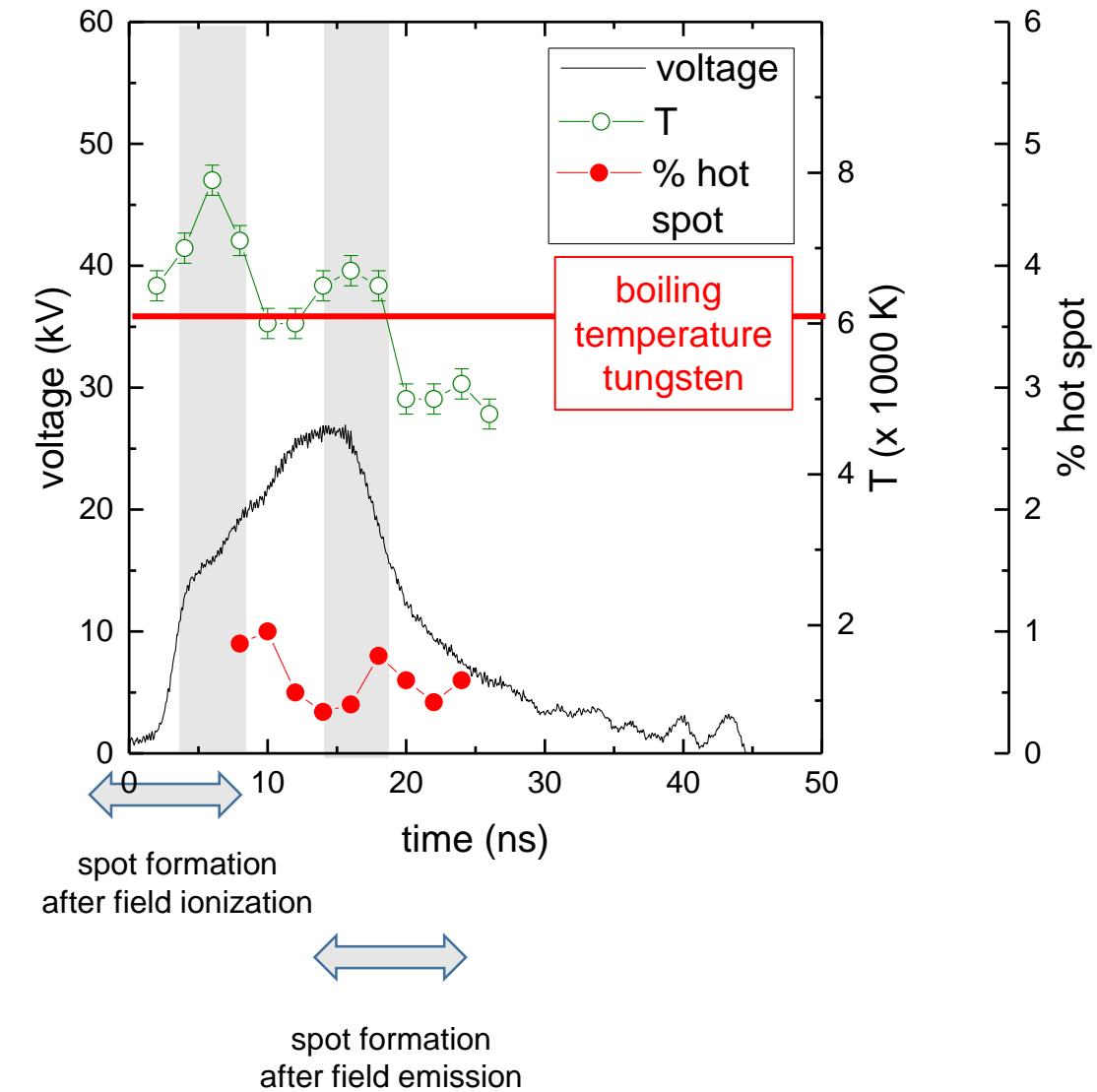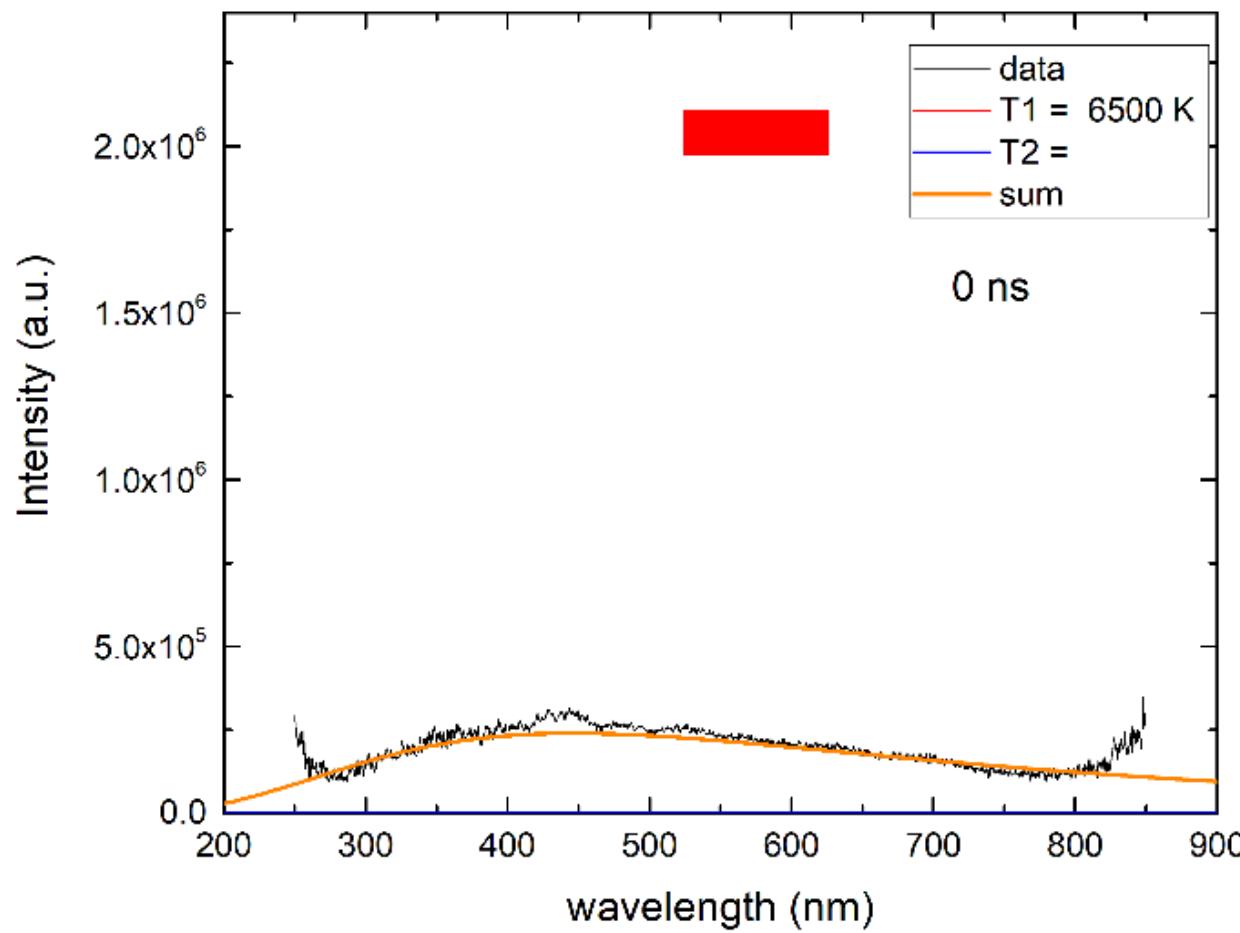
distilled water

