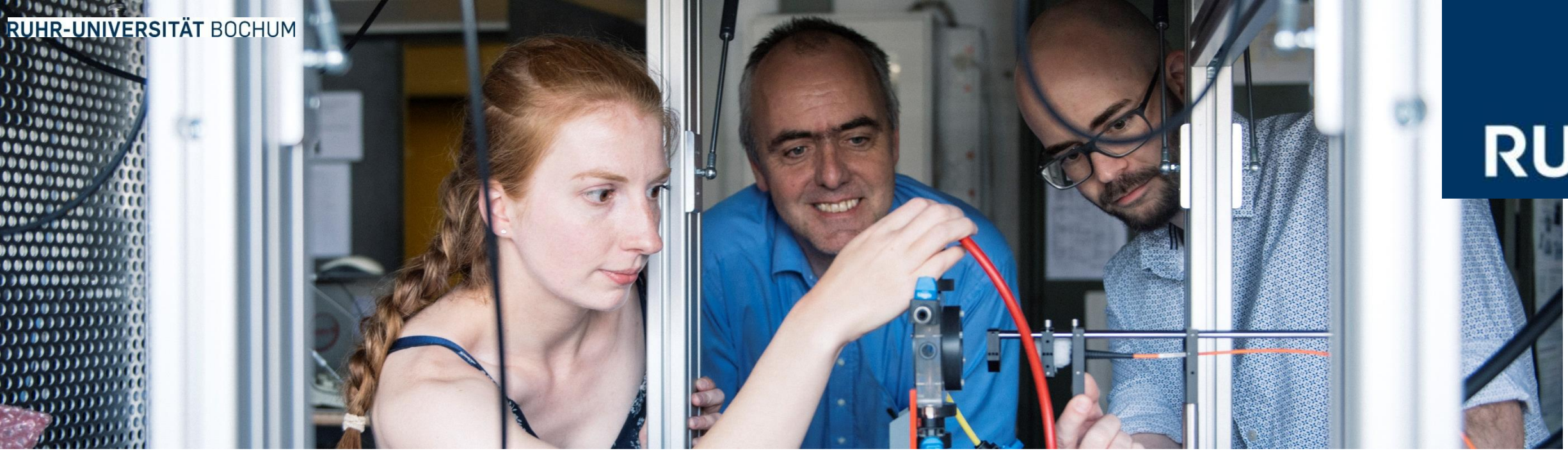


Nanosecond Plasmas in Liquids – Dynamic Plasmas at GPa pressures

A. von Keudell, K. Grosse, J. Held, V. Schulz-von der Gathen, M. Kai, C. Nenbangkaeo, F. Seferoglu, L. Chauvet

Experimental Physics II, Ruhr University Bochum

SFB 1316 Transient Atmospheric Plasmas
from plasmas to liquids to solids

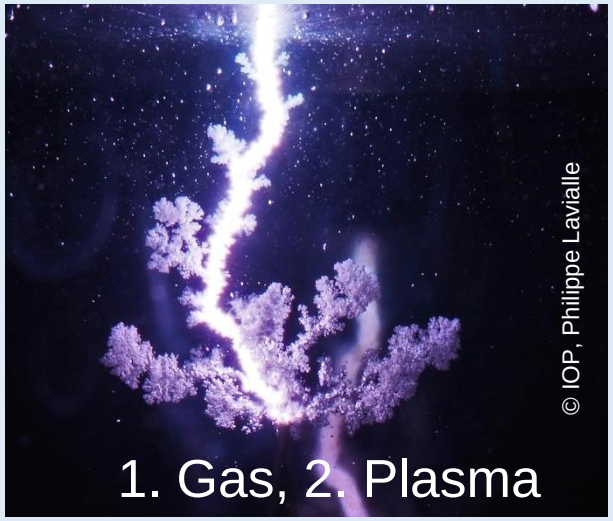
Plasma Chemistry in liquids – example H_2O_2 generation

Nanosecond plasmas

- 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

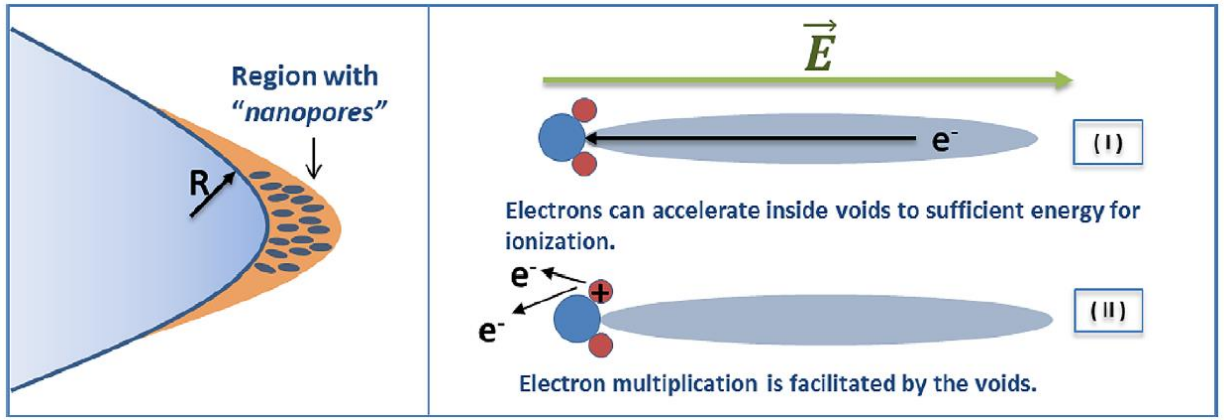


- Long microsecond pulses
- Initial formation of a gas bubble due to Ohmic heating or E-field rupture
- Plasma ignition inside the water vapor in the bubble

Moderate high pressures and temperatures
10 bar, 20000 K

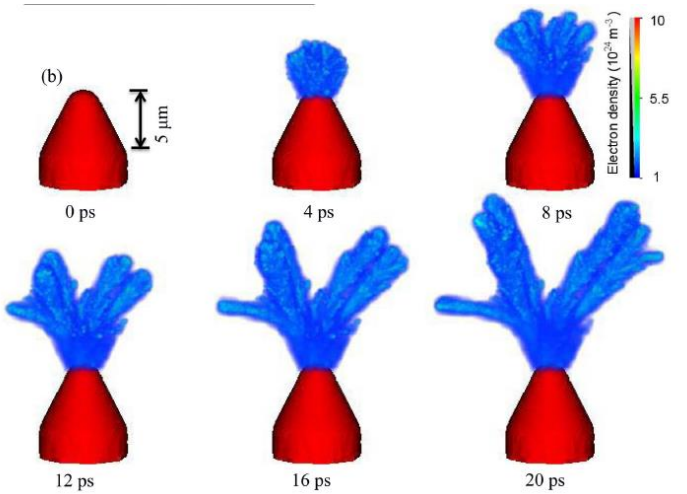
The big puzzle regarding the ignition in ns plasmas in liquids

e^- acceleration in nanopores



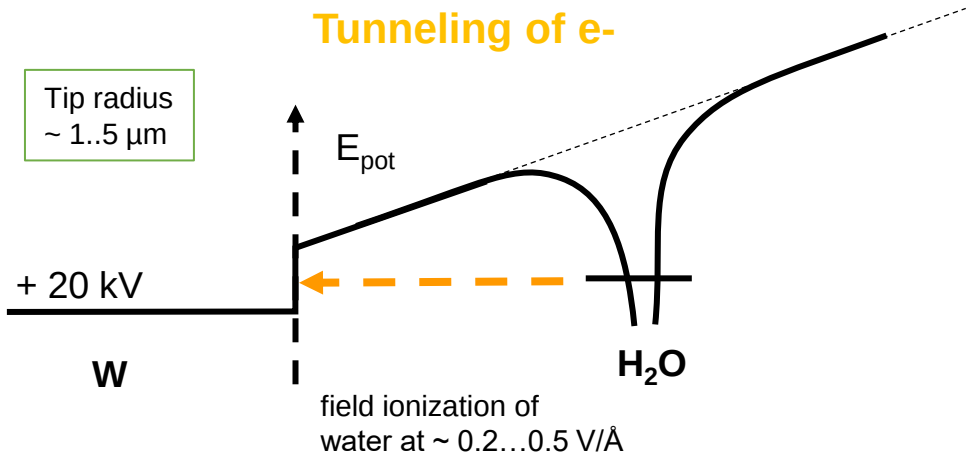
(Dobryn et al. JPD 46, 355201 (2013)

Field emission, field ionization

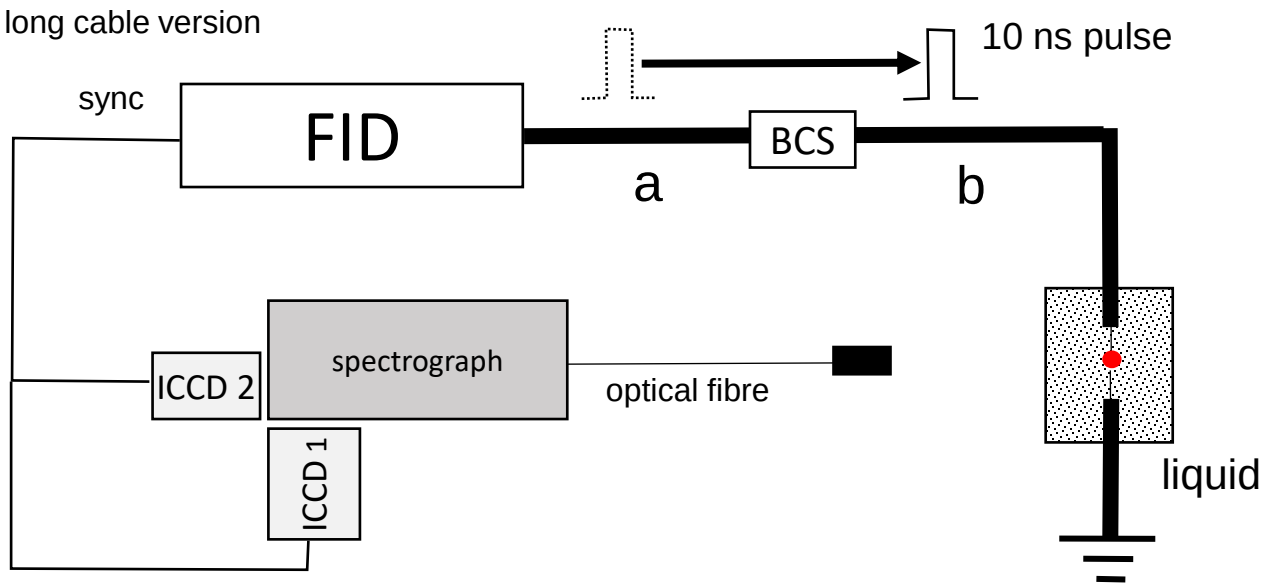


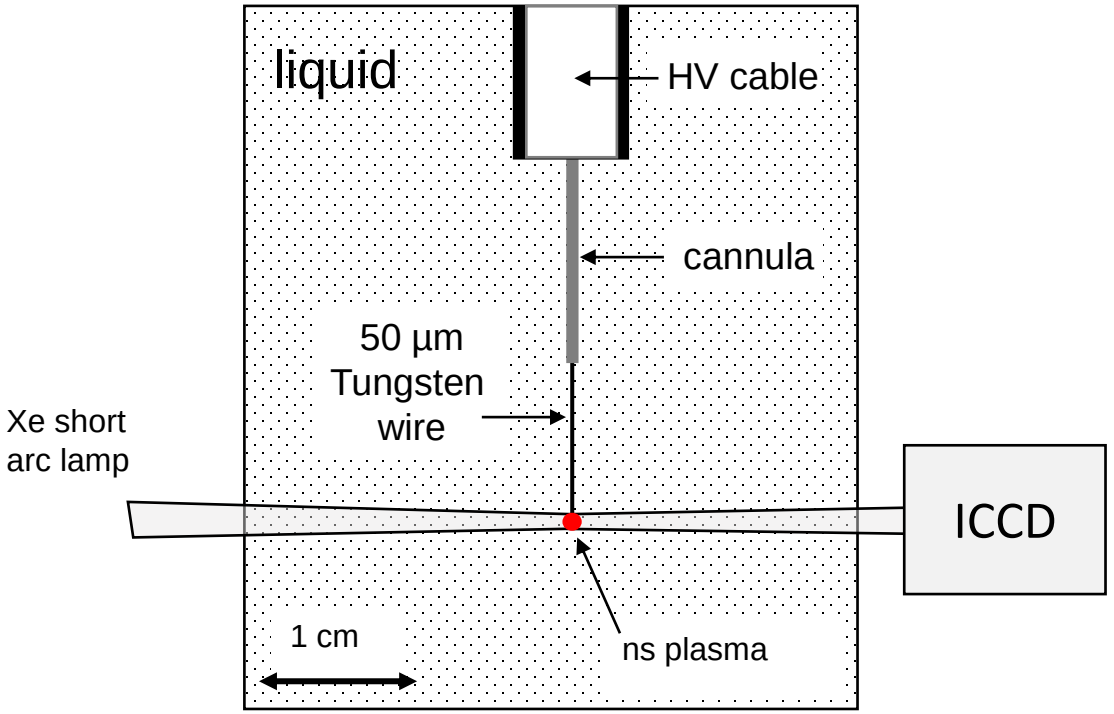
From A. Sun, J. Teunissen, U. Ebert
IEEE Trans. Plas. Sci. 42, 2416 (2014)

Tunneling of e-



Plasma Chemistry in liquids – example H_2O_2 generation

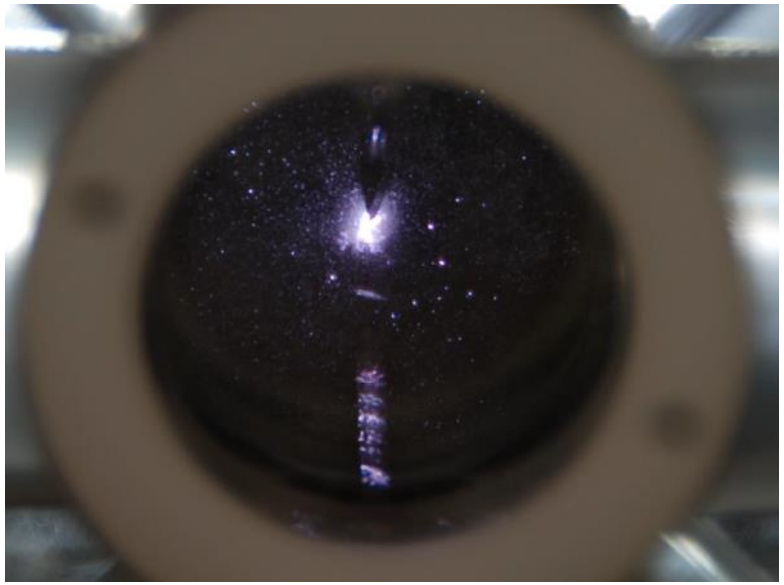




- 10 ns pulses, 14…30 kV, distilled water
- Shadowgraphy 2 ns … 70 ns gate widths
- Optical emission spectroscopy with 2ns and 30 ns gate time

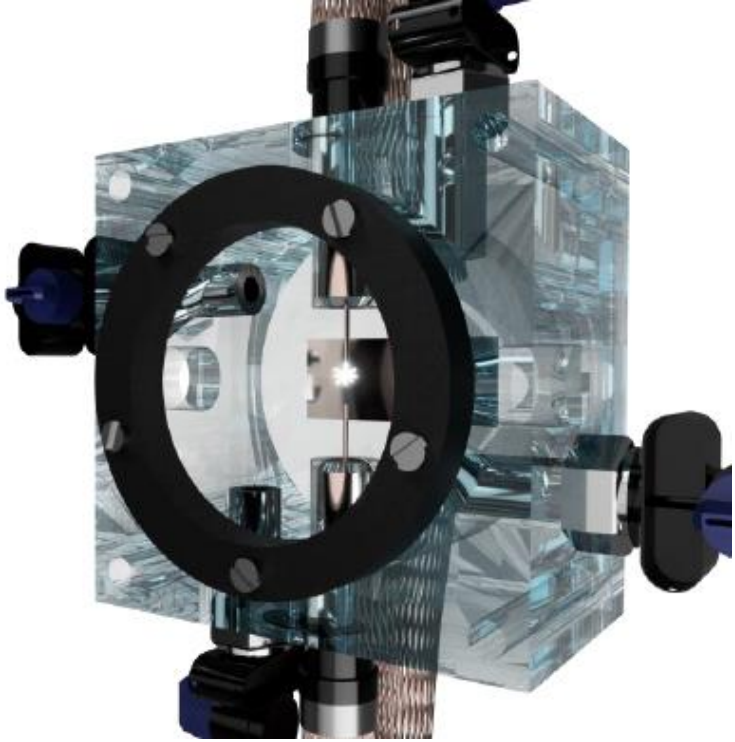
Goals:
- reactive liquid production
- regeneration of catalysts for plasma enhanced electrolysis

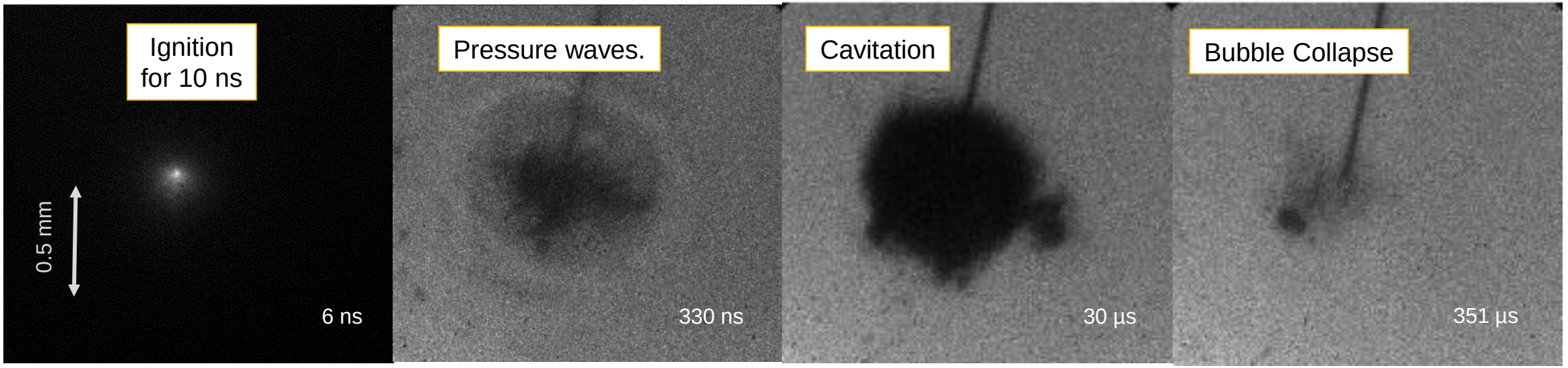
Plasma Chemistry in liquids – example H_2O_2 generation



Temporal evolution of the discharge

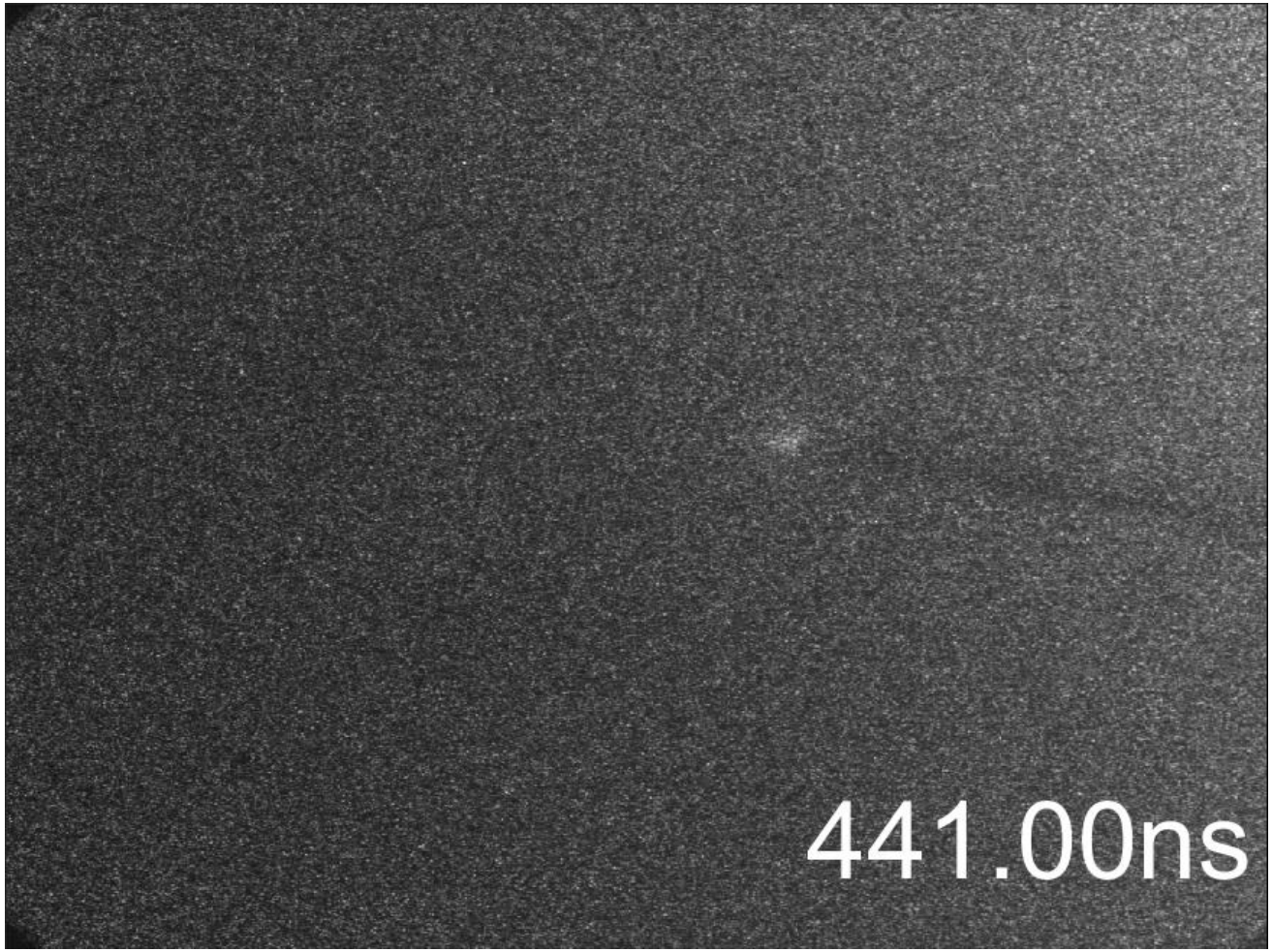
4 phases
- Ignition (Streamer)
- Pressure waves propagate
- Conversion of water into plasma and vapor
- Expansion of a cavitation bubble



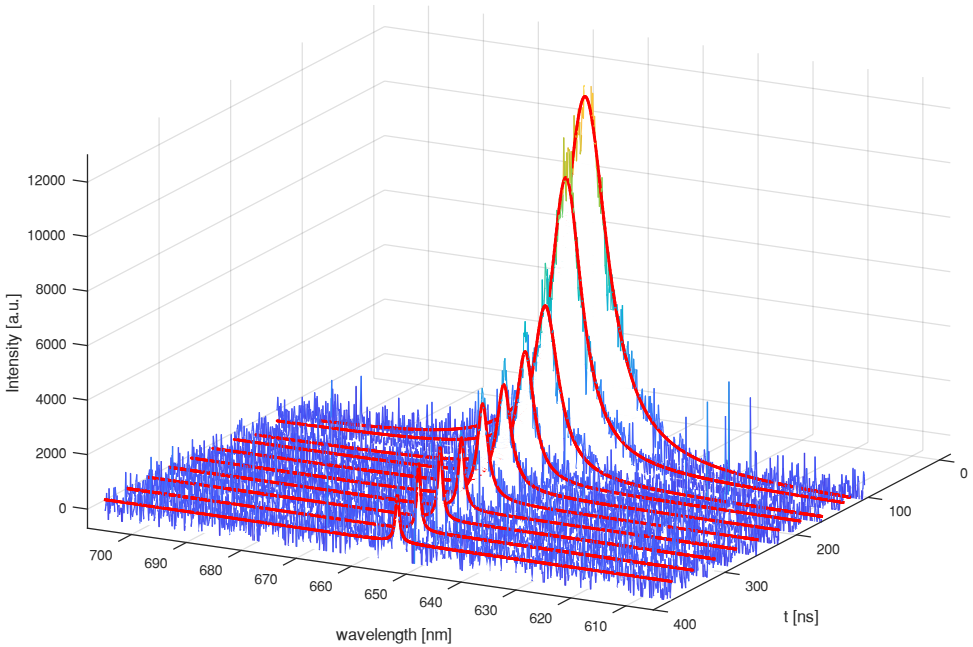


Plasma Chemistry in liquids – example H_2O_2 generation

Temporal evolution of the discharge

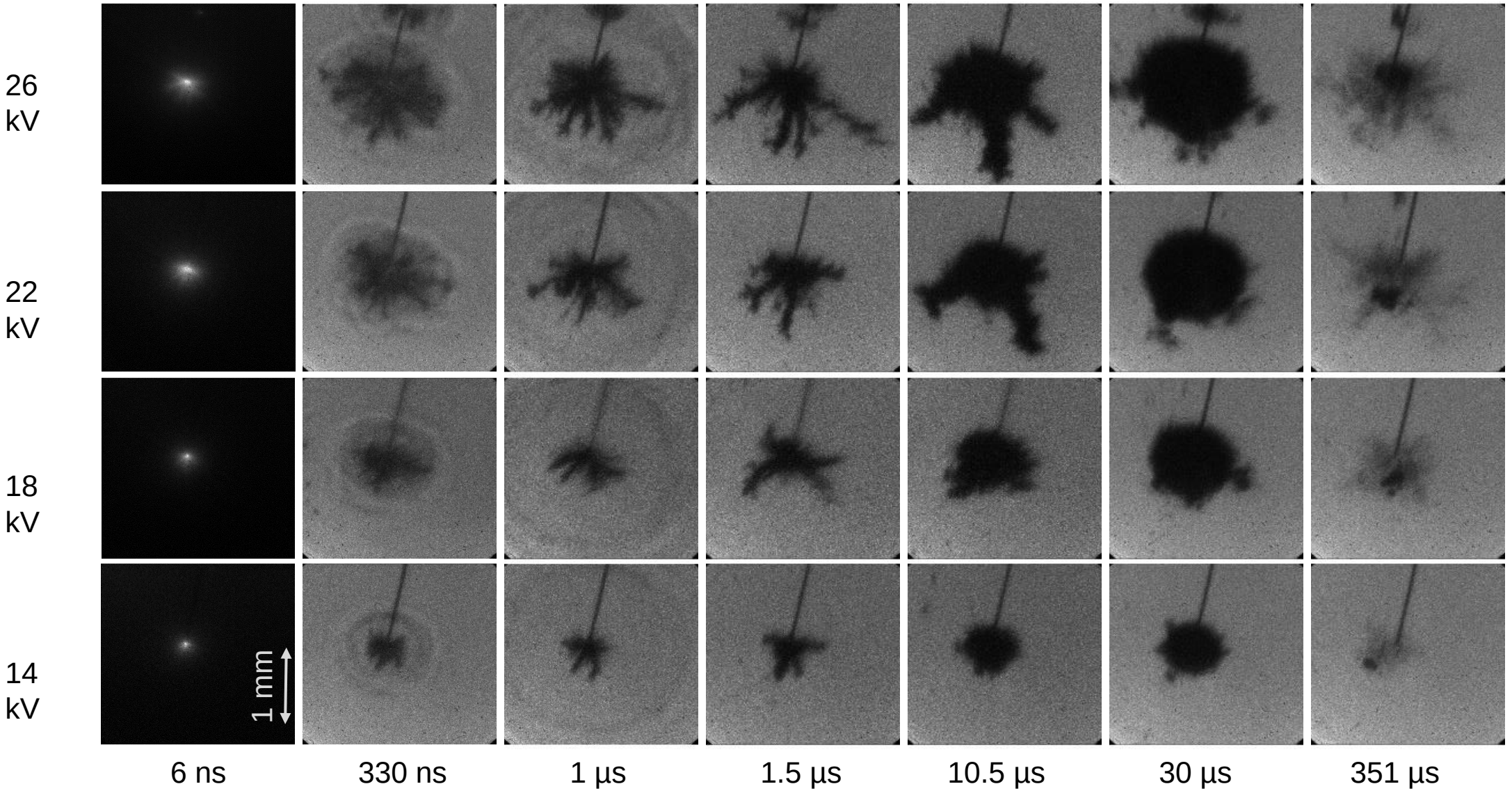


H alpha emission after the plasma pulse



60 ns gate, 30 ns steps

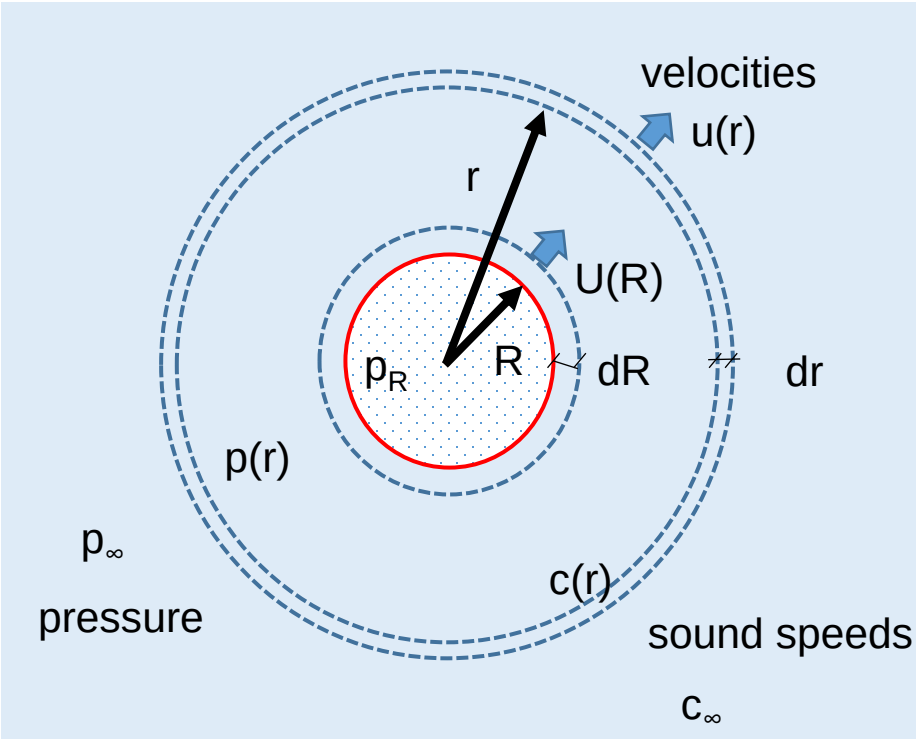
Monitoring Bubble Expansion with Shadowgraphy – monitoring sound waves and cavitation

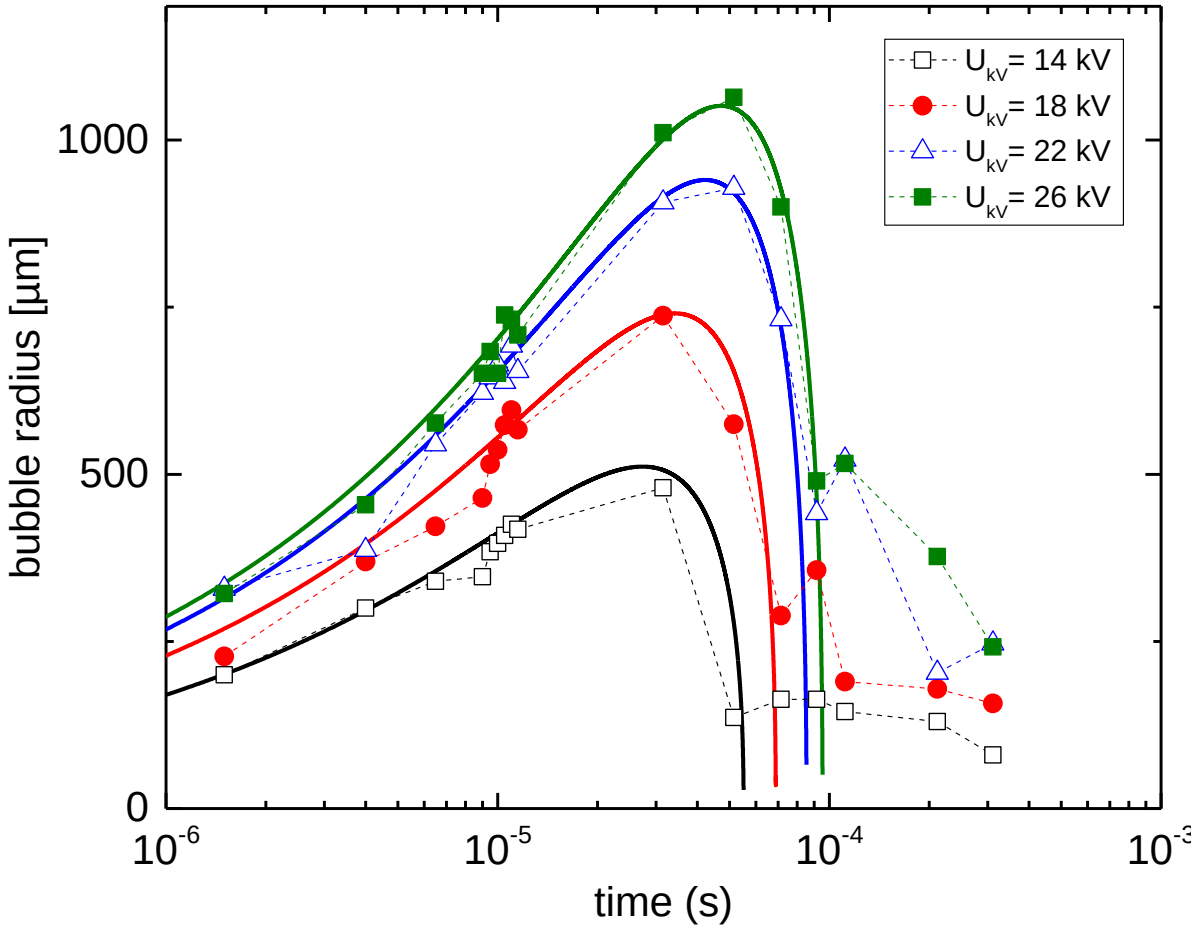


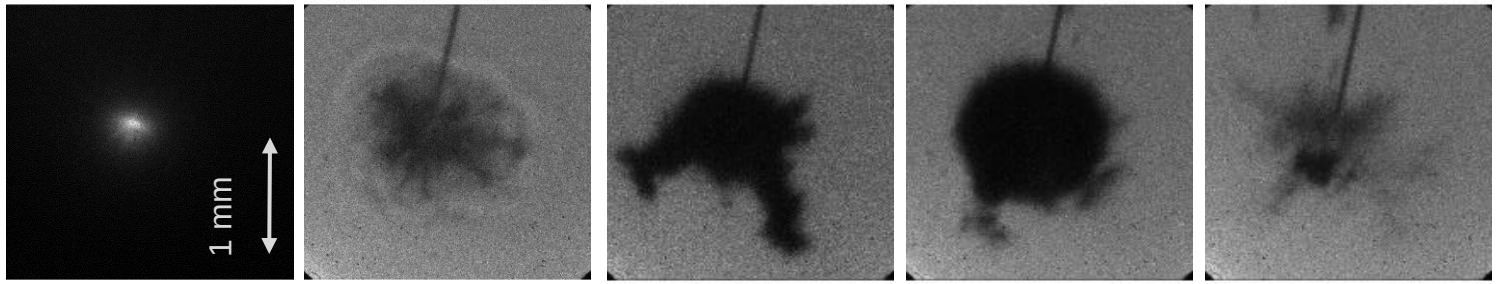
Comparison of Bubble Expansion with cavitation theory

Rayleigh Plesset equation:

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



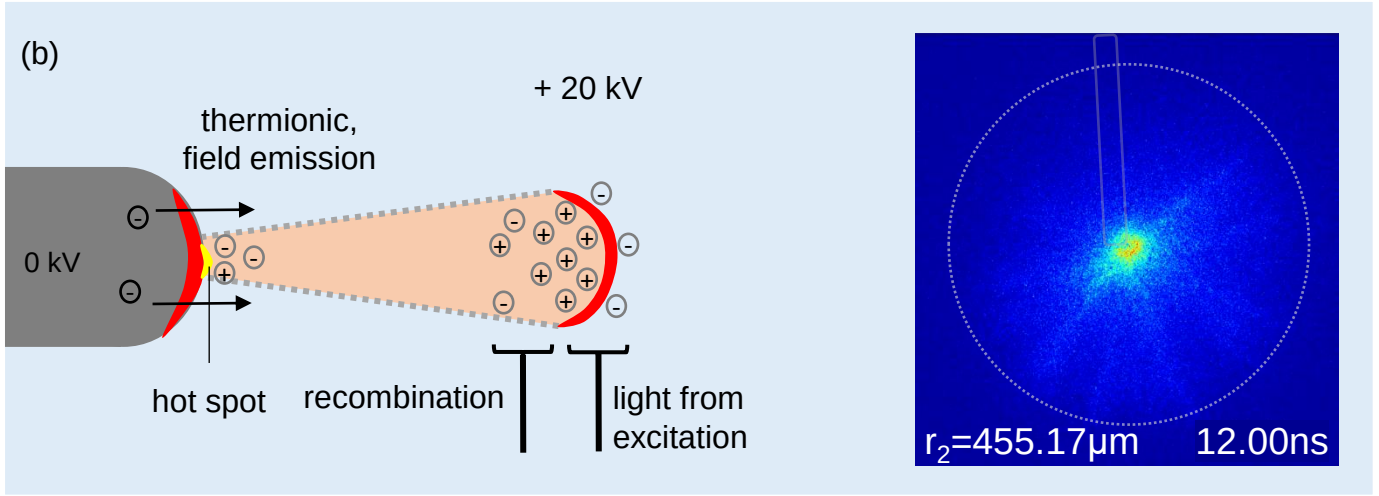


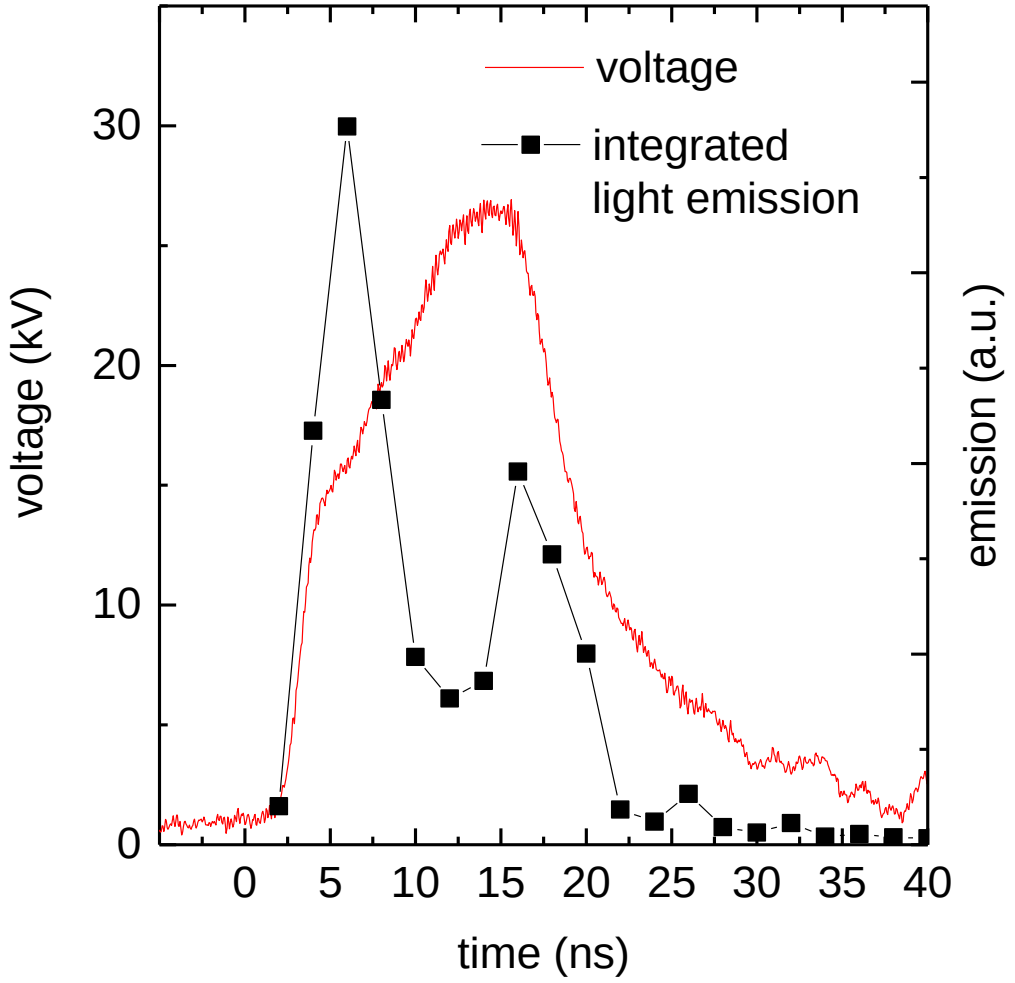


6 ns | 330 ns | 10.5 µs | 30 µs | 351 µs

How does the plasma Ignites ?

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

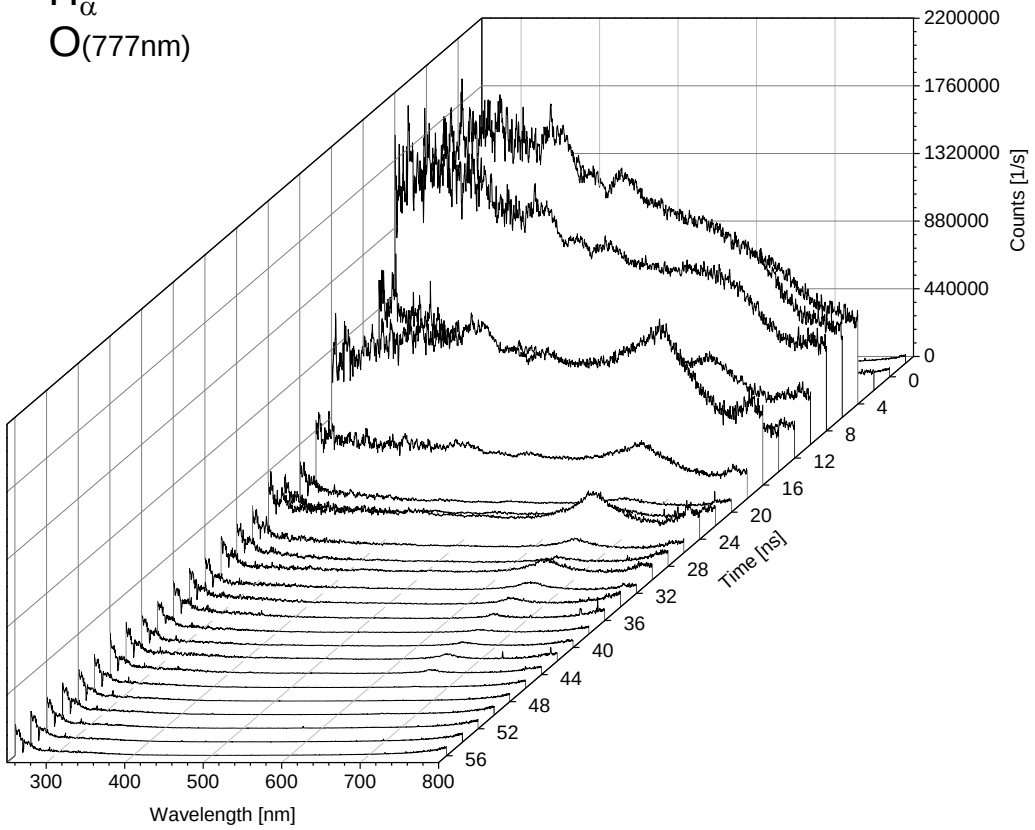


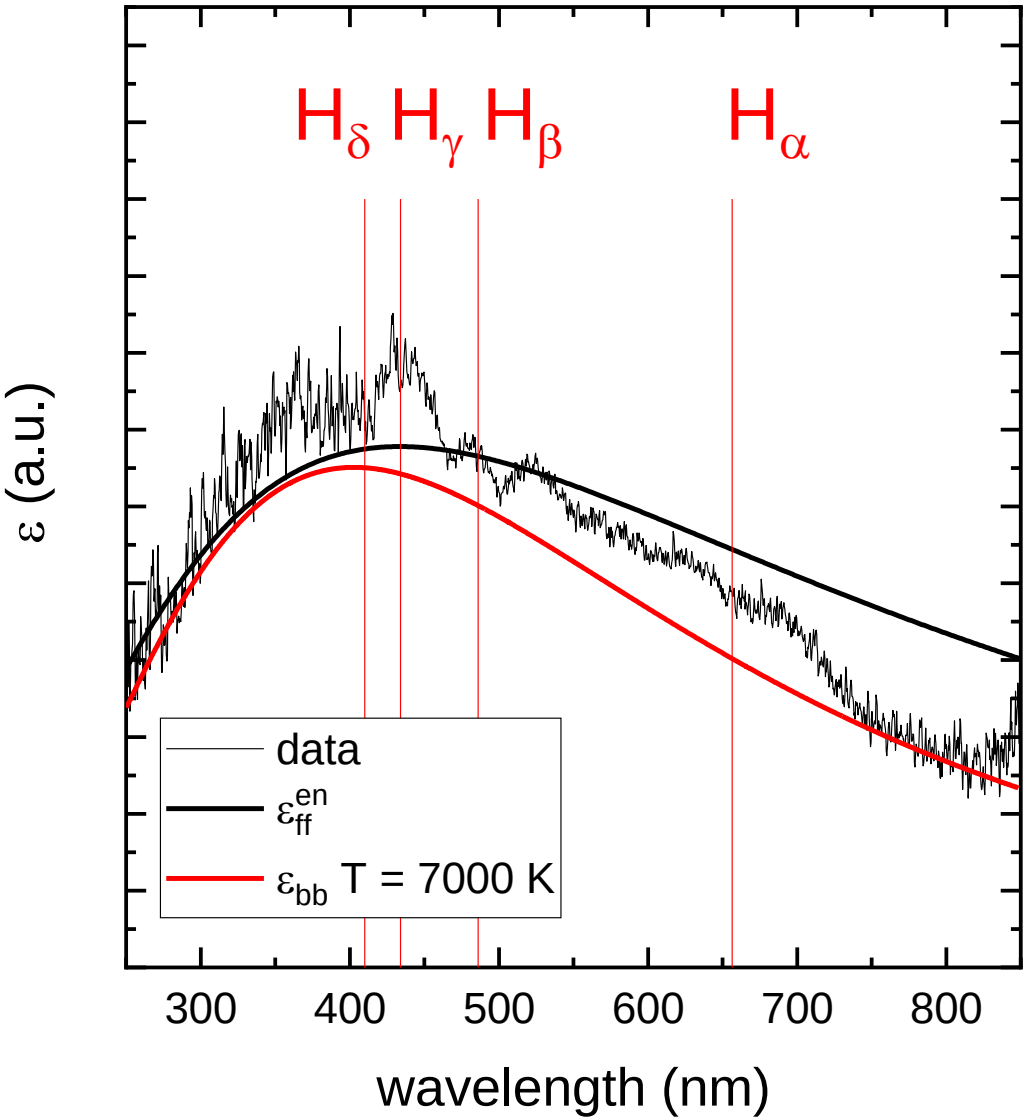


Temperatures from emission spectra of the plasma into the UV

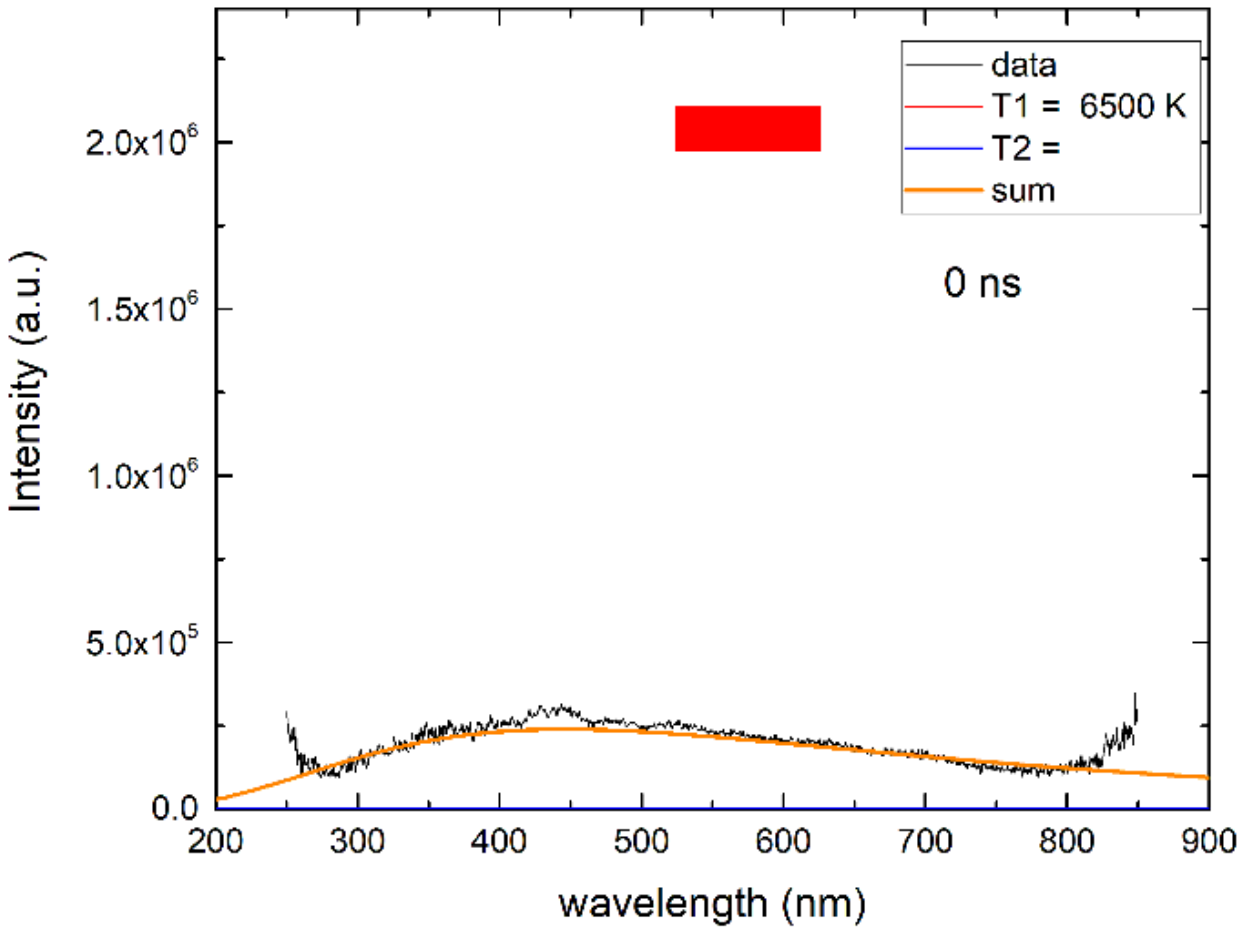
Spectrum (first 50 ns, time resolution 2 ns)