dist. Water + 0.0035M KCl

26 kV

P. Grosse, B. Roldan et al.

Reference plasma based low pressure creation of CuO nanocubes

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Nature of the 1/λˣ background in emission – cathode spots on the tungsten electrode

**Chemistry in Plasma Treated Liquids** | A. von Keudell et al.

Line emission – Electron densities from Stark broadening of Hydrogen Balmer Series
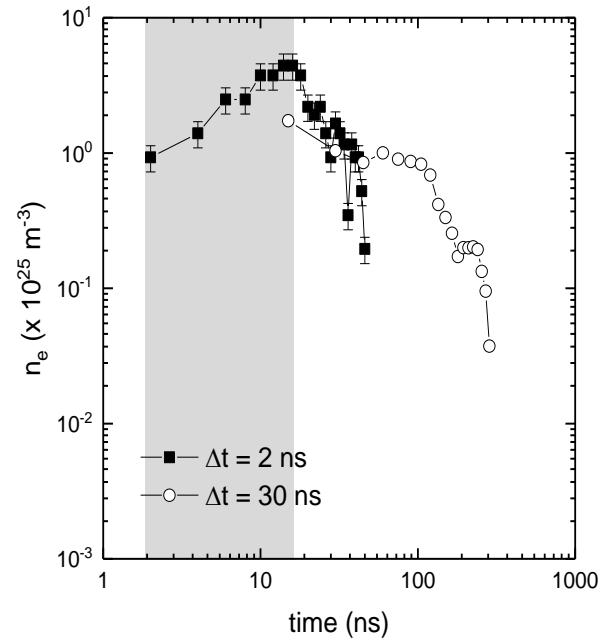
electron density from Stark broadening