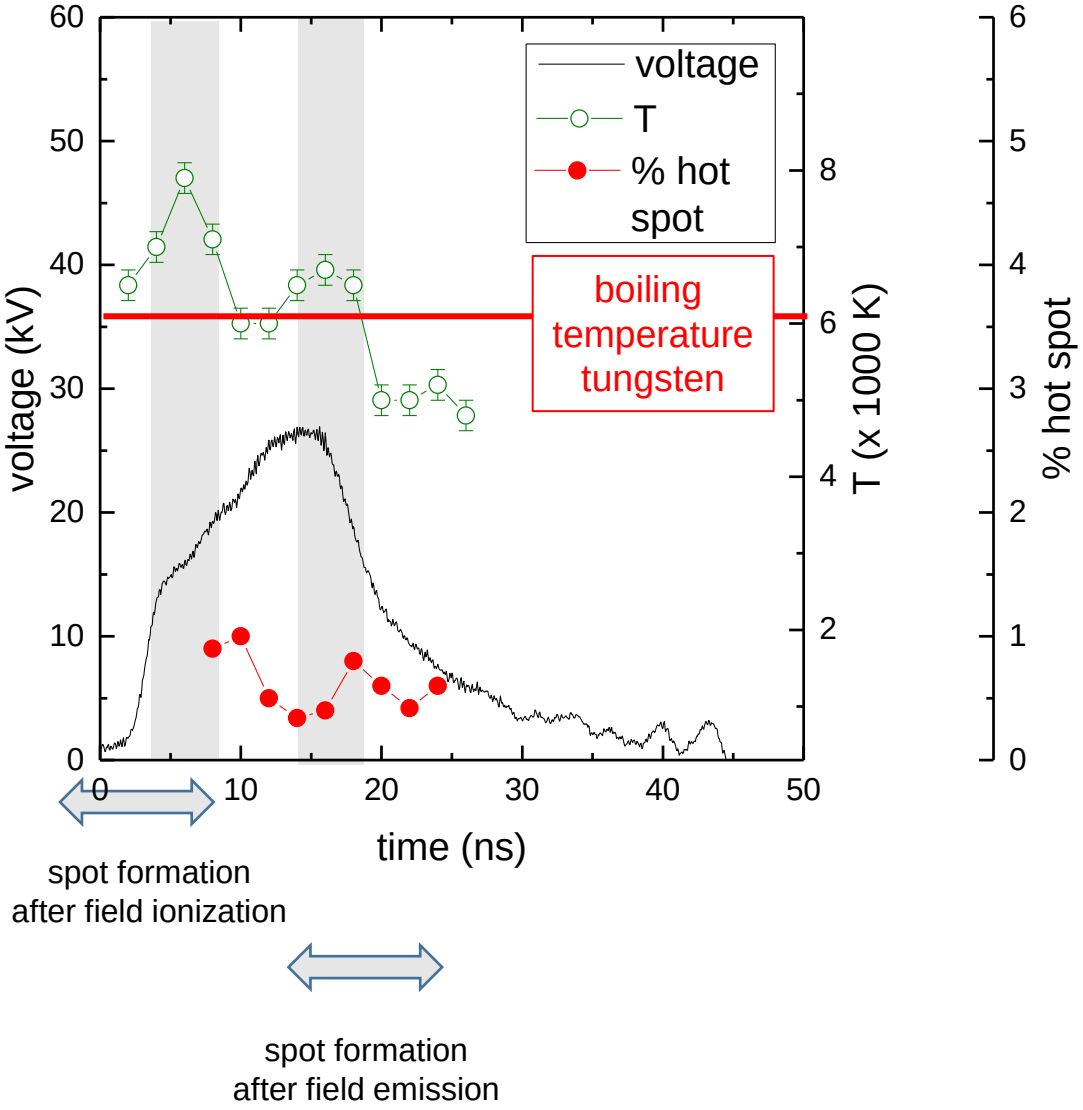
- Recombination
- H_2 , H_2O recomb. continuum
- OH, OH^+, H_2O, H_2O^+ bands
- Black body radiation (W)
- H_α
- $O_{(777nm)}$





Nature of the 1/λ^x background in emission – cathode spots on the tungsten electrode

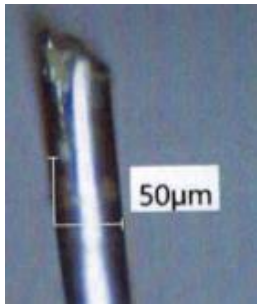




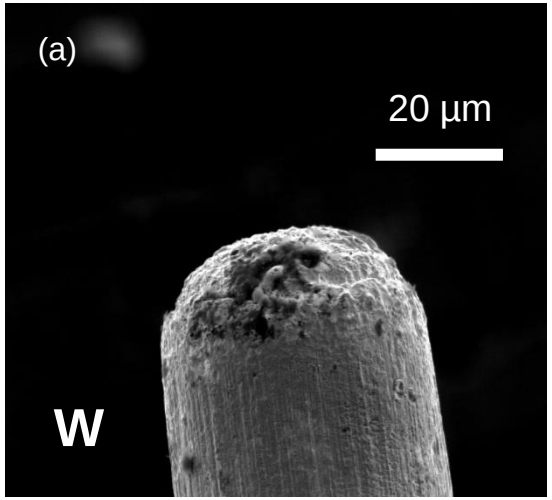
spot formation
after field ionization

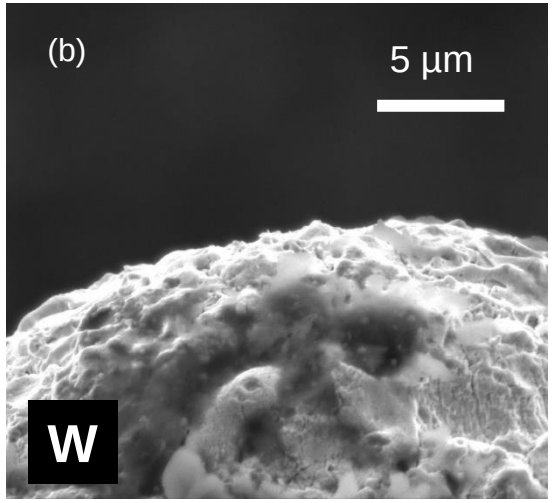
spot formation
after field emission

Tungsten tip vs. Platinum/Iridium tip



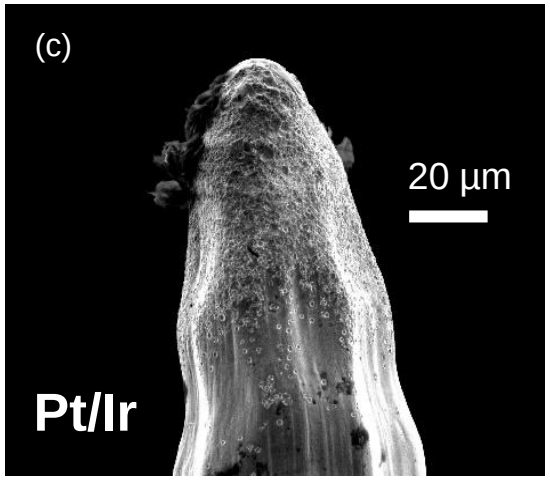
- W as high melting temperature
  3700 K
- W therm. conduct.
  115 W / m K
- W oxidizes, Crystallites are formed

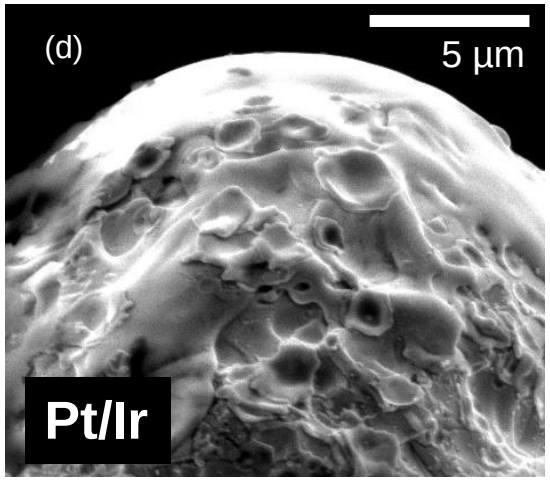




Permanent operation possible

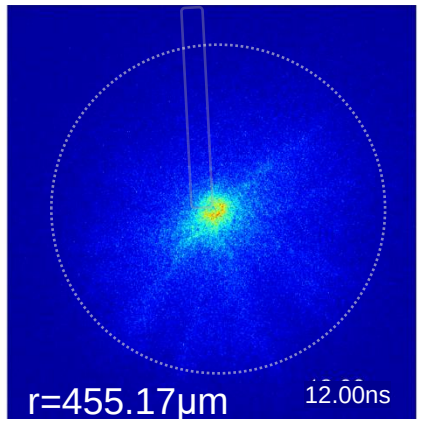
- Pt melting temperature
  2100 K
- Pt thermal conduct.
  82 W/ m K
- Ir melting temperature
  2700 K

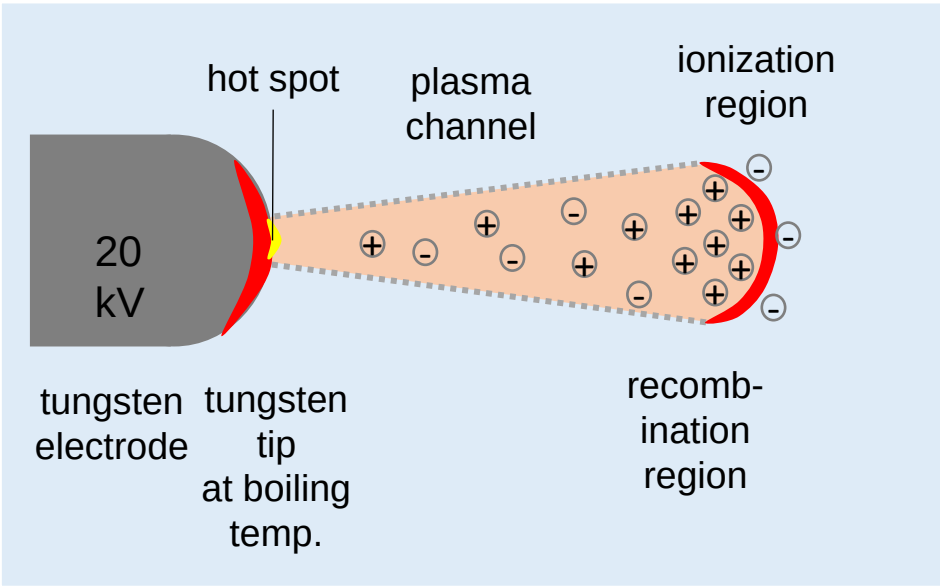


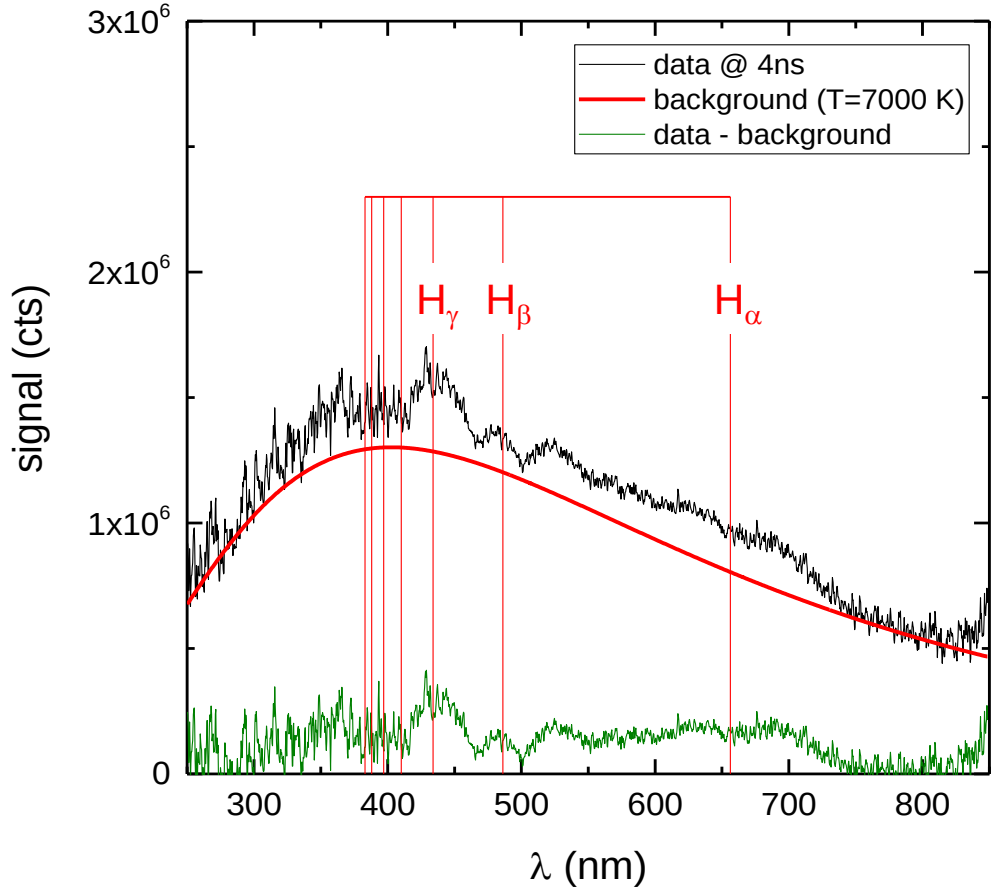


Ignition stops after 1 h of operation

Line emission – Hydrogen Balmer Series

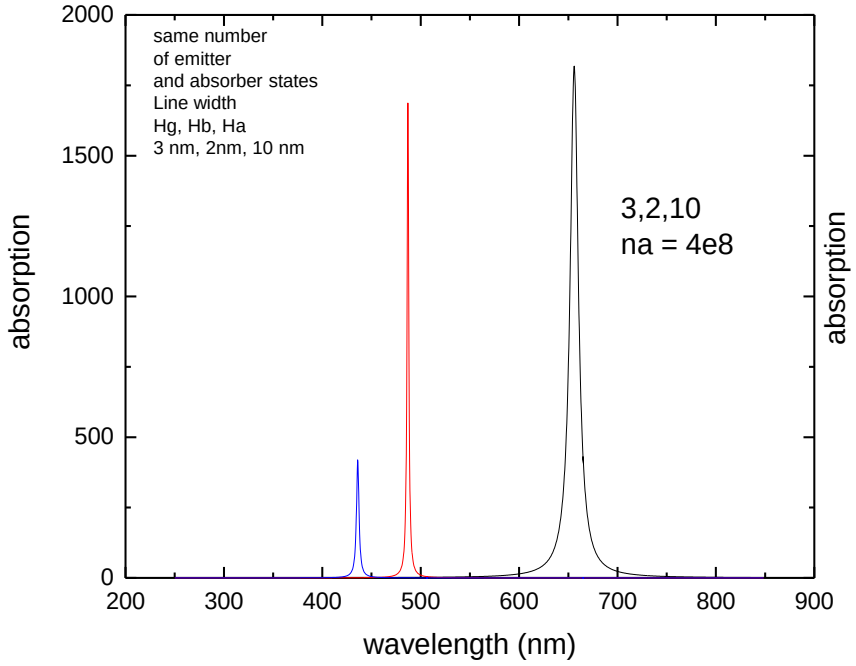


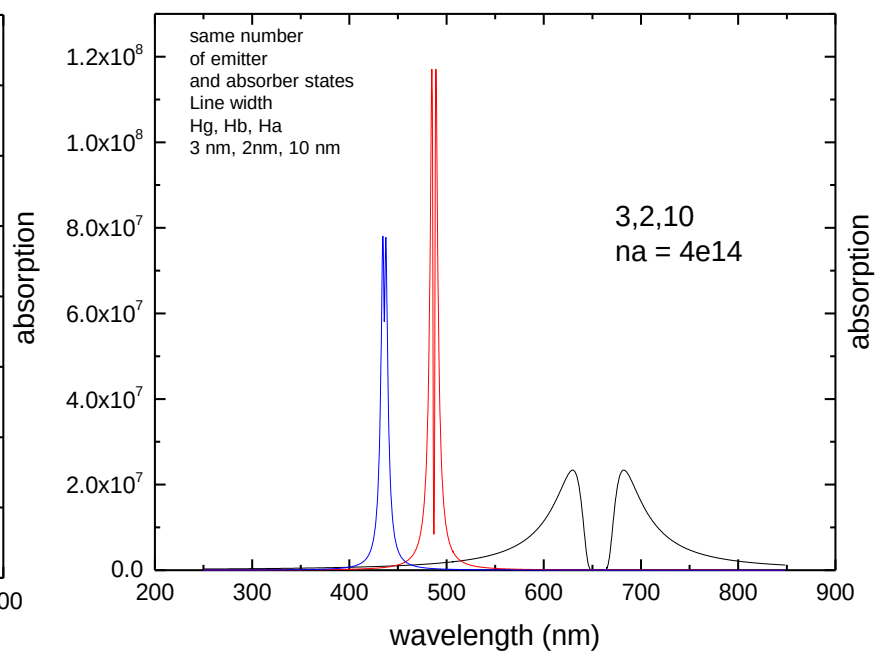


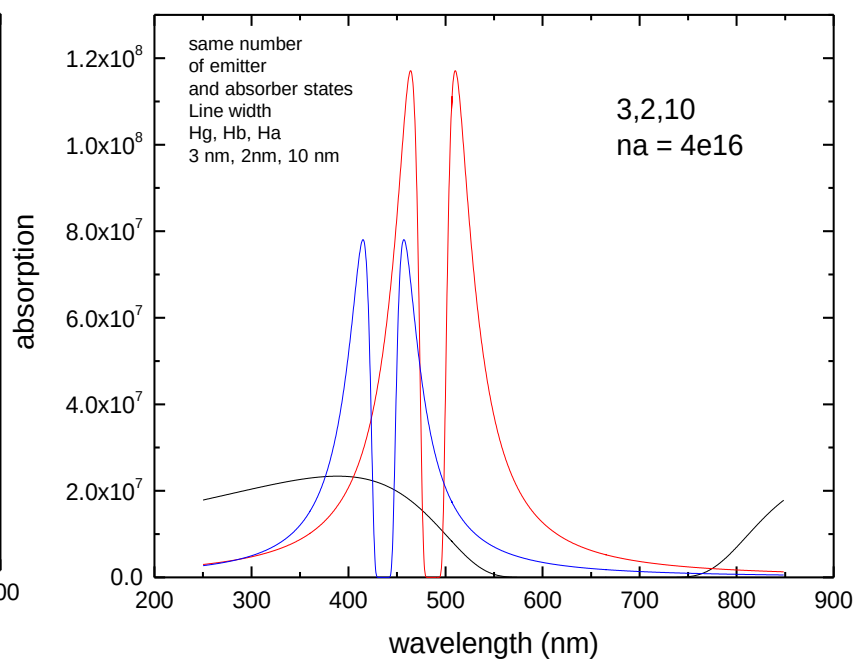


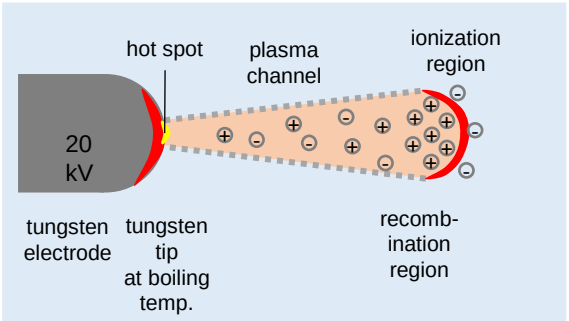
- H Balmer lines clearly visible
- Why is Hγ more pronounced than Hα ?

Line emission – Selfabsorption of Hydrogen Balmer Series









6000 K

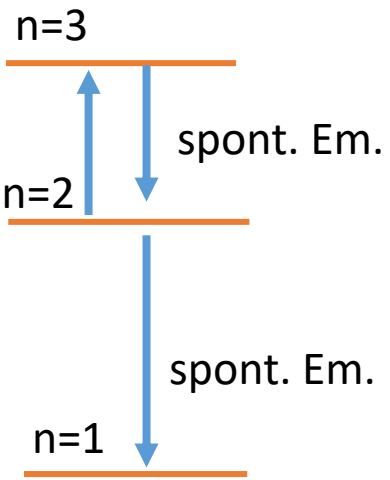
N_a species

H_α emission

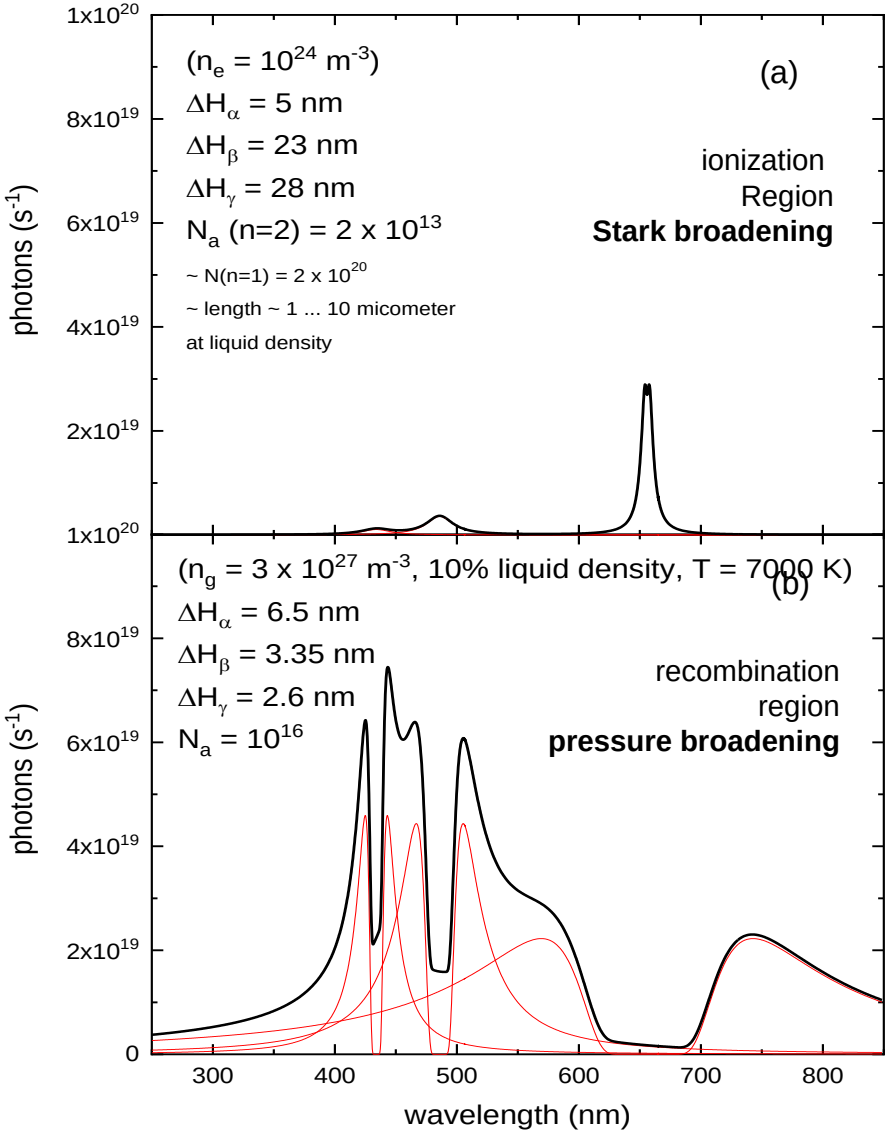
N_a species

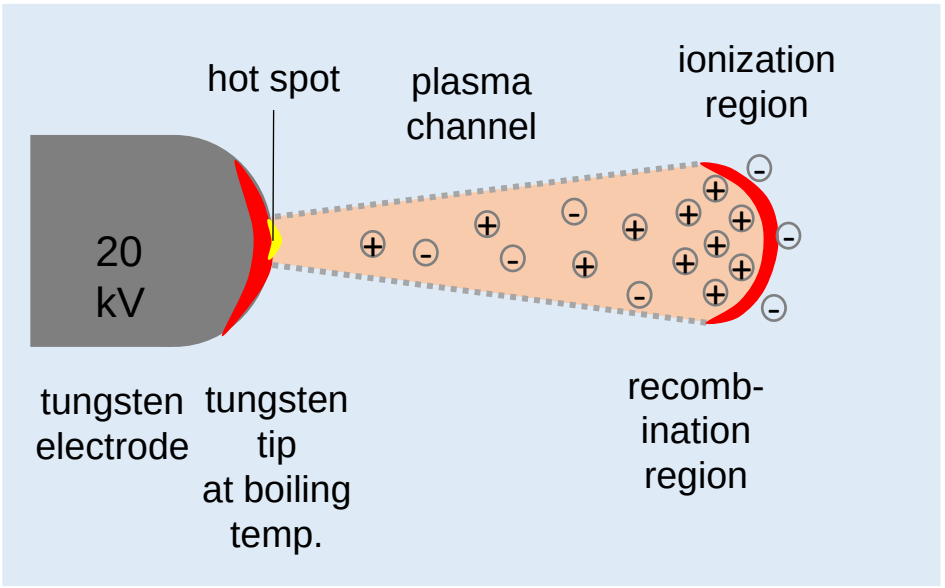
H_α absorption

Det.