- n_e follows directly voltage (no delay as in ns air plasmas) ionization and recombination on ps time scales at liquid densities)
- decay follows the voltage

$n_e \sim 5 \times 10^{25}$ m^{-3}

ionization degree $\sim 10^{-3}$
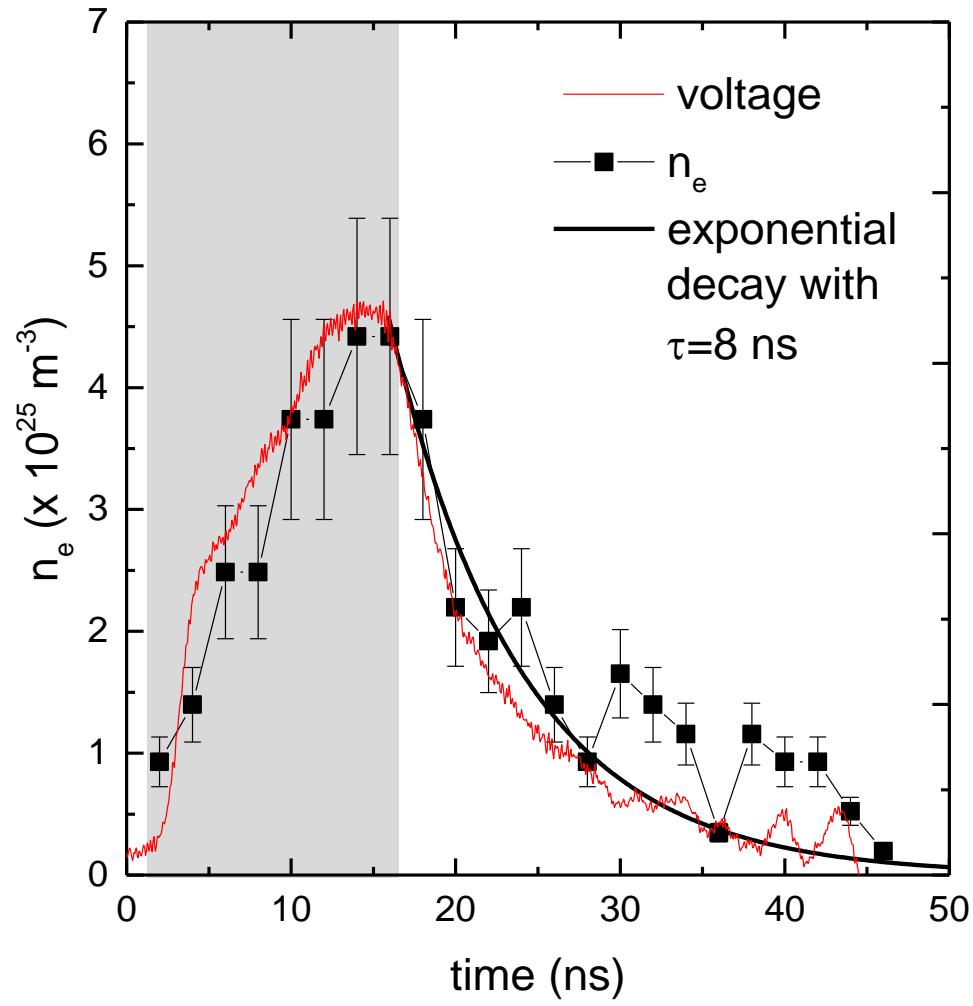
Comparison to ne decay in the re-ignited plasmas During bubble expansion

Chemistry in Plasma Treated Liquids | A. von Keudell et al.