Line emission – Selfabsorption of Hydrogen Balmer Series

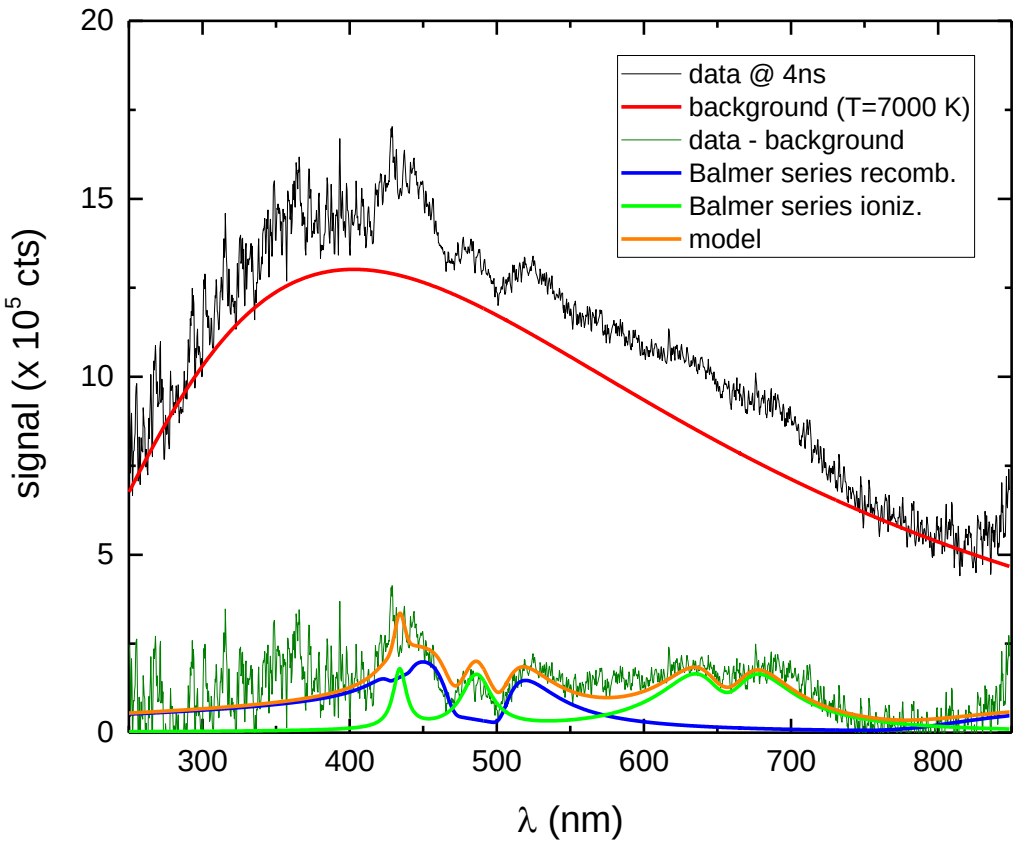




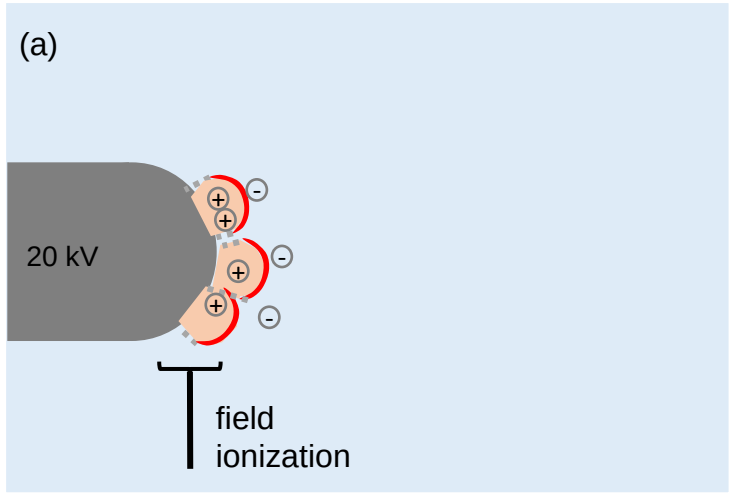
Three contributions

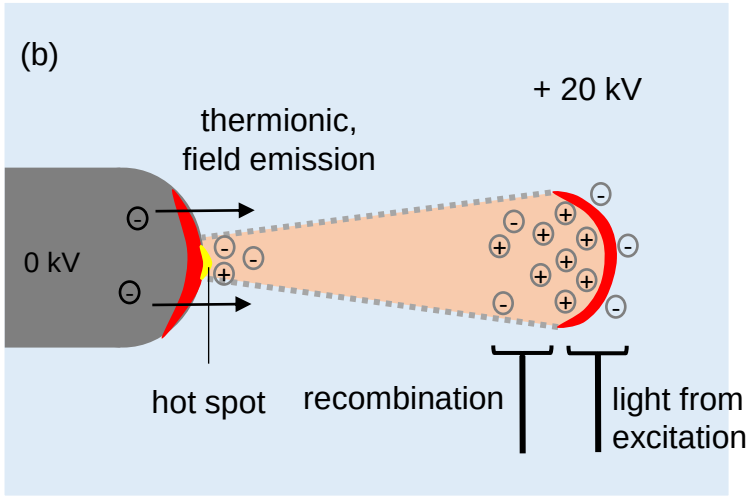
- Continuum blackbody ~ 6000 – 7000 K
- H Balmer strong self absorption - recombination region (Hγ dominates) – Number of absorbers ~ 50 µm region
- H Balmer small self absorption - ionization region (Hα dominates) - Number of absorbers ~ 1 µm region

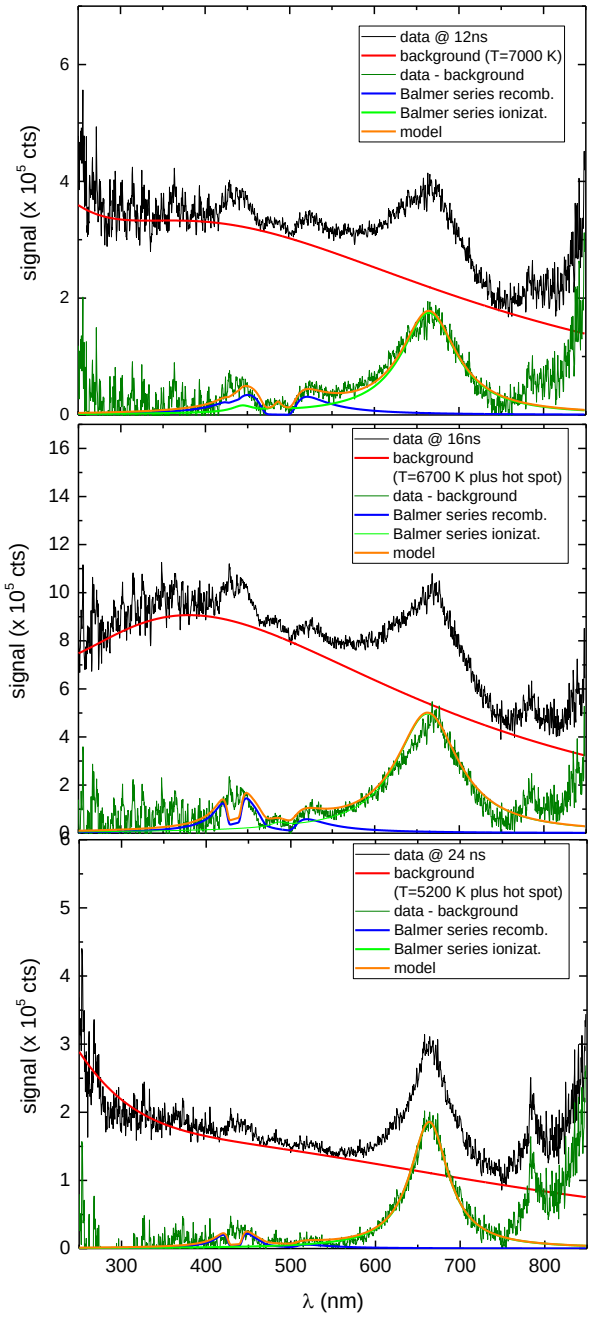
Line emission – Selfabsorption of Hydrogen Balmer Series



Degree of self-absorption of Hα requires liquid density H atoms along an optical path of 1 µm
→ Ionization occurs in high density regions
→ field effects







RUHR UNIVERSITÄT BOCHUM RUB

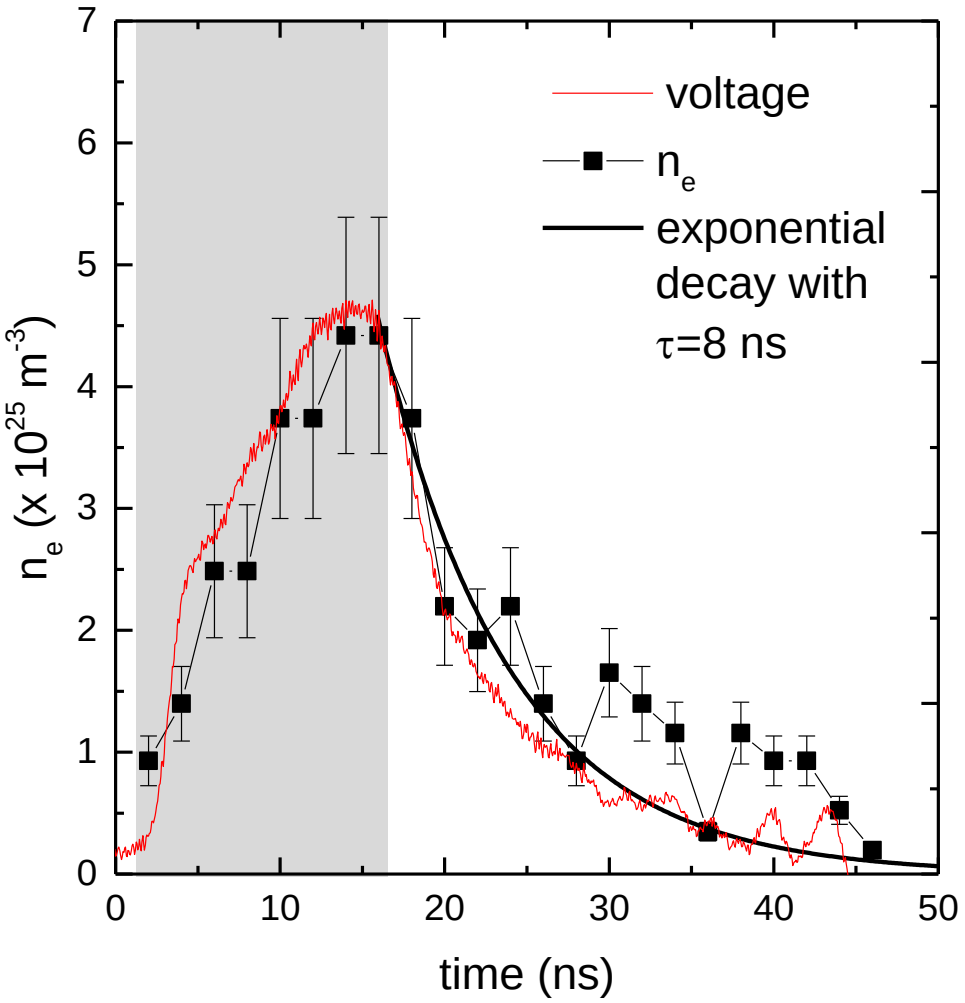
Line emission – Electron densities from Stark broadening of Hydrogen Balmer Series

electron density from Stark broadening

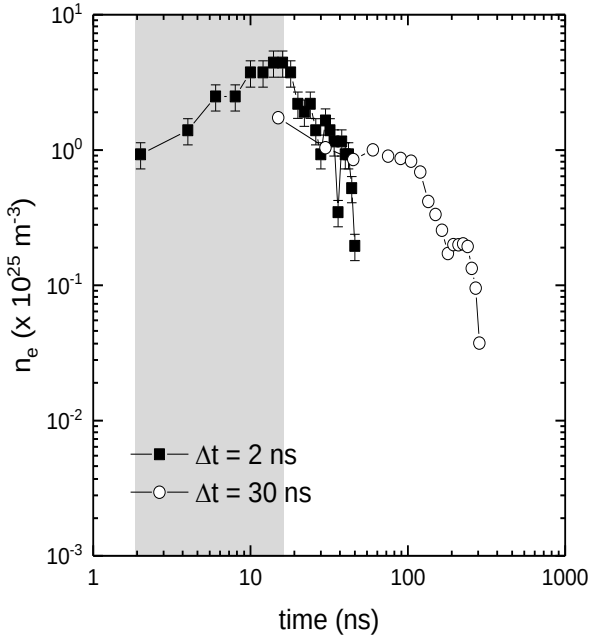
- n_e follows directly voltage (no delay as in ns air plasmas) ionization and recombination on ps time scales at liquid densities)
- decay follows the voltage

n_e ~ 5 x 10^{25} m^{-3}

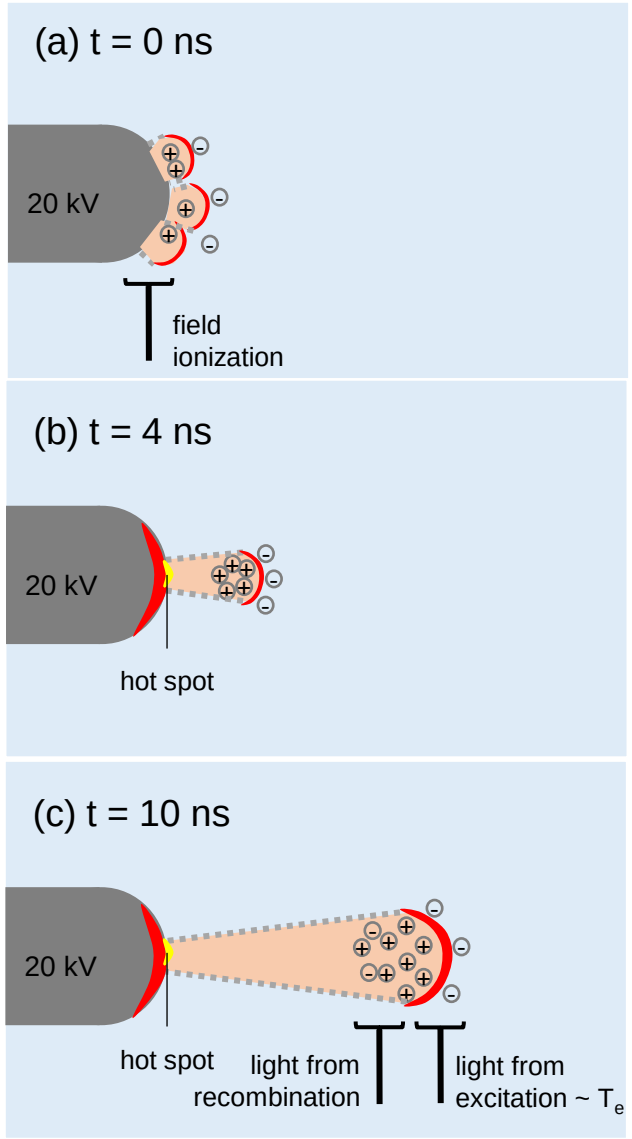
ionization degree ~ 10^{-3}



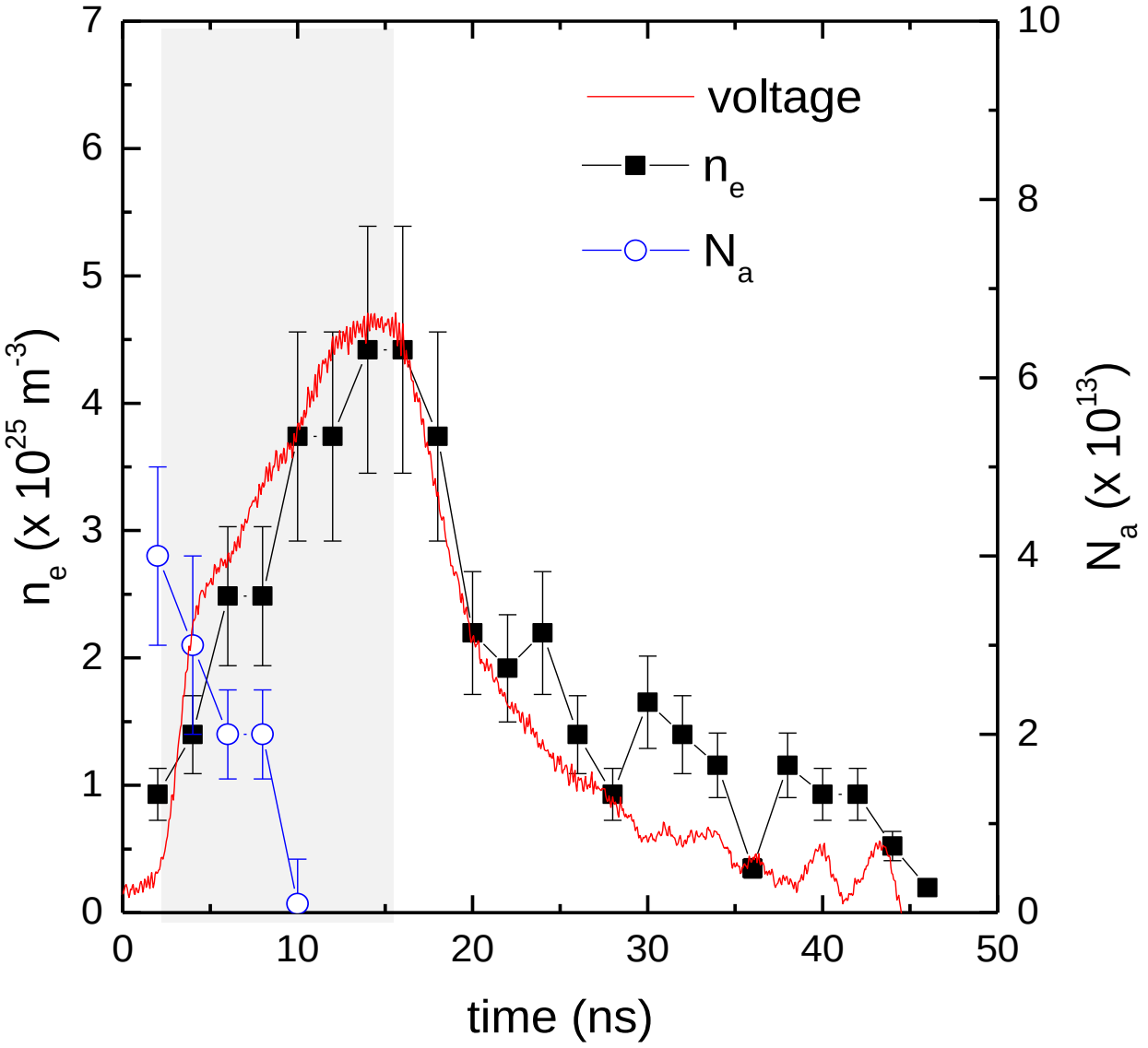
Comparison to ne decay in the re-ignited plasmas During bubble expansion



Line emission – Ionization front propagates Hydrogen Balmer Series



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



Conclusion

ns plasmas in liquids for species conversion

- 10 ns plasma ignition in the liquid creating super critical water
- Subsequent expansion can be well described by cavitation theory
- Temperatures in the range of a few 10000 K in the beginning
- Emission dynamic dominated by black body radiation tip and cathode spot
- Pressures in the range of a few 10000 bar in the beginning
- Ignition by field emission is favored.

Nanosecond plasmas in water: ignition, cavitation and plasma parameters
Katharina Grosse, Julian Held, Maike Kai, Achim von Keudell
Plasma Sources Sci. Technol. 28, 085003 (2019)

Chemistry in Nanosecond plasmas in water
L. Chauvet, C. Nenbangkaeo, K. Grosse, A. von Keudell
Plasma Processes and Polymers 201900192 (20019)

Nanosecond pulsed discharges in distilled water - Part I: Continuum radiation and plasma ignition
K. Grosse, V. Schulz-von der Gathen, A. von Keudell
Plasma Sources Sci. Technol. 29, 095008 (2020)

Nanosecond pulsed discharges in distilled water - Part II: Line emission and plasma propagation
A. von Keudell, K. Grossse, V. Schulz-von der Gathen
Plasma Sources Science and Technology 29, 085021 (2020)

DFG Deutsche Forschungsgemeinschaft

SFB 1316

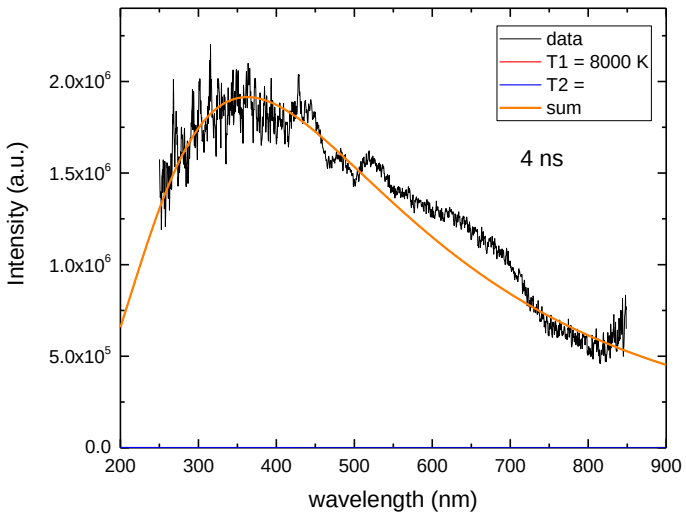
https://sfb1316.rub.de/

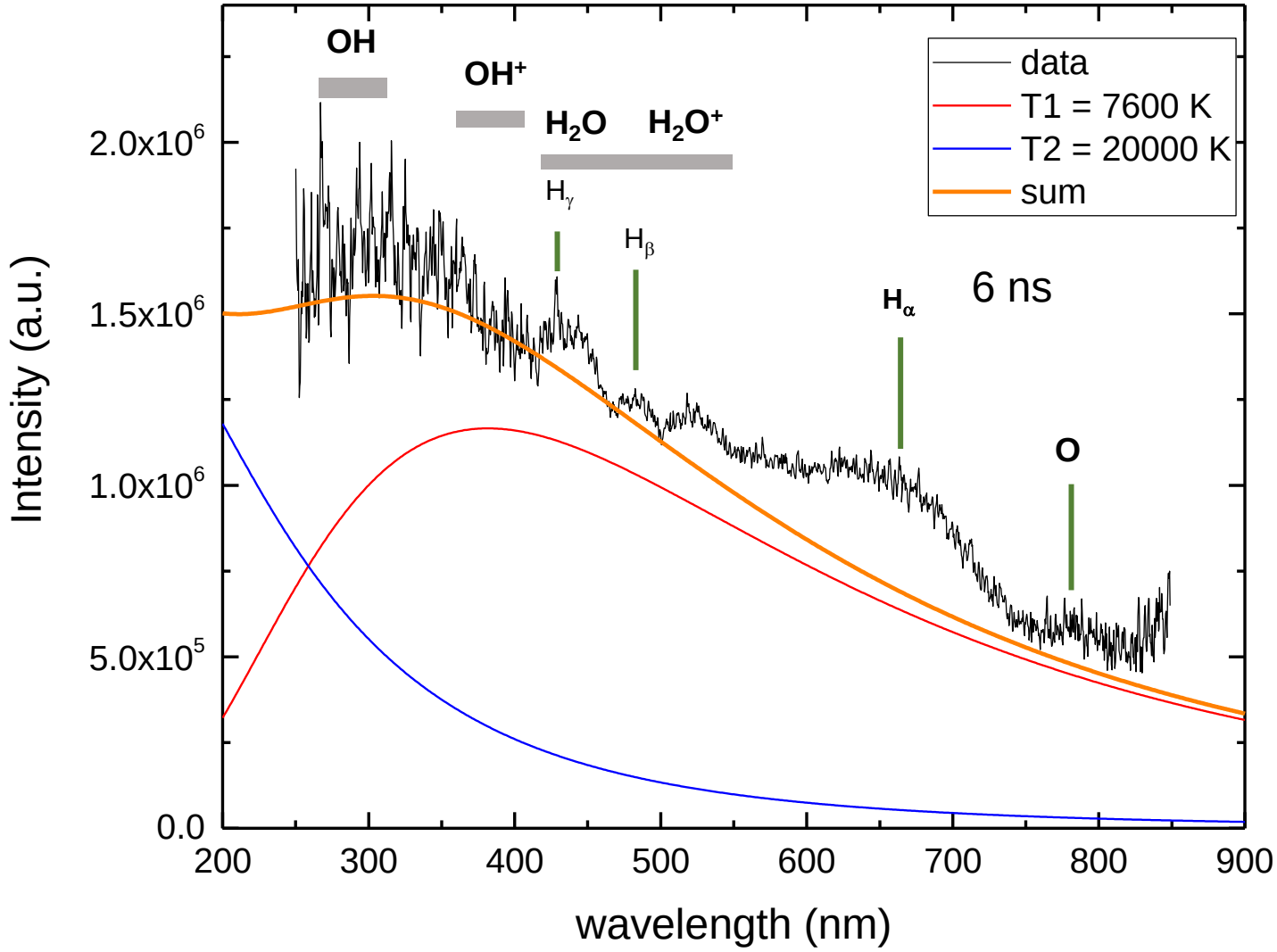
Backup Slides

Temperatures from emission spectra of the plasma UV part

Spectrum (first 50 ns, time resolution 2 ns)

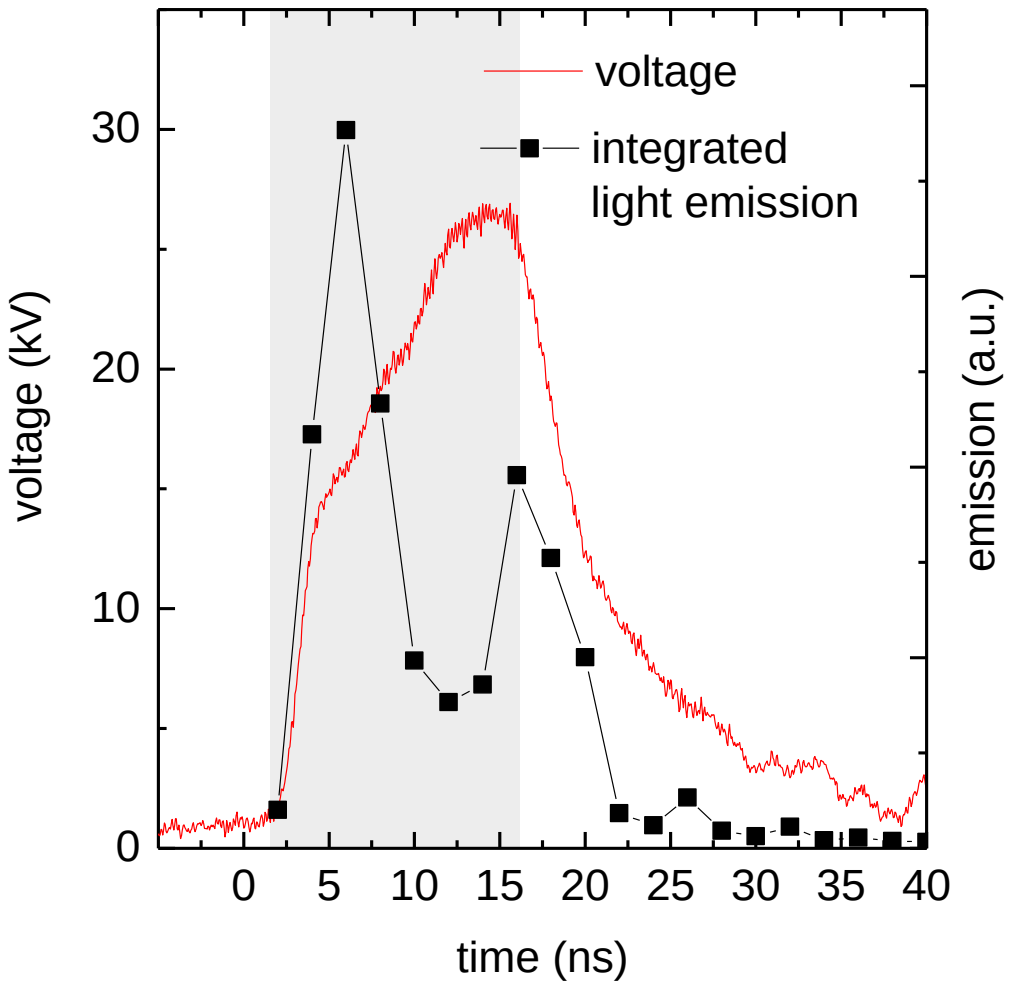
- Recombination
- H_2 , H_2O recomb. continuum
- OH, OH^+, H_2O, H_2O^+ bands
- Black body radiation (W)
- H_α
- O(777nm)

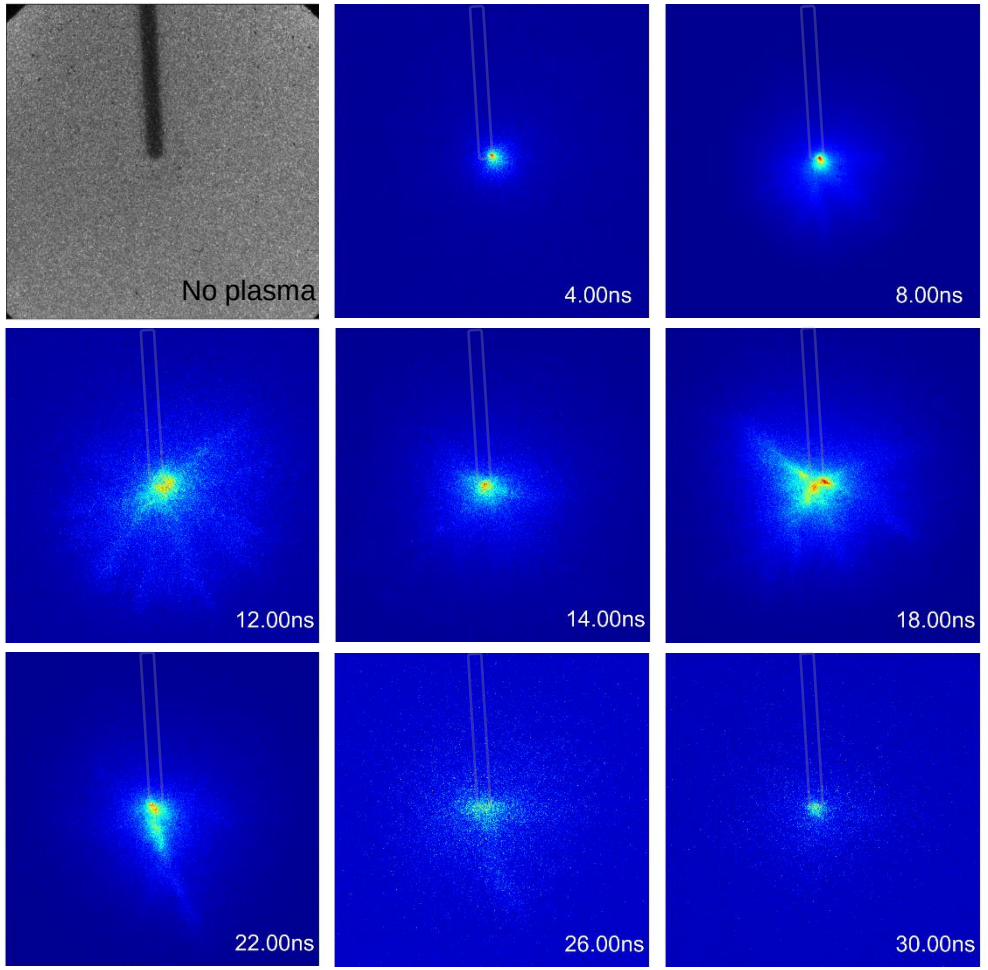




How does the plasma Ignites ?

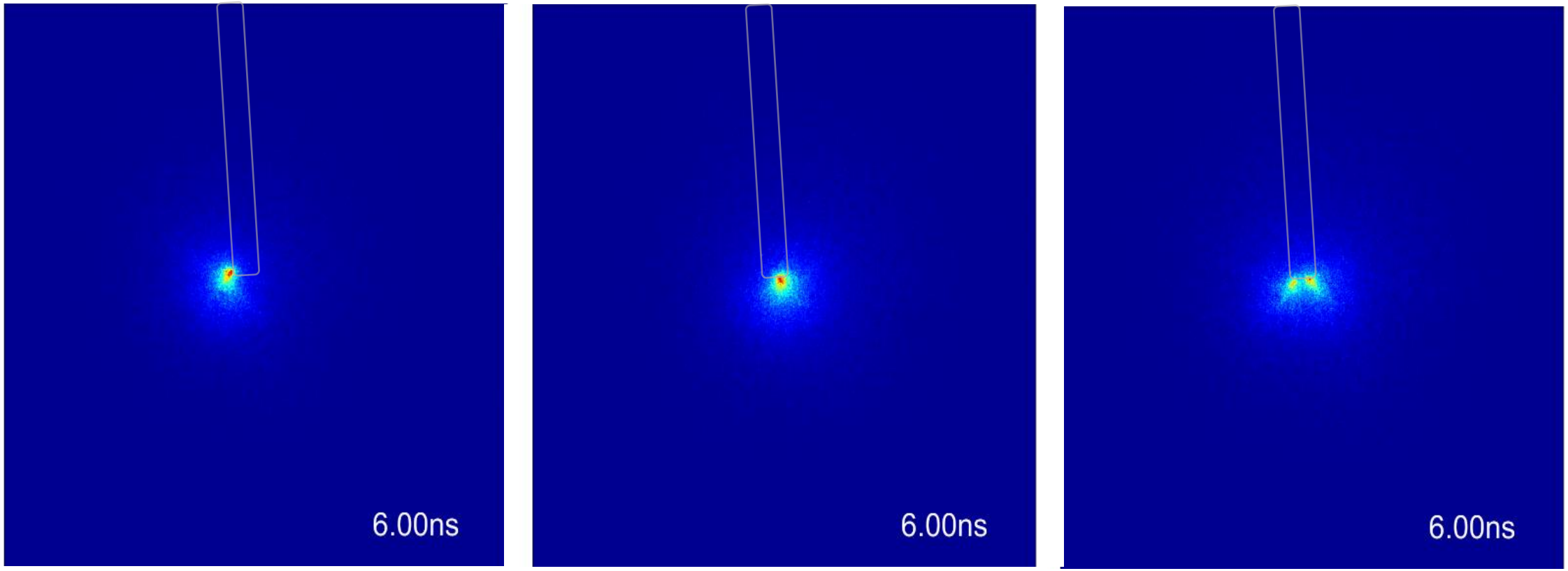
Experiment 22kV, 1Hz, distilled water, t_{gate}=2ns, t_{step}=2ns



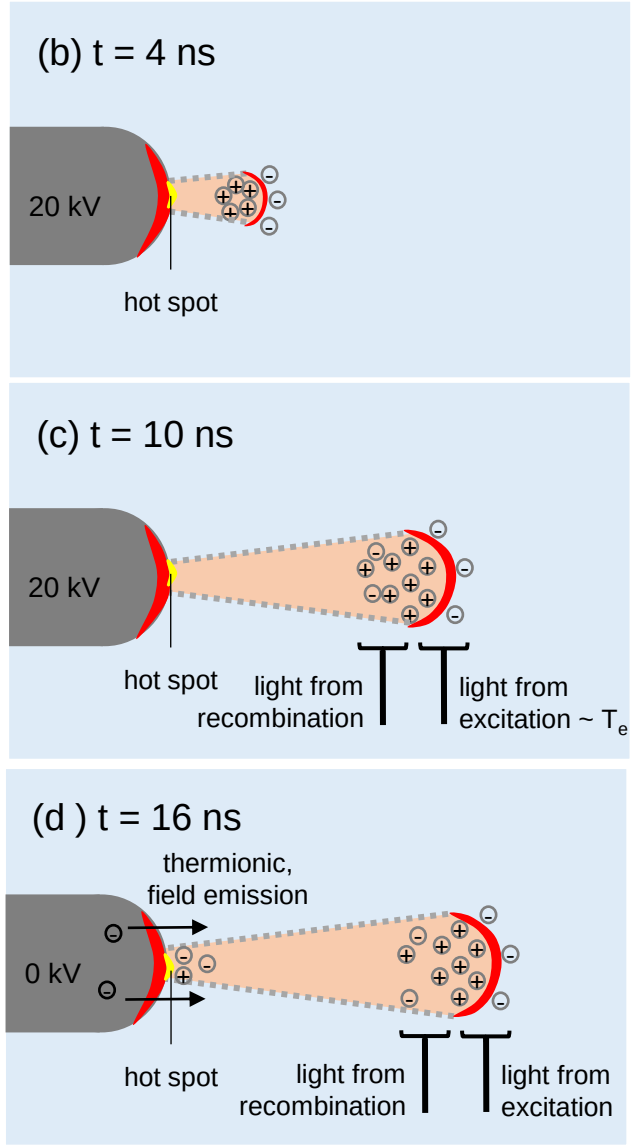


How does the plasma Ignites ?

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

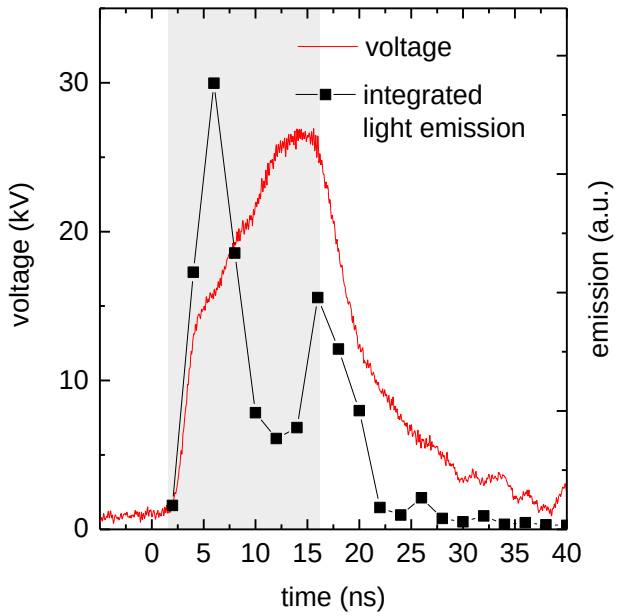


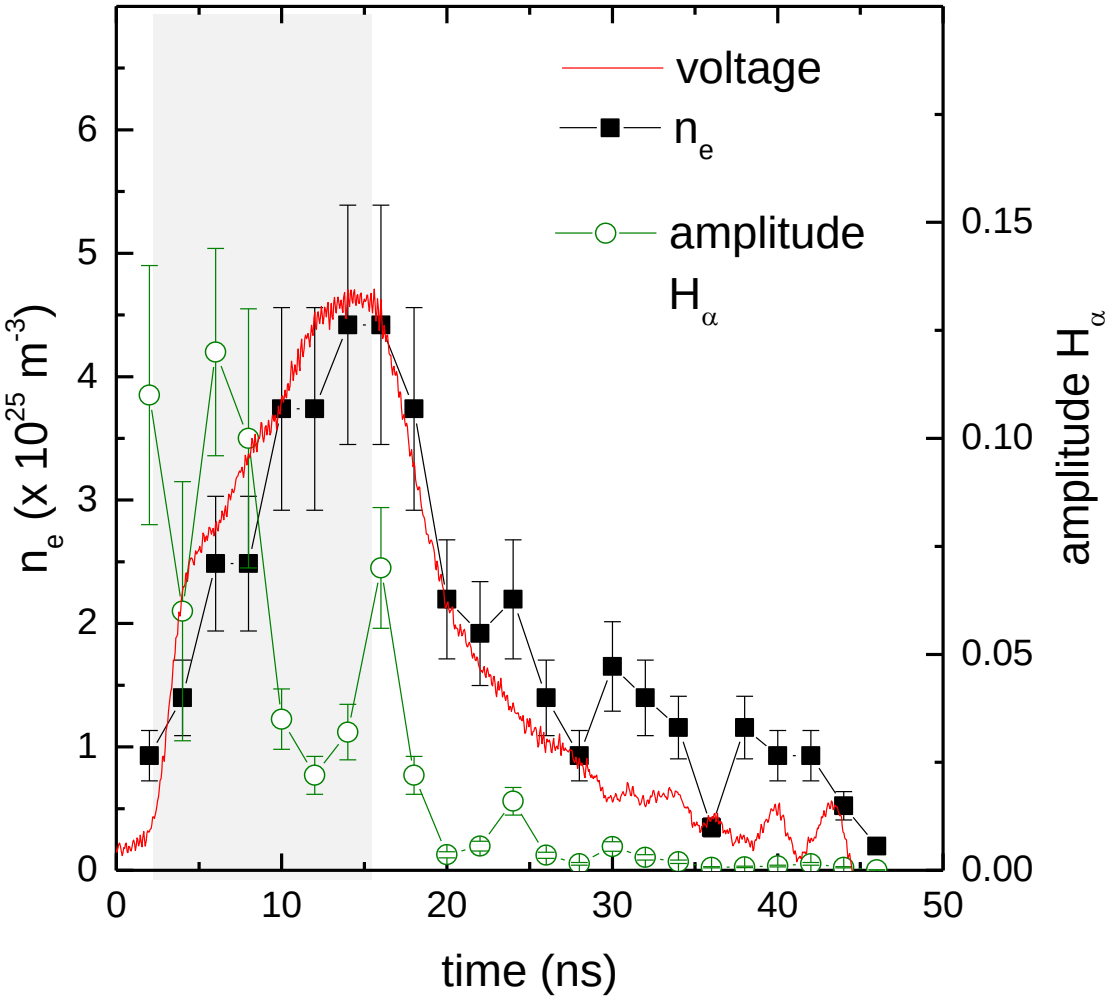
Line emission – H alpha from ionization region of Hydrogen Balmer Series



H alpha from ionization region dominates when electrons are being accelerated

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

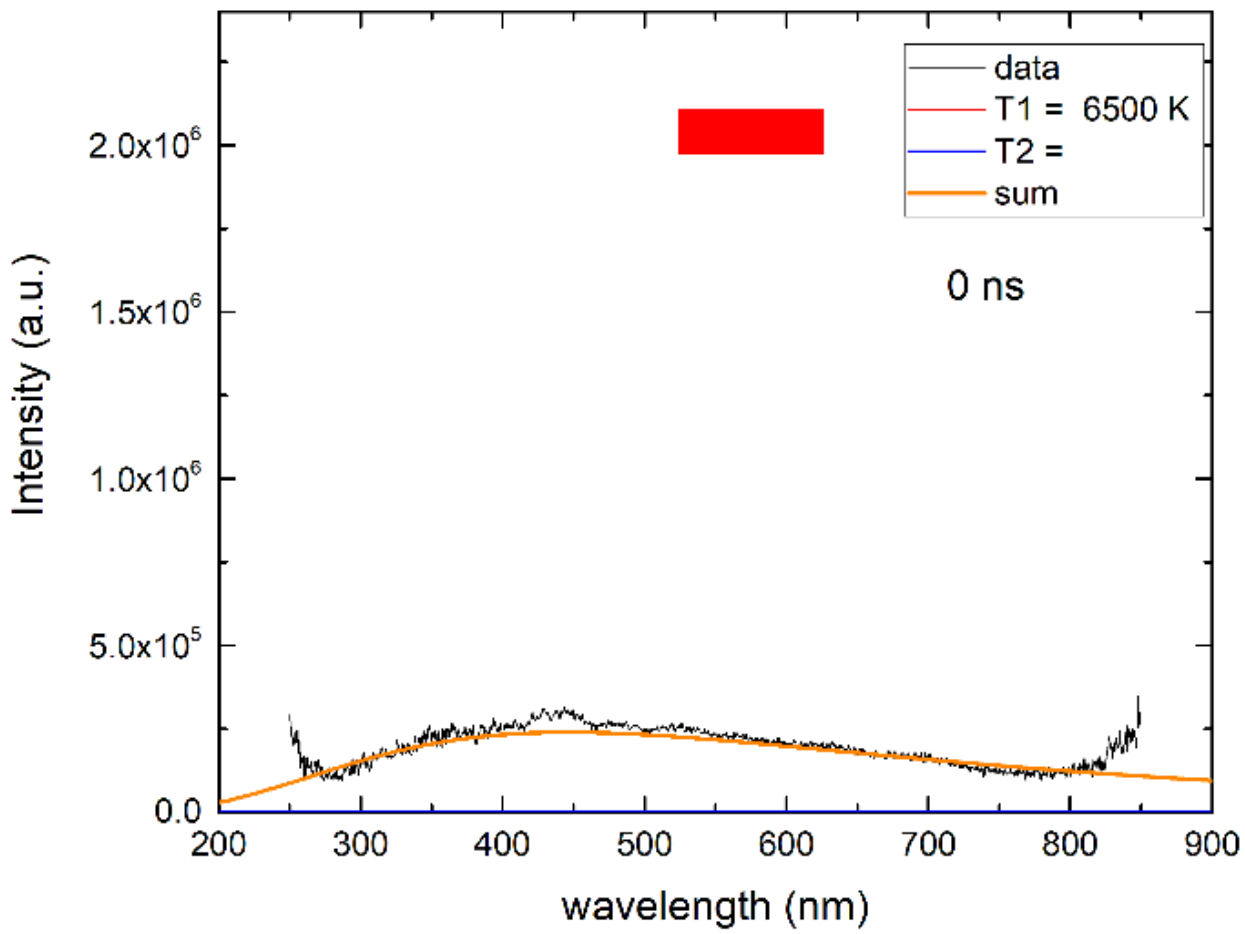




Temperatures from emission spectra of the plasma into the UV

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
- $O_{(777nm)}$



Efficiency to create H_2O_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:

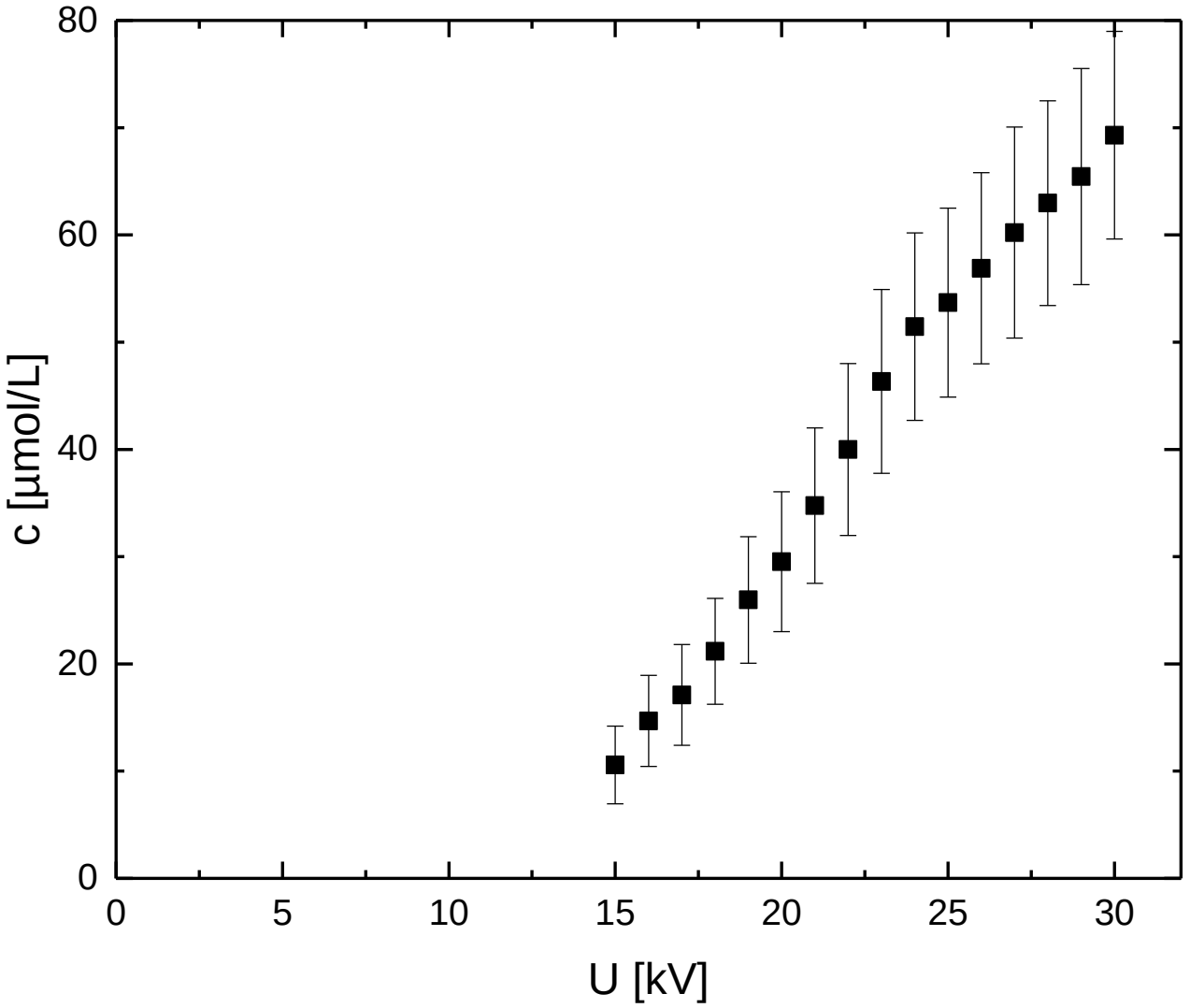
@ 20 kV, 30 µmol/l in 25 ml liquid is equivalent to 4×10^{17} species in total