Efficiency to create H$_2$O$_2$ with these plasmas
Measurement of the concentration with a colorimetric kit

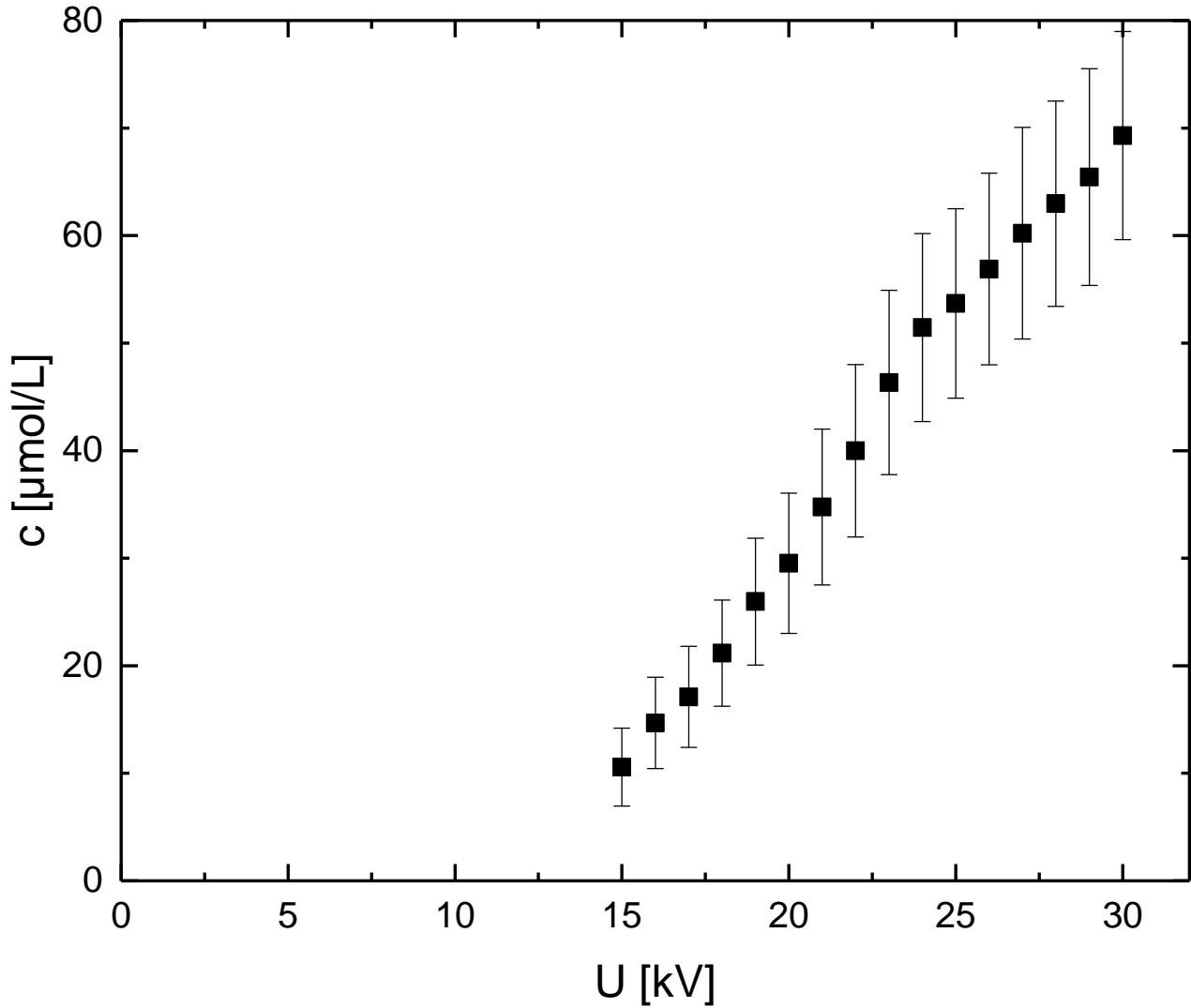$H_2O_2 \rightarrow H_2O + 0.5\ O_2$: $\Delta G = -119$ kJ/mol

Measurement:
@ 20 kV, 30 µmol/l in 25 ml liquid is equivalent to 4×10^{17} species in total

Estimate:
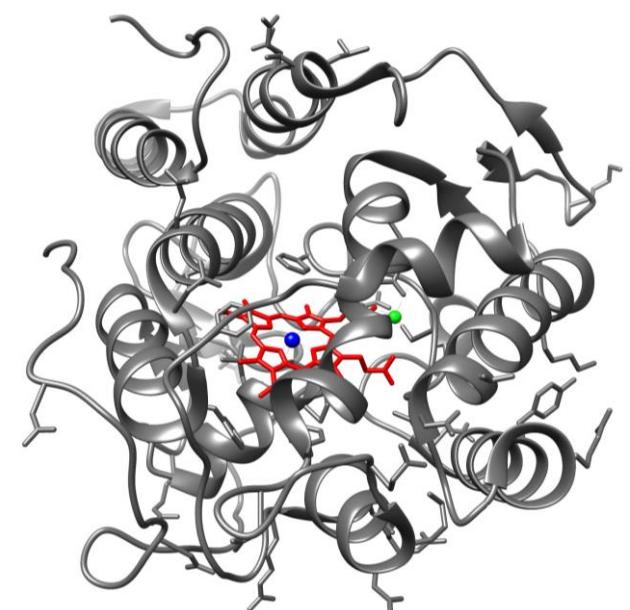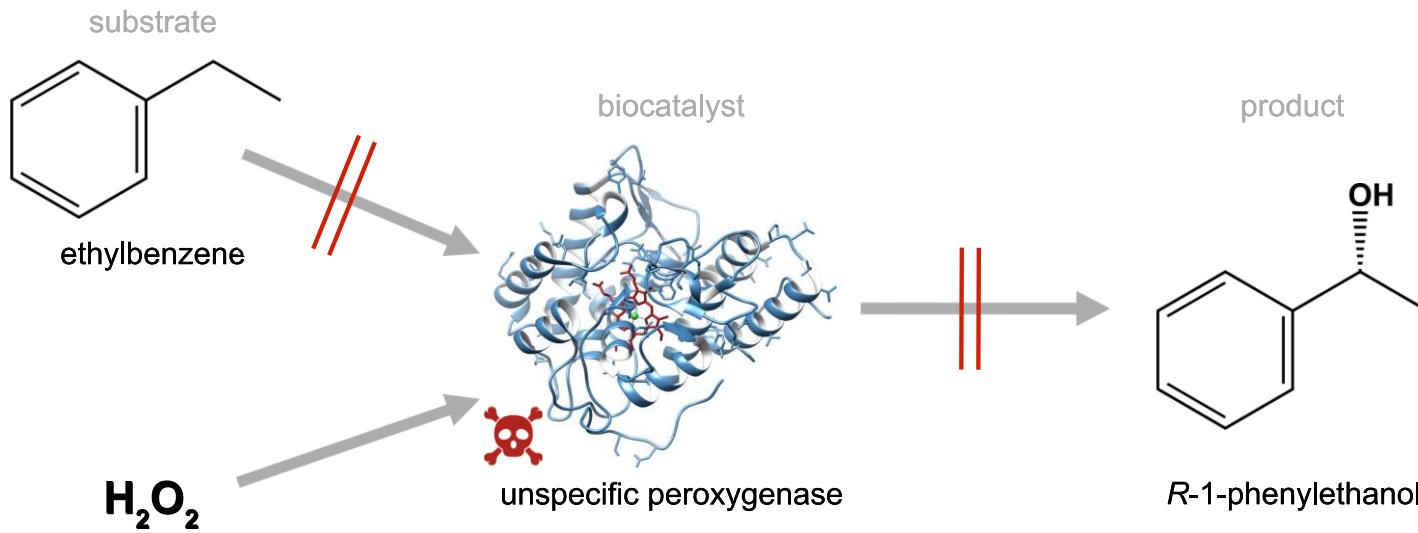Species in 25 µm radius spheres at density of liquid water $3\ 10^{22}$ cm^{-3}: 2×10^{15} species

Total number of species treated in 10 min @ 15 Hz, 10 ns pulses: 3.8×10^{19} molecules are exposed to plasma

efficiency 1.1%

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Biocatalysis

- use of H_2O_2-dependent enzymes → oxidoreductases

- redox reaction → one substrate reduced, one oxidized

  peroxygenases: $H_2O_2 + AH → A\text{-}OH + H_2O$

- industrial application is limited → excess of H_2O_2 leads to suicide inactivation

substrate

ethylbenzene

H_2O_2

biocatalyst

unspecific peroxygenase

product

OH

R-1-phenylethanol

unspecific peroxygenase of *Agrocybe aegerita* (*Aae*UPO) (PDB: 5OXU)

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