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%

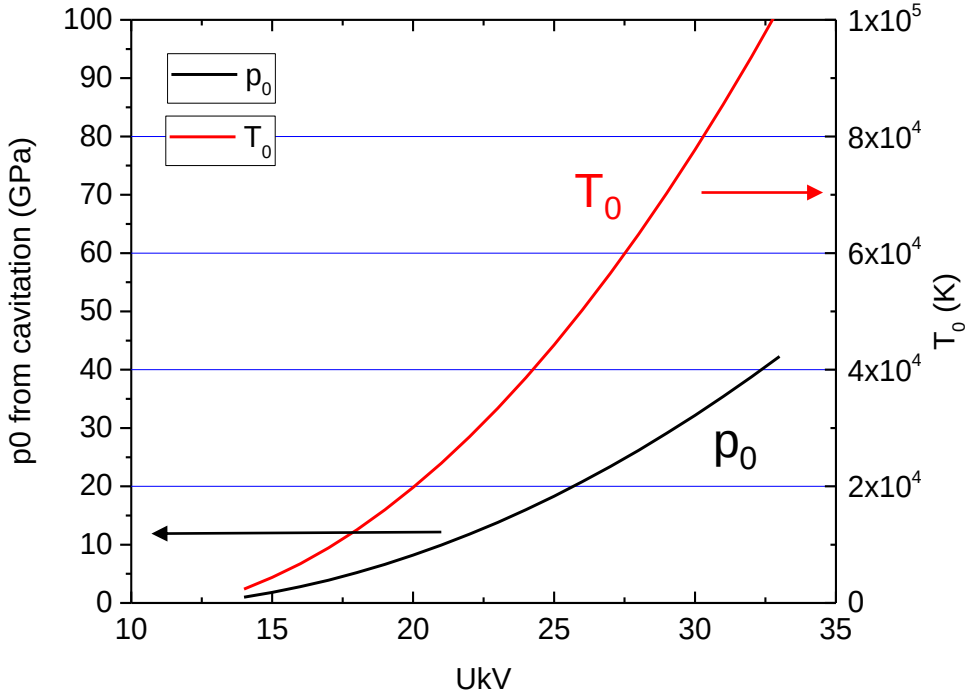


Efficiency to create H_2O_2 with these plasmas
Modeling the chemistry

*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	$k_{81} = 4.55 \cdot 10^{-12}\,(T/298)^{0.4} \cdot \exp[3090(RT)^{-1}]$
$OH + H$	$\rightarrow H_2O$	300-2100 K	$k_{82} = 2.69 \cdot 10^{-10} \exp[-620(RT)^{-1}]$
$H + OH$	$\rightarrow O + H_2$	300-2500 K	$k_{83} = 6.68 \cdot 10^{-14}(T/298)^{2.8} \cdot \exp[-16210(RT)^{-1}]$
$H_2O_2 + OH$	$\rightarrow HO_2 + H_2O$	300-2500 K	$k_{84} = 2.91 \cdot 10^{-12} \cdot \exp[-1330(RT)^{-1}]$
$O_2 + OH$	$\rightarrow HO_2 + O$	300-2500 K	$k_{85} = 3.7 \cdot 10^{-11} \cdot \exp[-220000(RT)^{-1}]$
$OH + OH$	$\rightarrow H_2O_2$	300-1500 K	$k_{86} = 1.51 \cdot 10^{-11}(T/298)^{-0.37}$
$OH + OH$	$\rightarrow 2\,O + 2H$	300-2500 K	$k_{87} = 4.09 \cdot 10^{-9} \cdot \exp[-416000(RT)^{-1}]$
H_2O_2 reactions			
$H_2O_2 + O$	$\rightarrow HO_2 + OH$	300-2500 K	$k_{88} = 1.42 \cdot 10^{-12}(T/298)^2 \exp[-16631(RT)^{-1}]$
$H_2O_2 + H$	$\rightarrow OH + H_2O$	300-2500 K	$k_{89} = 4.01 \cdot 10^{-11} \exp[-16630(RT)^{-1}]$
$H_2O_2 + H$	$\rightarrow HO_2 + H_2$	300-2500 K	$k_{810} = 8 \cdot 10^{-11} \exp[-33260(RT)^{-1}]$
$H_2O_2 + O_2$	$\rightarrow 2\,HO_2$	300-2500 K	$k_{811} = 9 \cdot 10^{-11} \exp[-166000(RT)^{-1}]$
HO_2 reactions			
$HO_2 + OH$	$\rightarrow H_2O + O_2$	300-2000 K	$k_{812} = 4.81 \cdot 10^{-11} \exp[2080(RT)^{-1}]$
$HO_2 + O$	$\rightarrow OH + O_2$	300-2500 K	$k_{813} = 2.91 \cdot 10^{-11} \exp[-1660(RT)^{-1}]$
$HO_2 + H$	$\rightarrow 2\,OH$	300-2500 K	$k_{814} = 2.81 \cdot 10^{-10} \exp[-3660(RT)^{-1}]$
$HO_2 + H$	$\rightarrow H_2 + O_2$	300-2500 K	$k_{815} = 1.1 \cdot 10^{-10} \exp[-8900(RT)^{-1}]$
$HO_2 + HO_2$	$\rightarrow H_2O_2 + O_2$	300-2500 K	$k_{816} = 3.01 \cdot 10^{-12}$
$HO_2 + H_2$	$\rightarrow H_2O_2 + H$	300-2500 K	$k_{817} = 5 \cdot 10^{-11} \exp[-109000(RT)^{-1}]$
$HO_2 + M$	$\rightarrow O_2 + H + M$	300-2200 K	$k_{818} = 2.41 \cdot 10^{-8}(T/298)^{-1.18} \exp[-2031000(RT)^{-1}]$
H reactions			
$O + H + M$	$\rightarrow OH + M$	300-2500 K	$k_{819} = 4.36 \cdot 10^{-32}(T/298)^{-1}$
$H + H + M$	$\rightarrow M + H_2$	300-2500 K	$k_{820} = 6.04 \cdot 10^{-33}(T/298)^{-1}$
$O_2 + H$	$\rightarrow OH + O$	500-2000 K	$k_{821} = 2.94 \cdot 10^{-10} \exp[-69680(RT)^{-1}]$
$O_2 + H + M$	$\rightarrow HO_2 + M$	200-2200 K	$k_{822} = 1.94 \cdot 10^{-32}(T/298)^{-1}$
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	$k_{823} = 2.97 \cdot 10^{-12}(T/298)^{1.21} \exp[-19710(RT)^{-1}]$
$O + H_2$	$\rightarrow OH + H$	300-2500 K	$k_{824} = 3.44 \cdot 10^{-13}(T/298)^{2.67} \exp[-26270(RT)^{-1}]$
O reactions			
$O + O + M$	$\rightarrow O_2 + M$	200-4000 K	$k_{825} = 5.21 \cdot 10^{-35} \exp[7480(RT)^{-1}]$
$O + H_2O$	$\rightarrow OH + OH$	300-2000 K	$k_{826} = 6.68 \cdot 10^{-13}(T/298)^{2.60} \exp[-63520(RT)^{-1}]$

Efficiency to create H_2O_2 with these plasmas
Modeling the chemistry

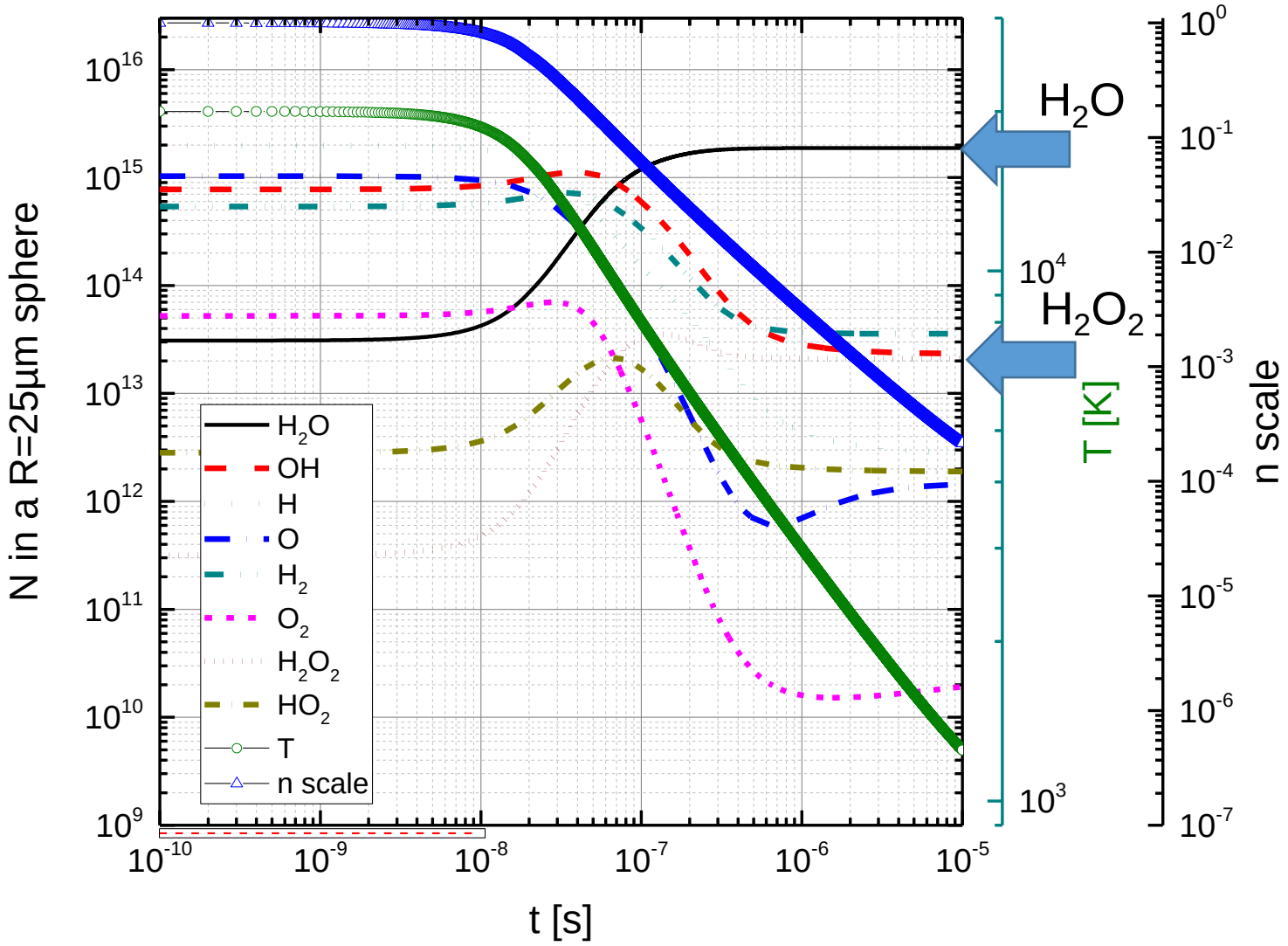
- Starting point
  gas density 3 x 10^{22} cm^{-3}
- Starting Temperature T = 20000 K
- **H_2O_2/H_2O ratio at 10 µs ~ 10^{-2}**

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, $H_2O \rightarrow H_2O_2 + H_2 + O + H$

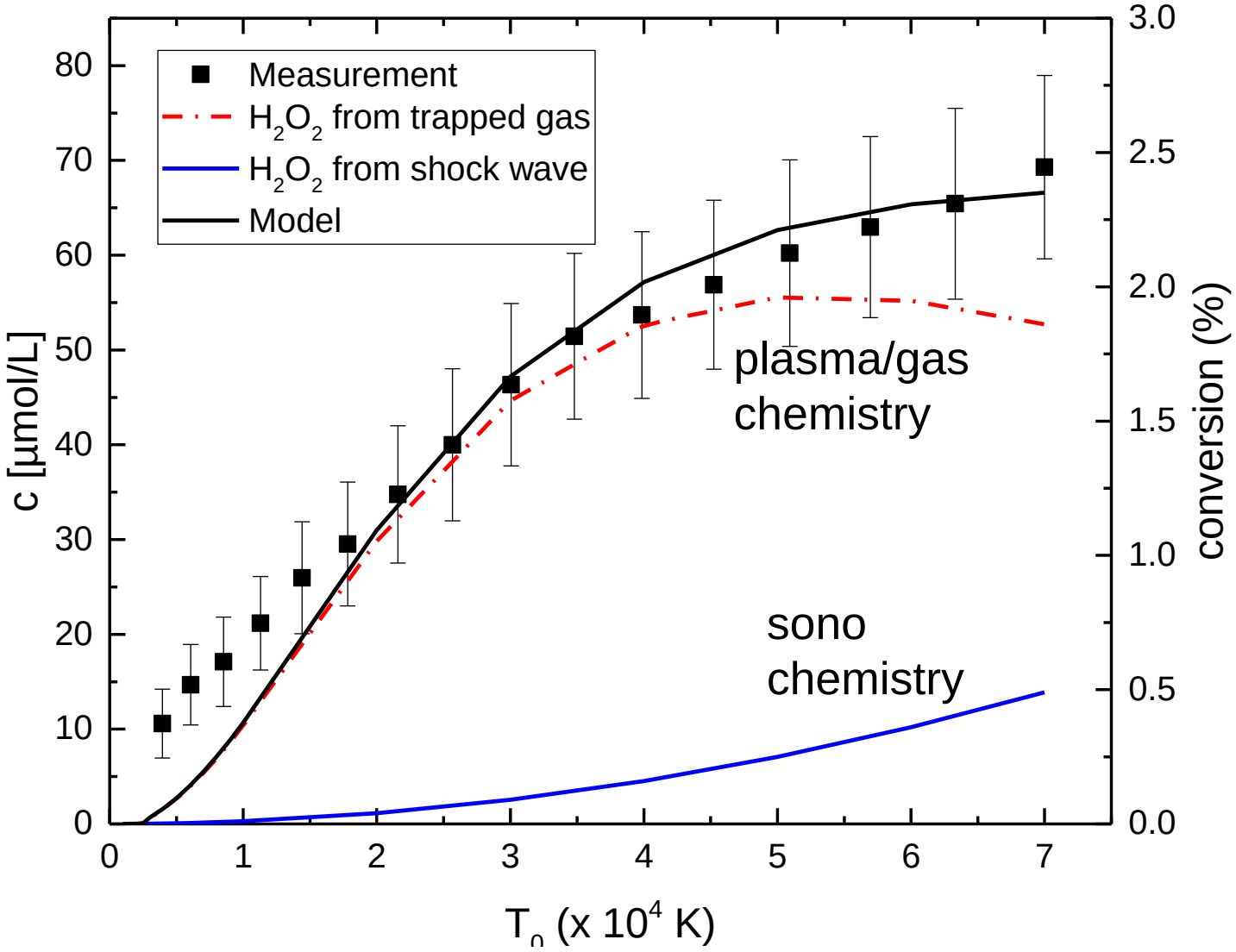
Efficiency to create H_2O_2 with these plasmas
Modeling the chemistry

- 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

efficiency 1.1%
@ 20 kV (20000 K)

- 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)



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)

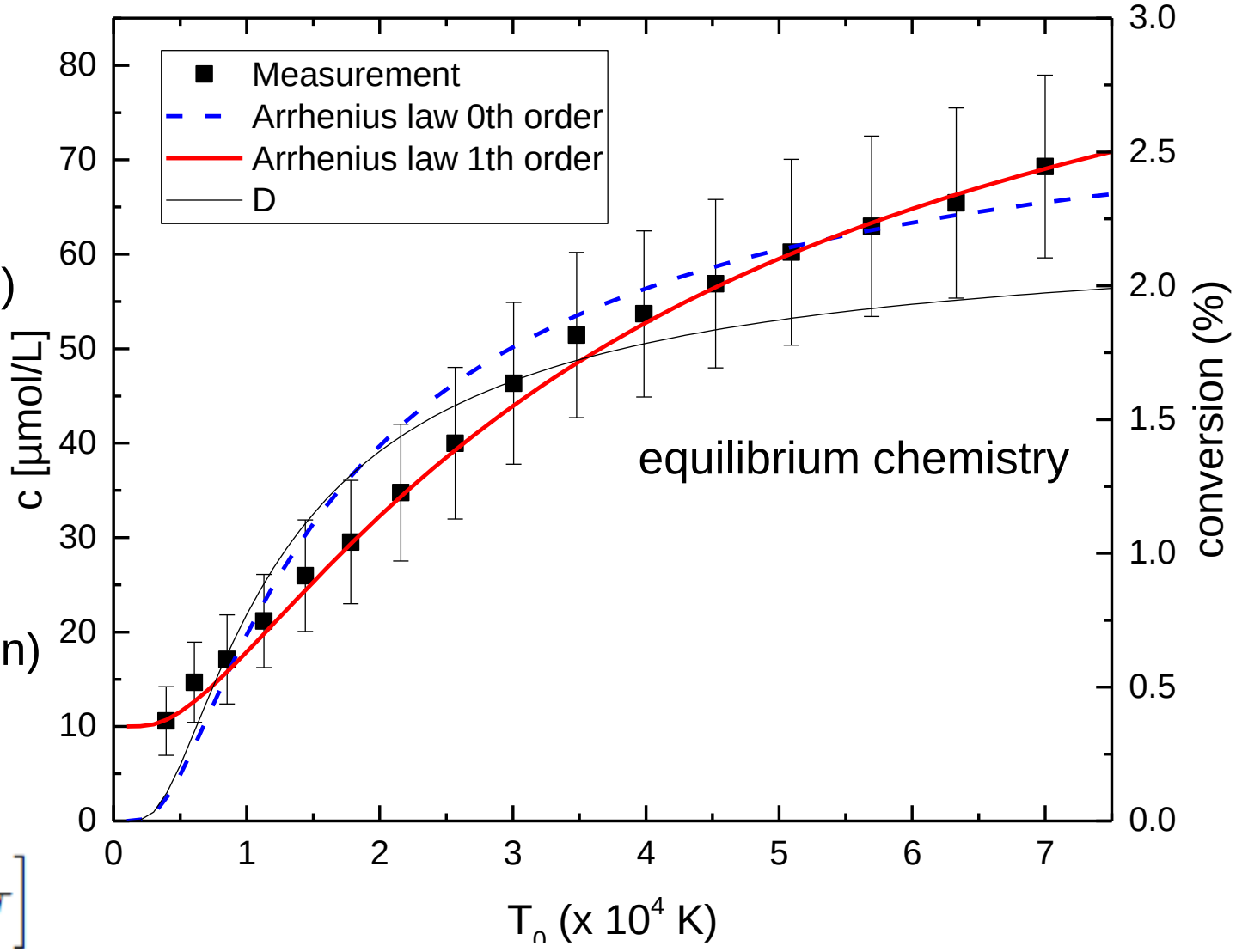
$$\frac{dn_{H_2O_2}}{dt} = k n_{H_2O}$$

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

1st order reaction (with local H_2O depletion)

$$\frac{dn_{H_2O_2}}{dt} = -\frac{dn_{H_2O}}{dt} = k n_{H_2O}$$

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

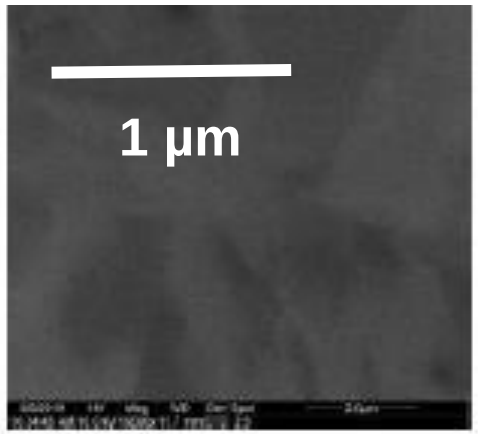


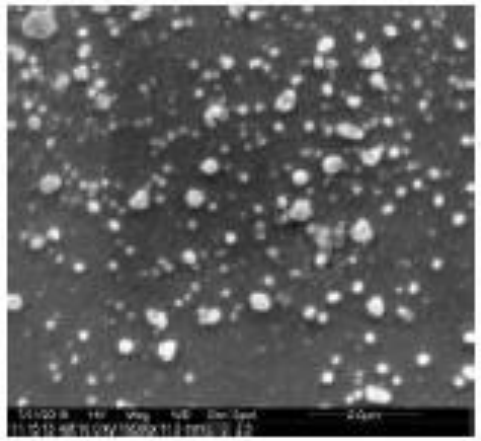
Nanosecond plasma based recovery of CuO nanocubes at copper electrodes

distilled water

dist. Water + 0.0035M KCl

20 kV

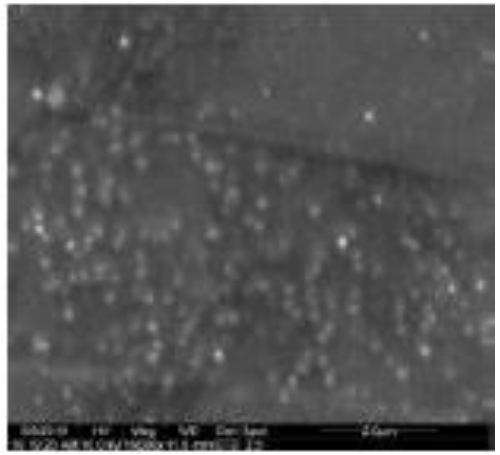


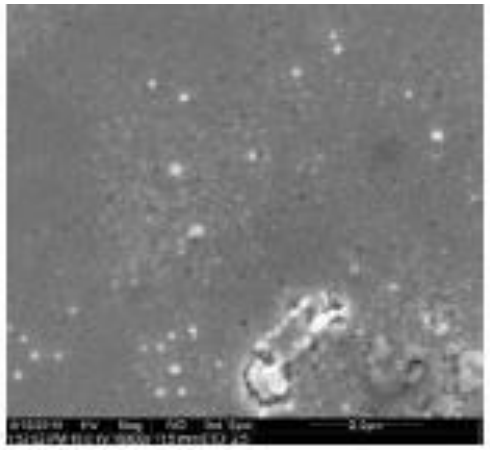


distilled water

dist. Water + 0.0035M KCl

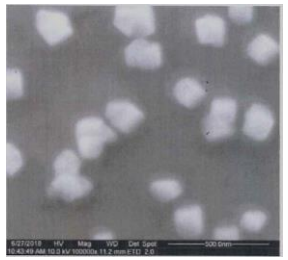
26 kV





Creation of Cu-nanocubes possible, if

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

$\langle p \rangle_{initial}$ scales with the dissipated energy

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

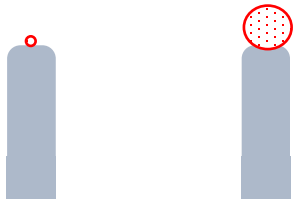
for R= 2.5 kOhm

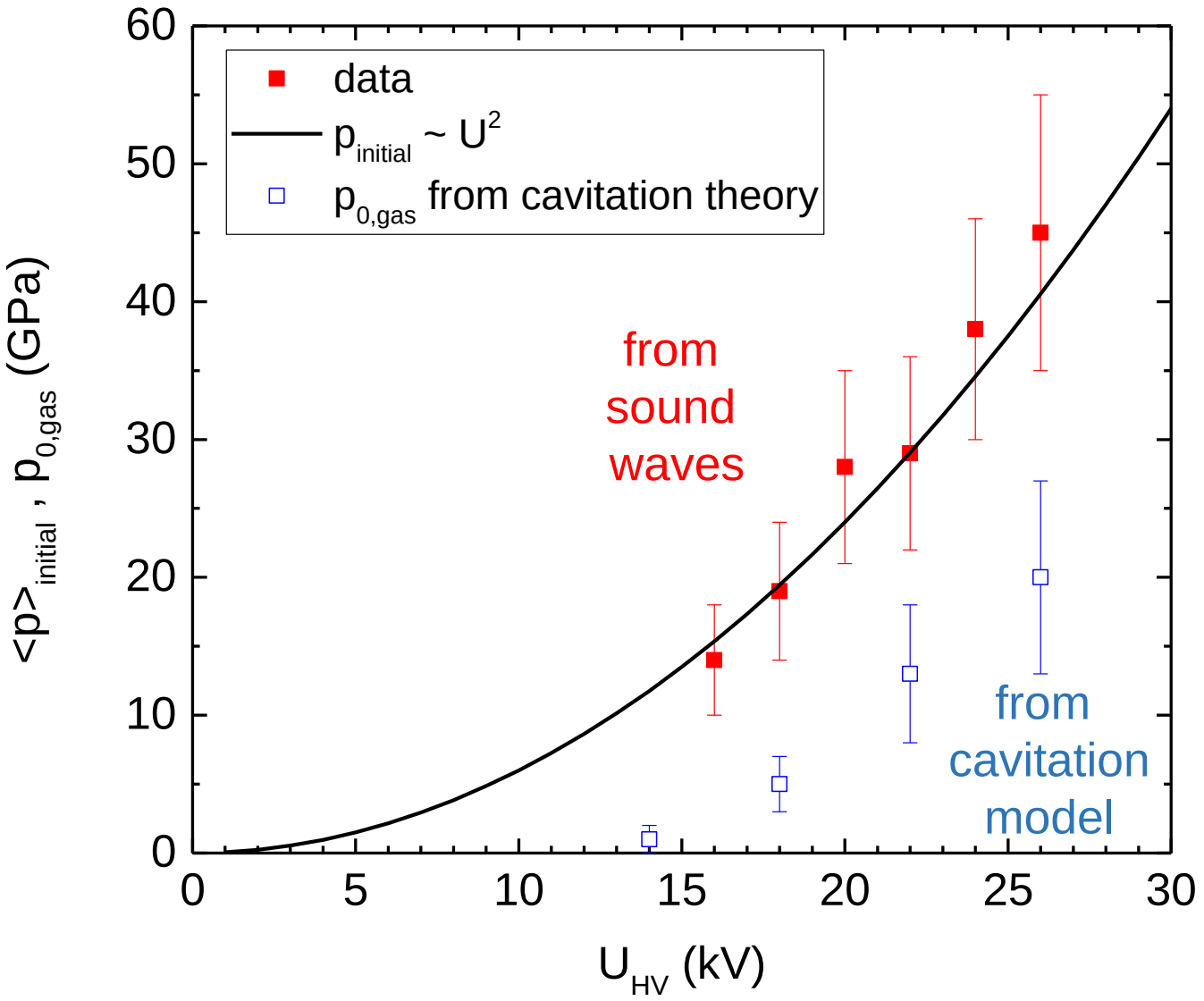
p_0, V_0

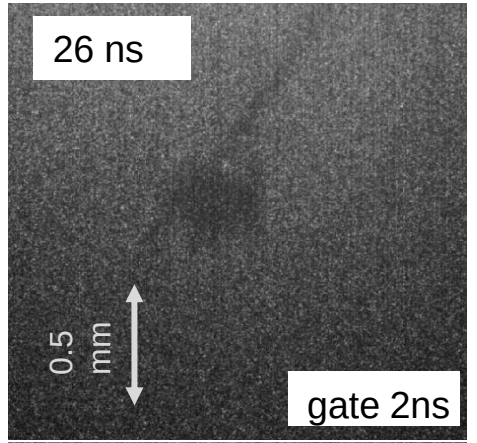
r = 25 µm
t = 10ns

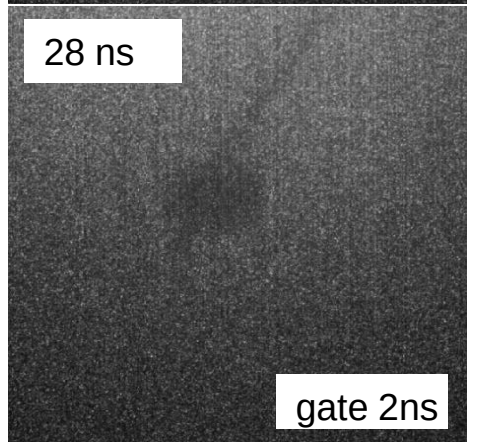
T ~ 2000… 70000 K

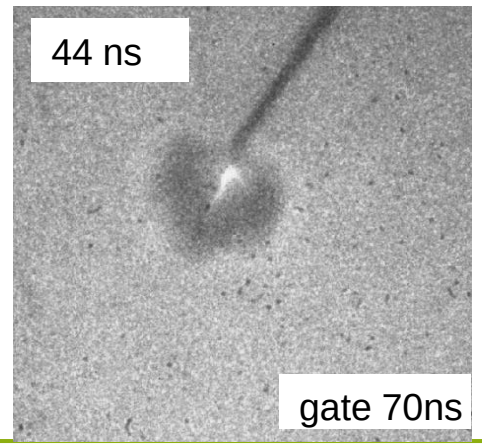
Ignition plasma



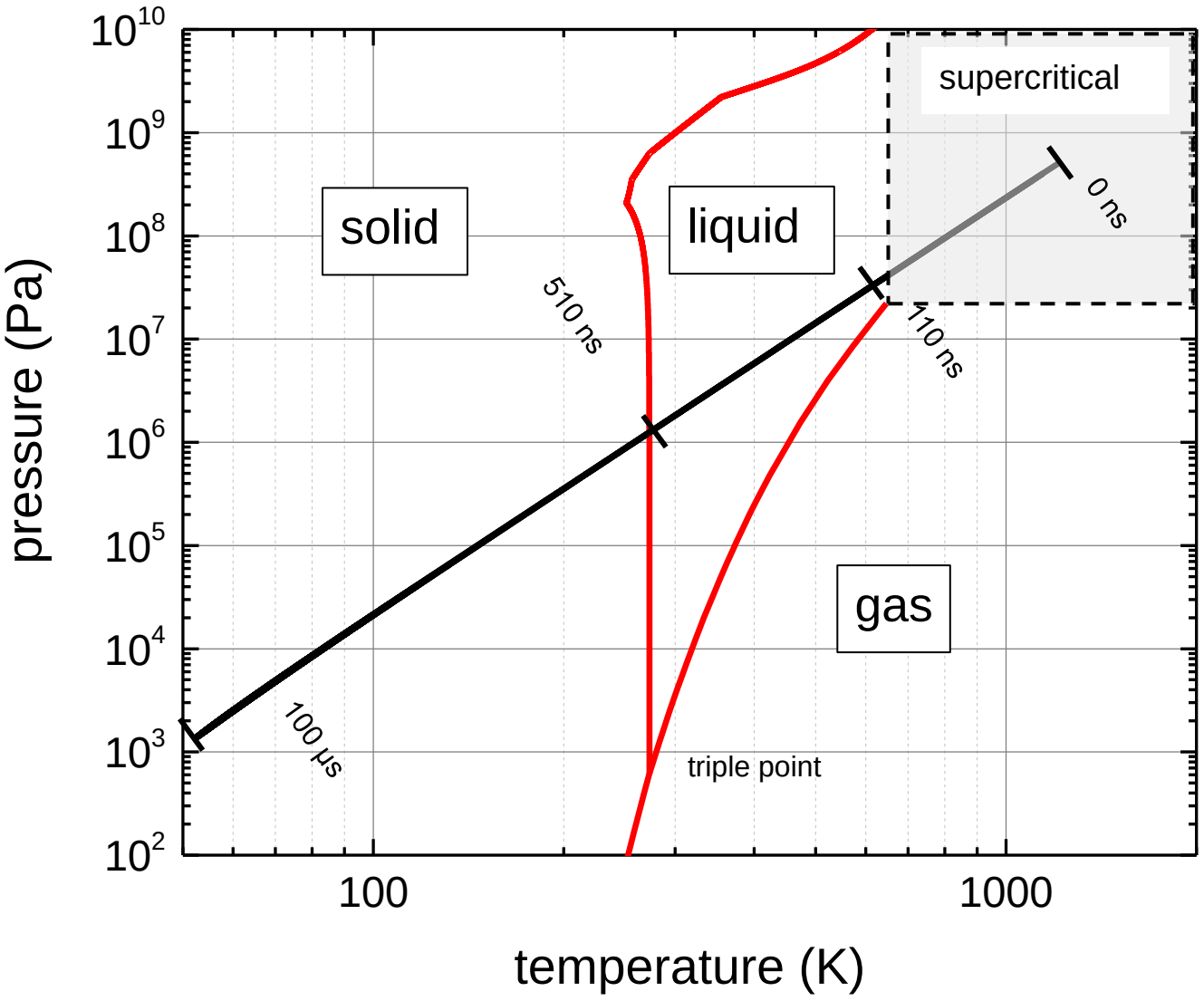


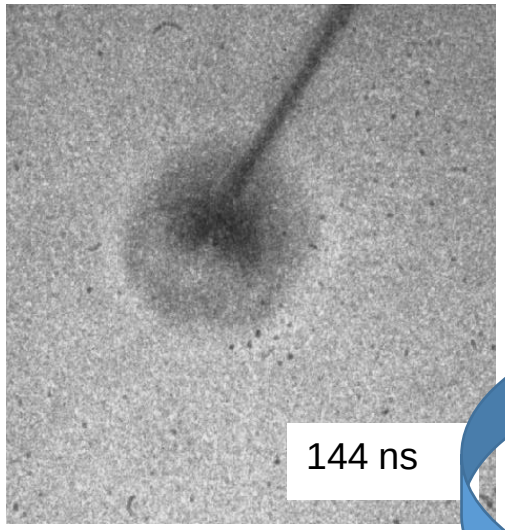


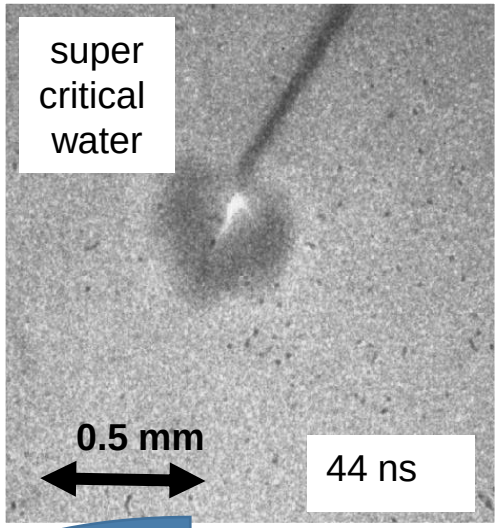


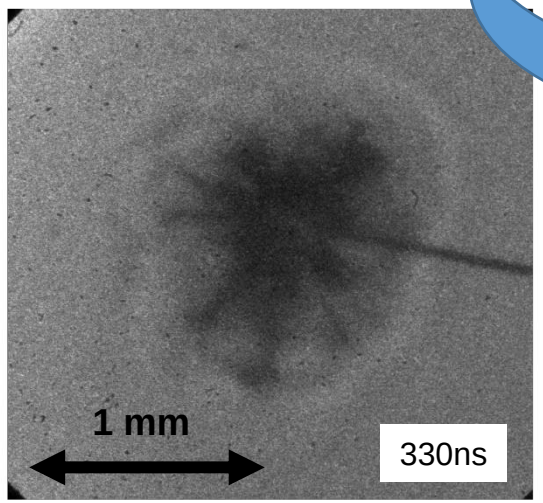


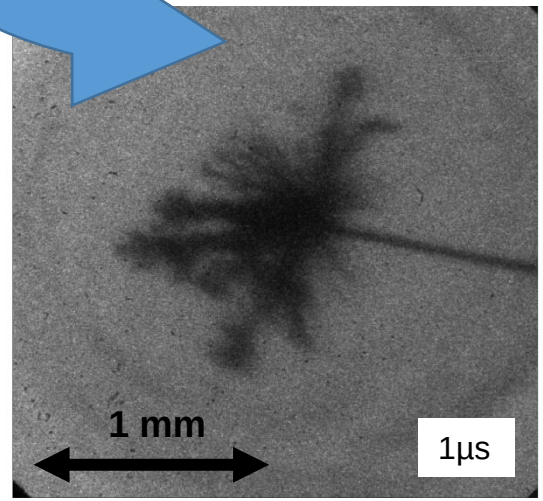
Transition of the water vapor in the bubble through the phase diagram of water











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

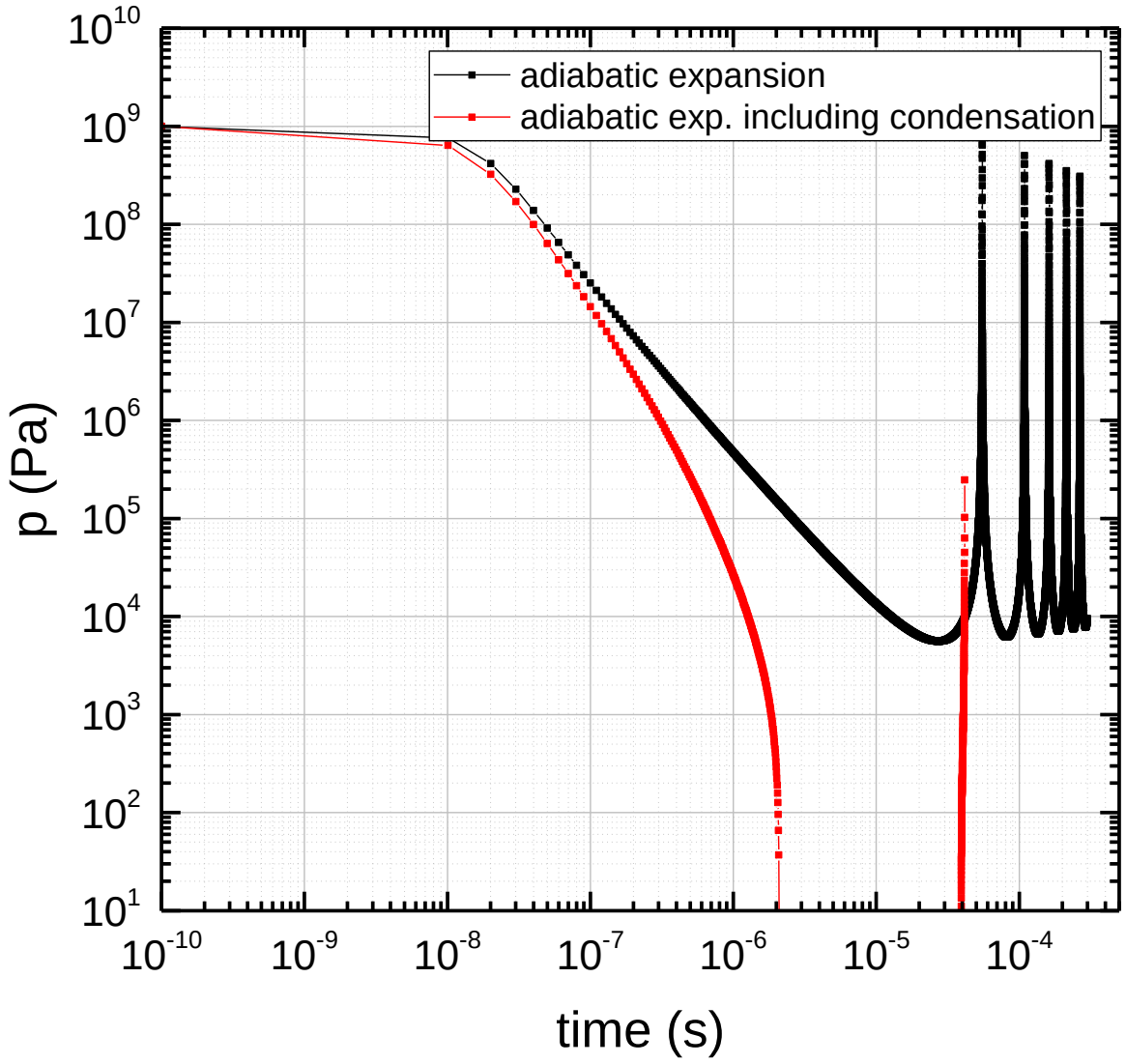
Balance between surface flux and volume loss depending on R,
β=sticking coeff. = 1

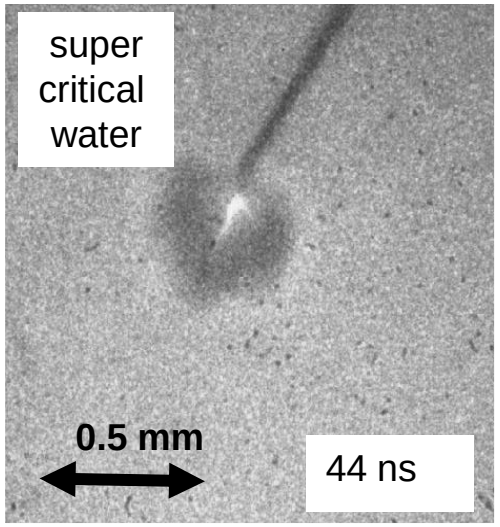
$$\frac{1}{4} n v_{therm} 4\pi R^2 \beta = \frac{4\pi}{3} R^3 n \frac{1}{\tau}$$

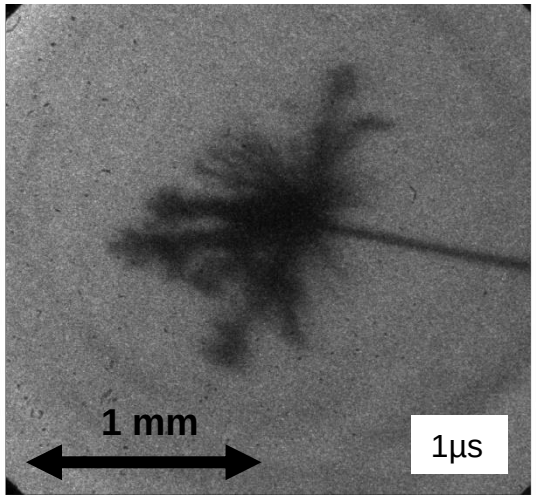
$$\tau = \frac{4R}{3 v_{therm} \beta}$$

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

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

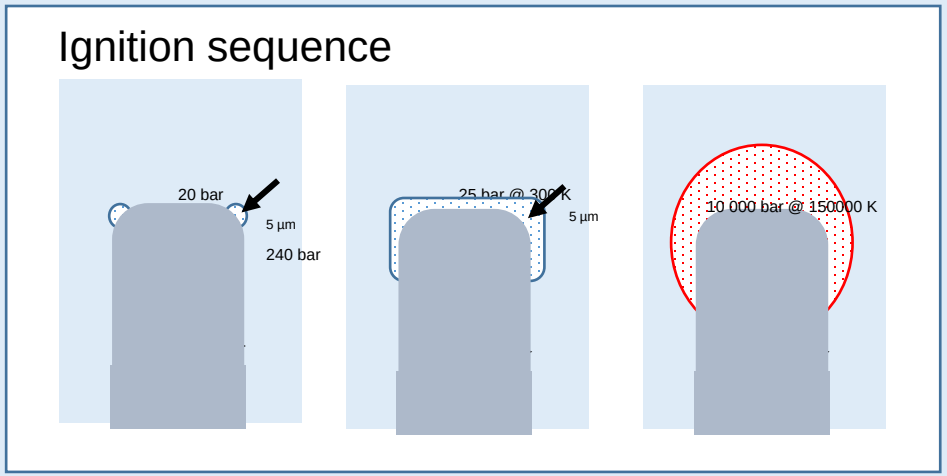






Plasma in a bubble expansion

everything to scale



r_{max} =600 µm
t=60 µs

r_{min} =5 µm
t=100 µs

sound wave

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

Ignition plasma

supercrit. vapor

sound wave

re-heated

re-heated

conden-sation

re-heated

gas

collapse

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

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

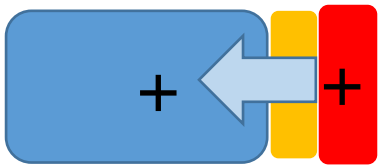
n_0=2.6 $10^{27}$$m^{-3}$
n_e=$10^{25}$$m^{-3}$
p=2 10^7 Pa
T=550 K

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

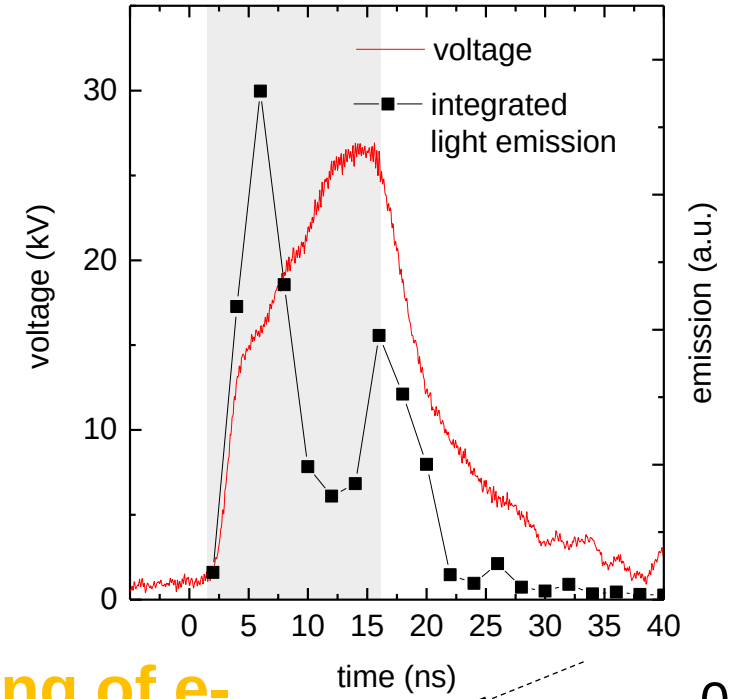
n_0=2.8 $10^{26}$$m^{-3}$
p=10^6 Pa
T= 260 K

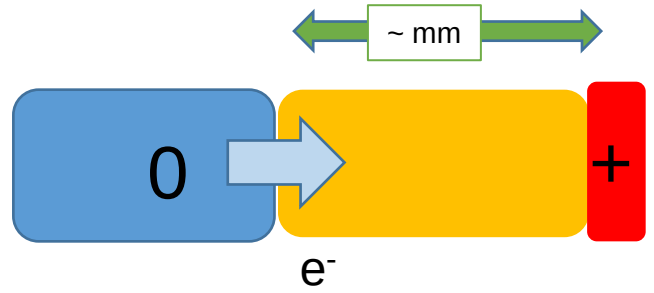
n_0=1.4 $10^{24}$$m^{-3}$
p=10^3 Pa
T=50 K

Field emission effects



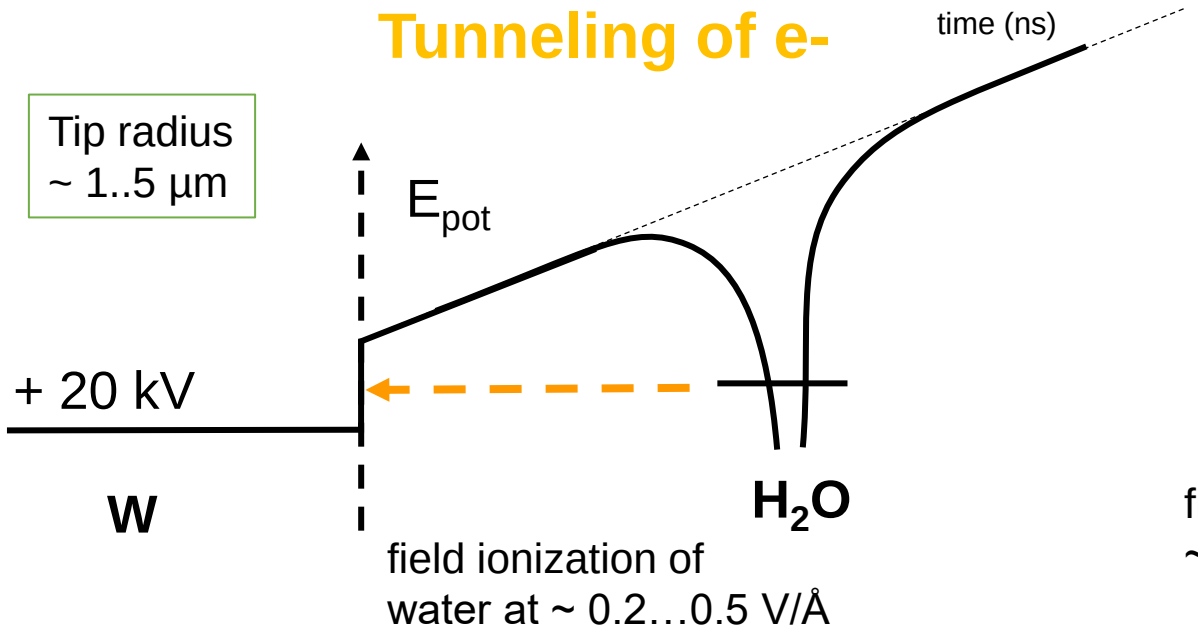
Start of the pulse water is polarized
Field ionization



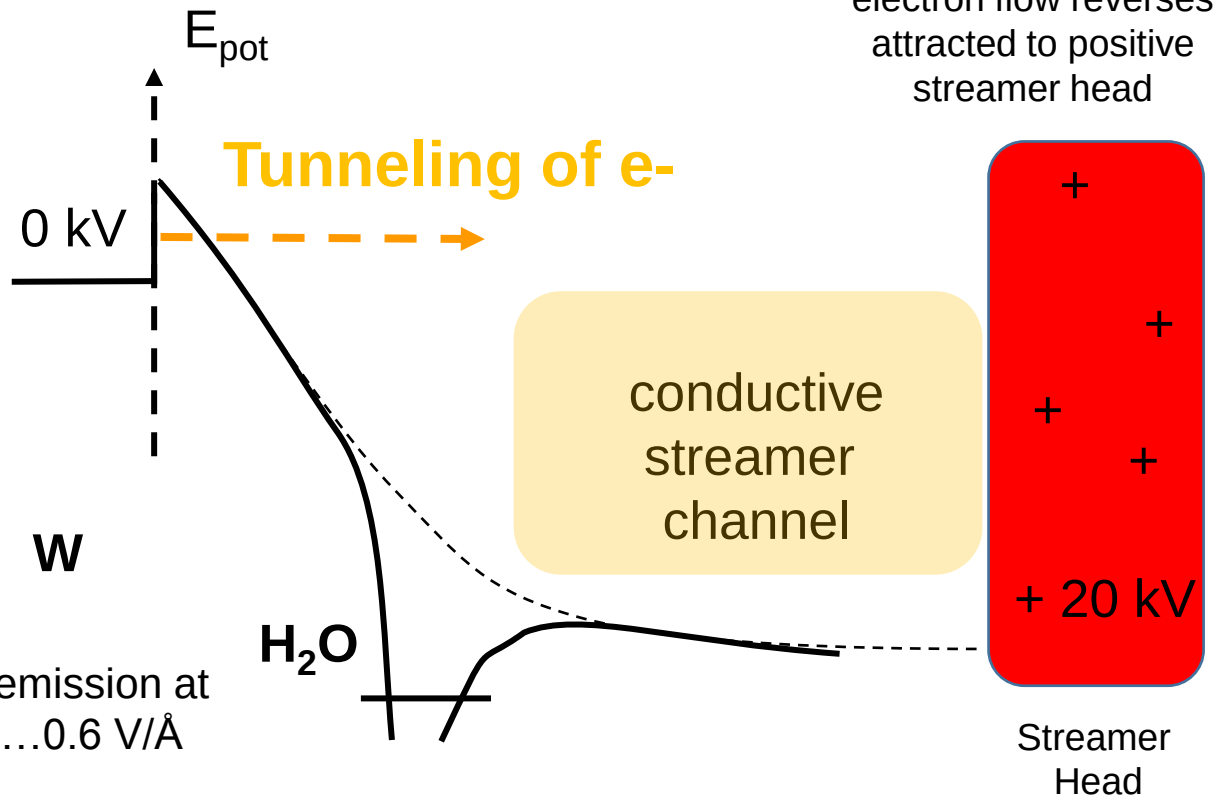


Voltage stops,
Field emission
electron flow reverses
attracted to positive
streamer head

Tip radius
~ 1..5 µm



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



field emission at
~ 0.3…0.6 V/Å

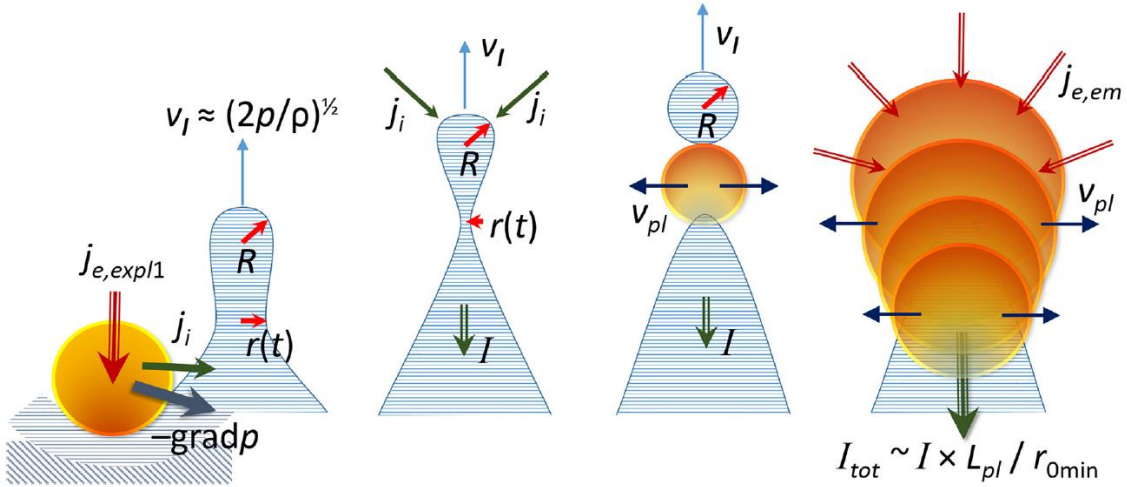
Streamer Head

Nature of the 1/λ^x background in emission

Possible sources for 1/λ^x background

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

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

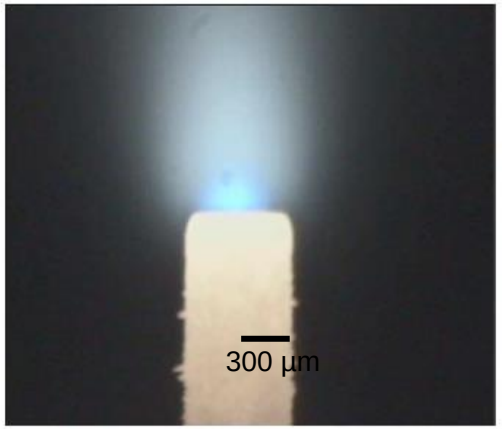


initial droplet R=1µm

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

Tsventoukh, Phys. Plasmas 25, 53504 (2018)

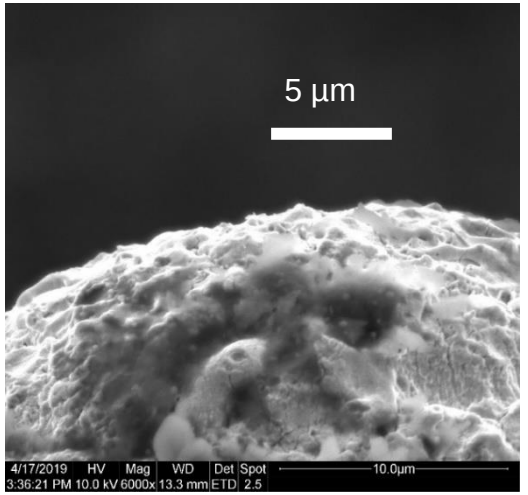
Example cathode spots in arc lamps

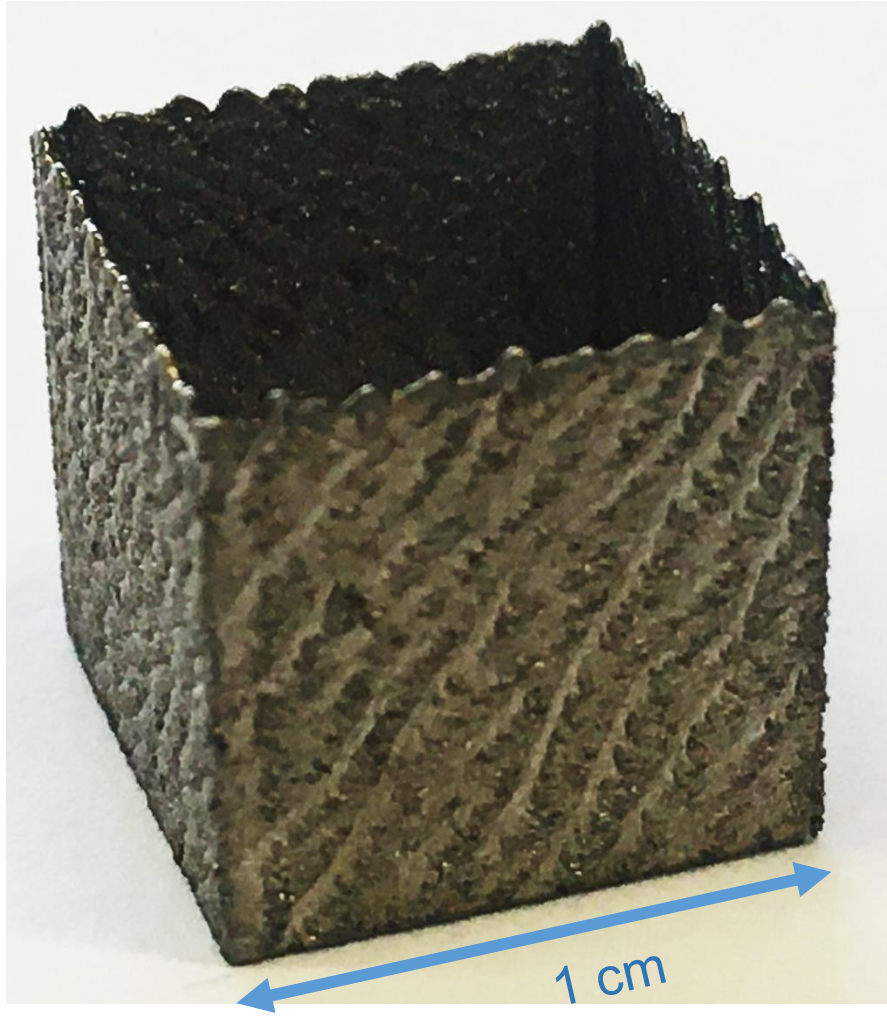


(d) $i_{arc} = 15.0$ A

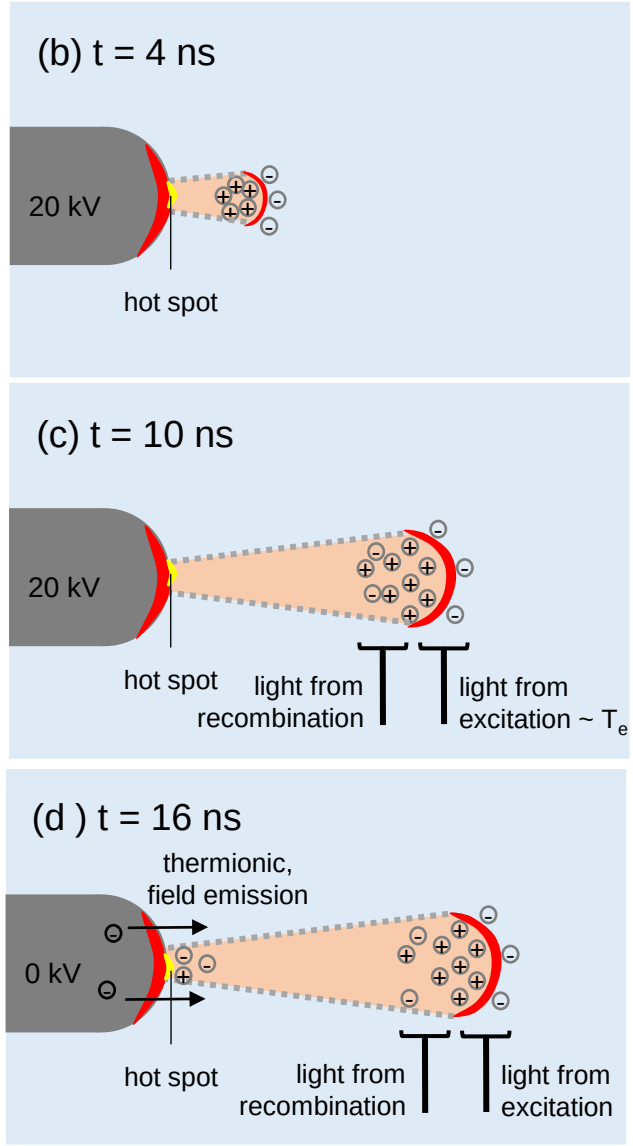
A. Bergner et al. PSST 23, 054005 (2014)

Cathode spots at W tips

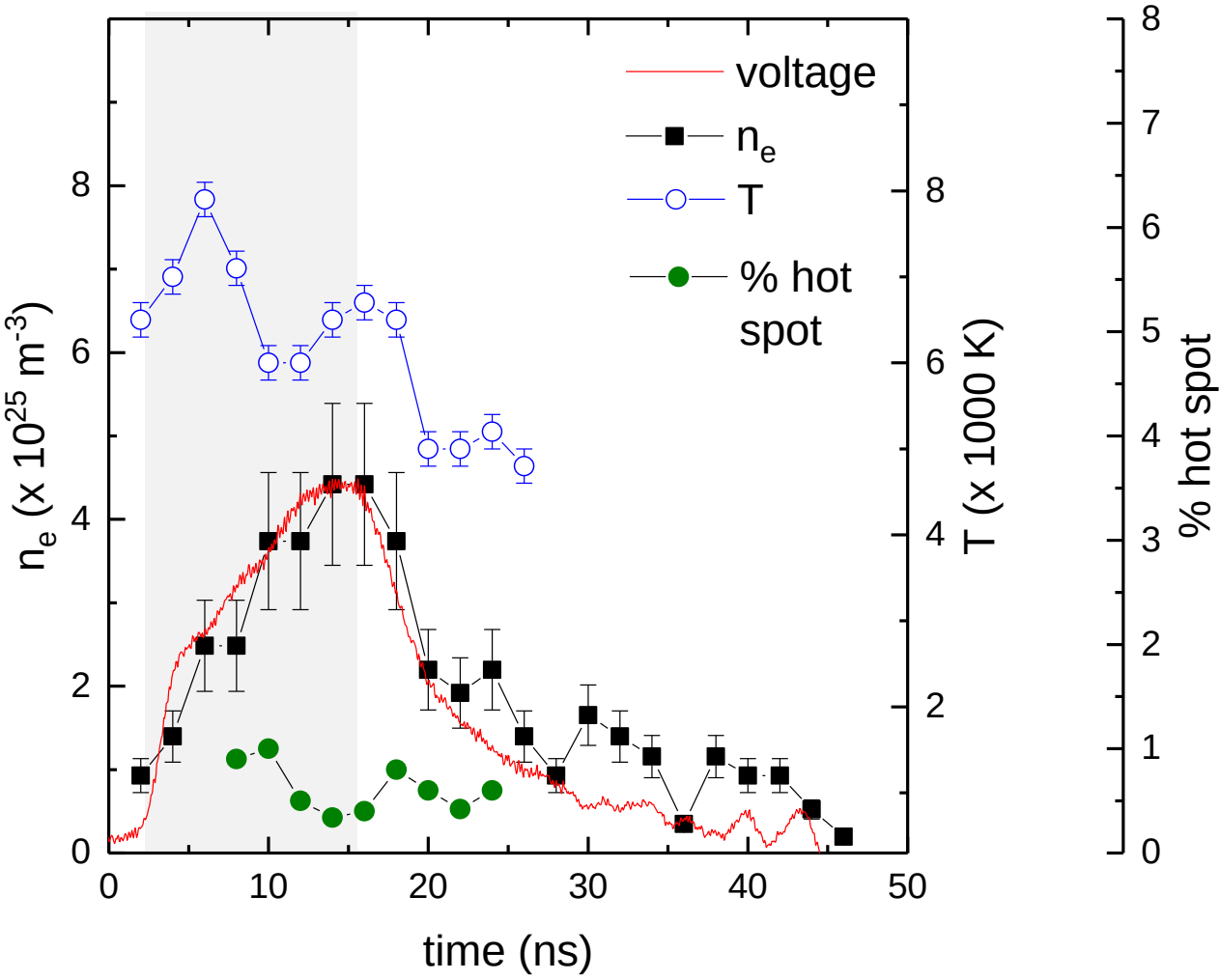



1 cm

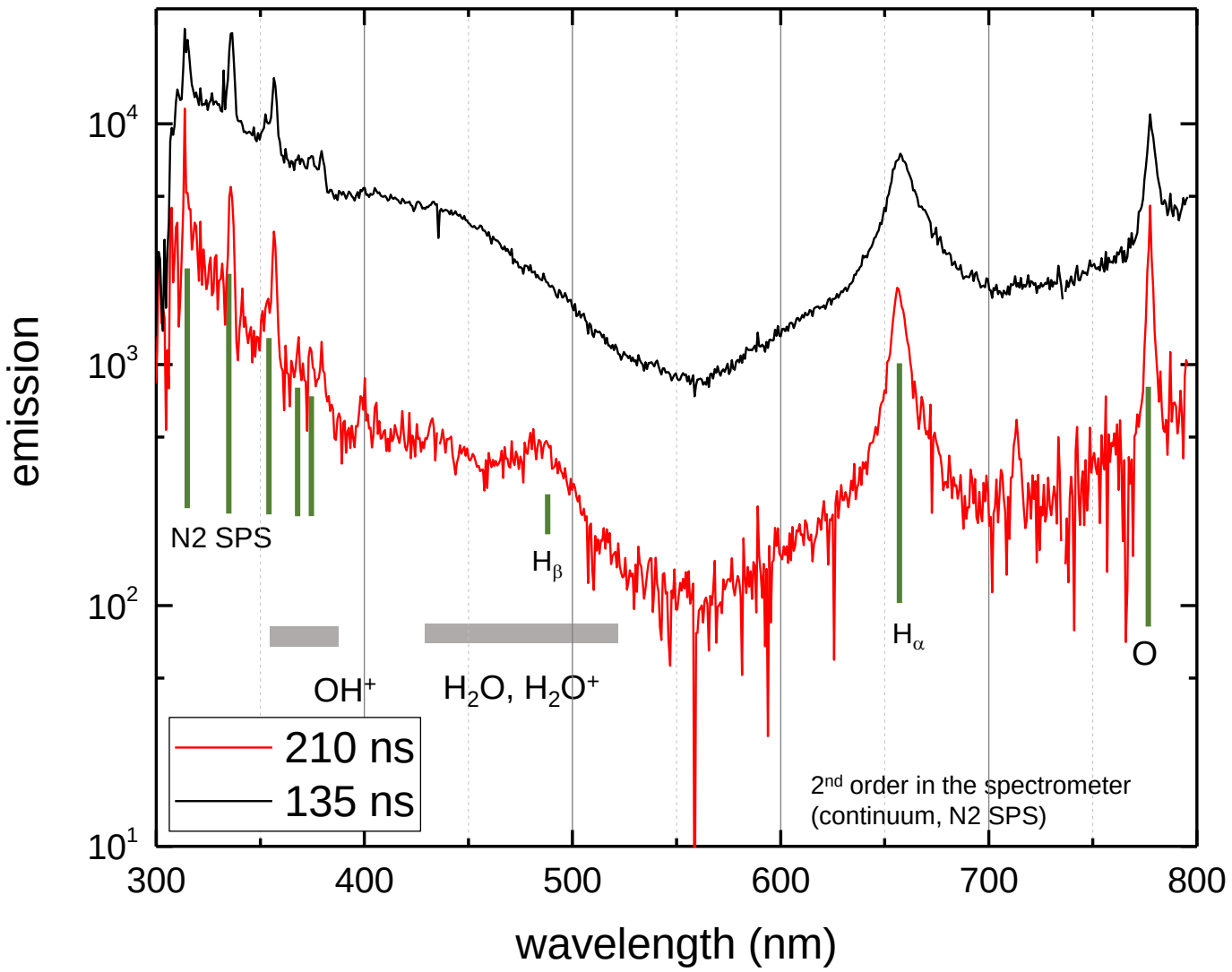
Line emission – H alpha from ionization region of Hydrogen Balmer Series



Temperature variation

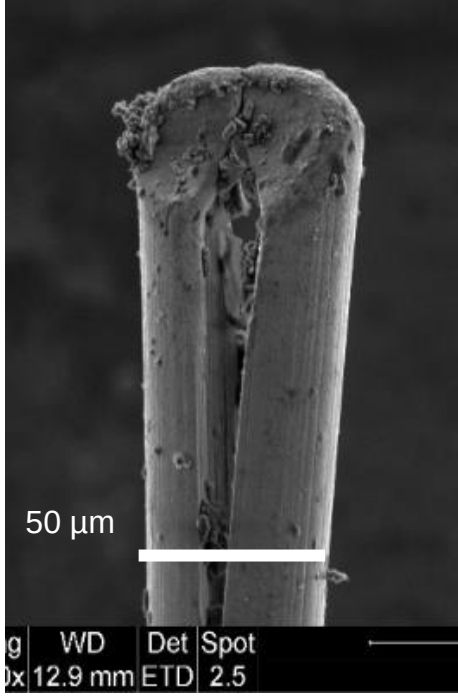


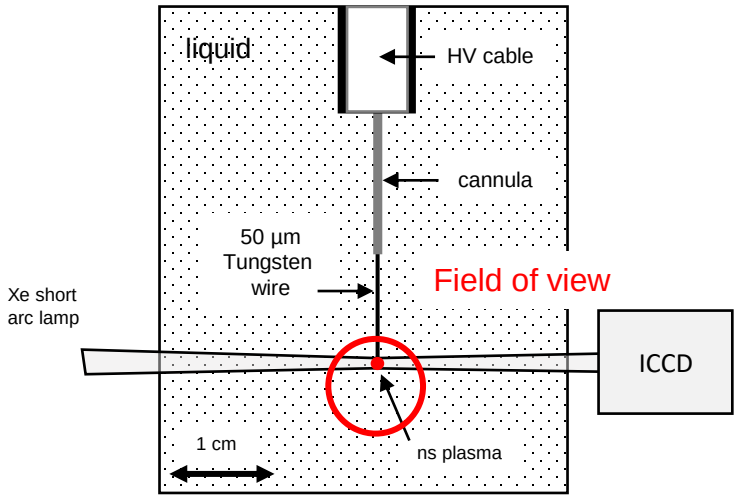
Temperatures from N2 SPS as thermometer for the later stages



Line identification

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

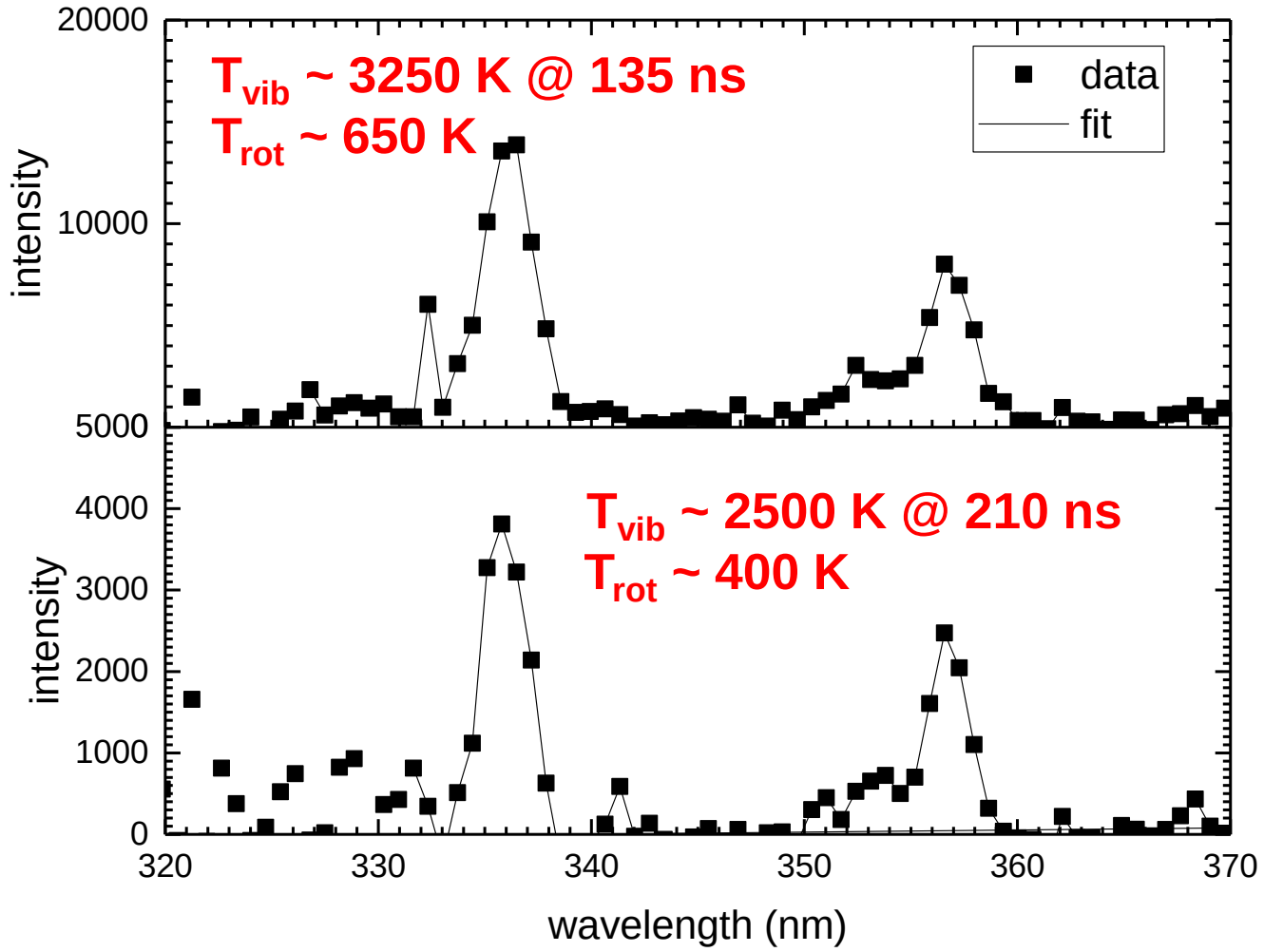


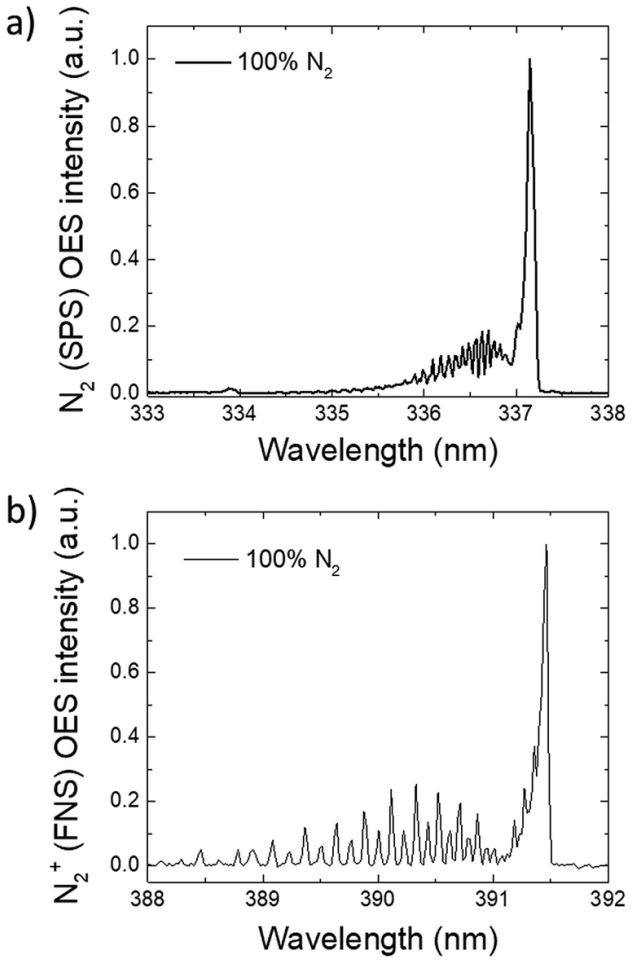


RUHR UNIVERSITÄT BOCHUM RUB

Temperatures from N2 SPS as thermometer for the later stages

For 20 kV Experiment





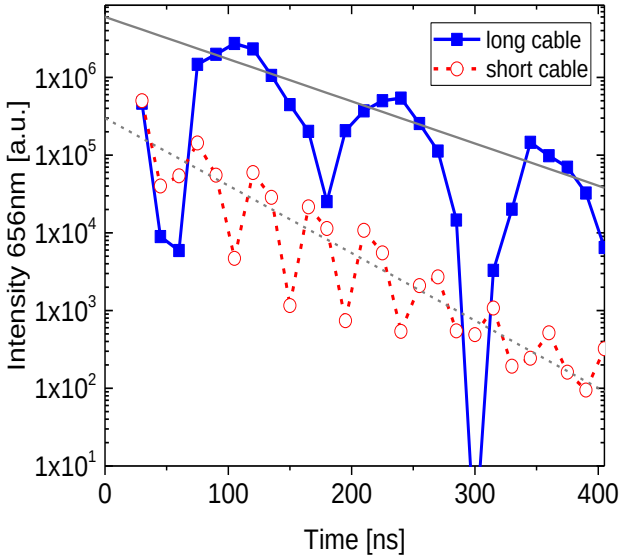
From Girard et al. PCCP 20, 2198 (2018)

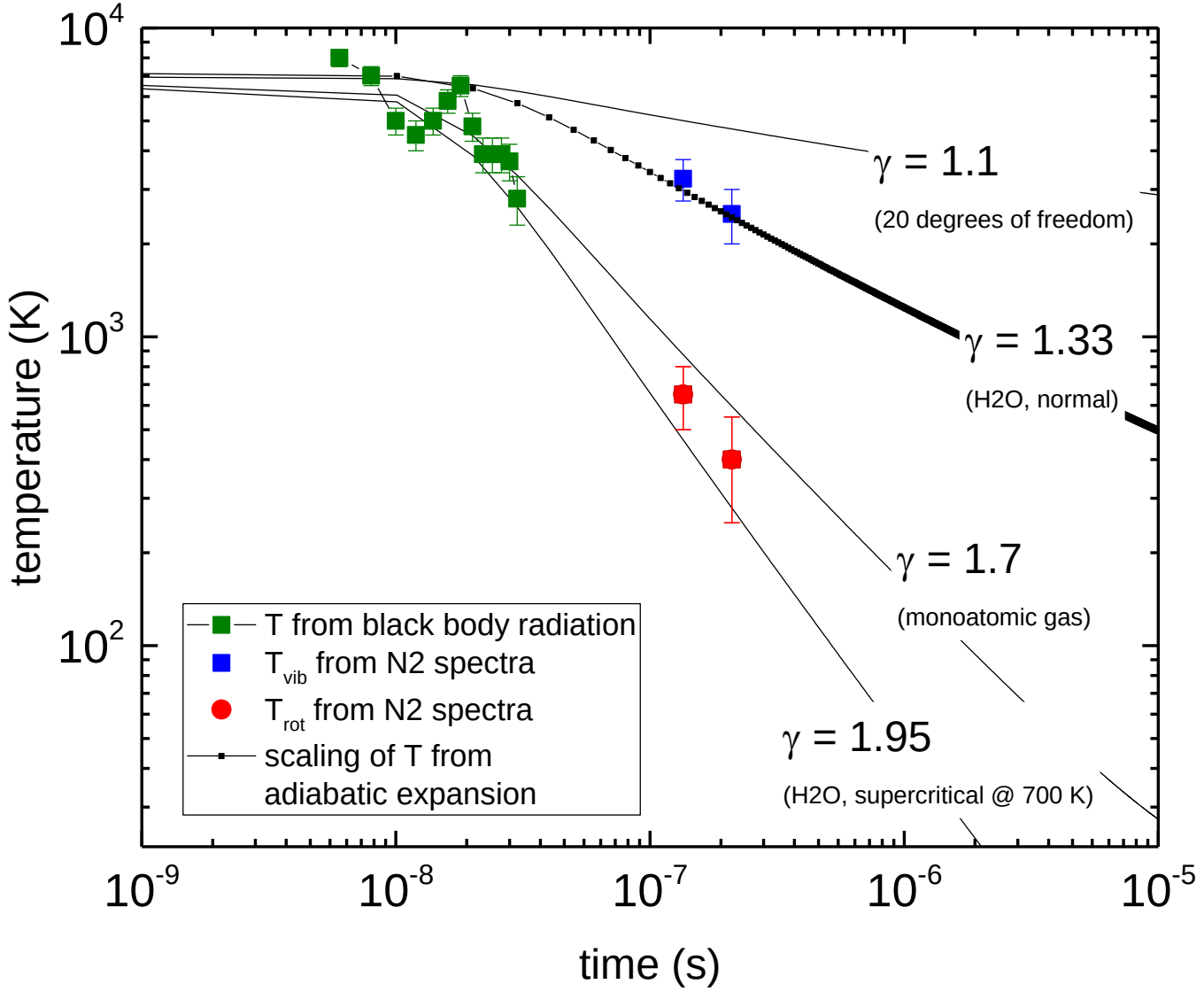
Temperatures from spectroscopies

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





Non-equilibrium in expanding ns plasmas

Rocket
Chemic
Hypersc
Ex

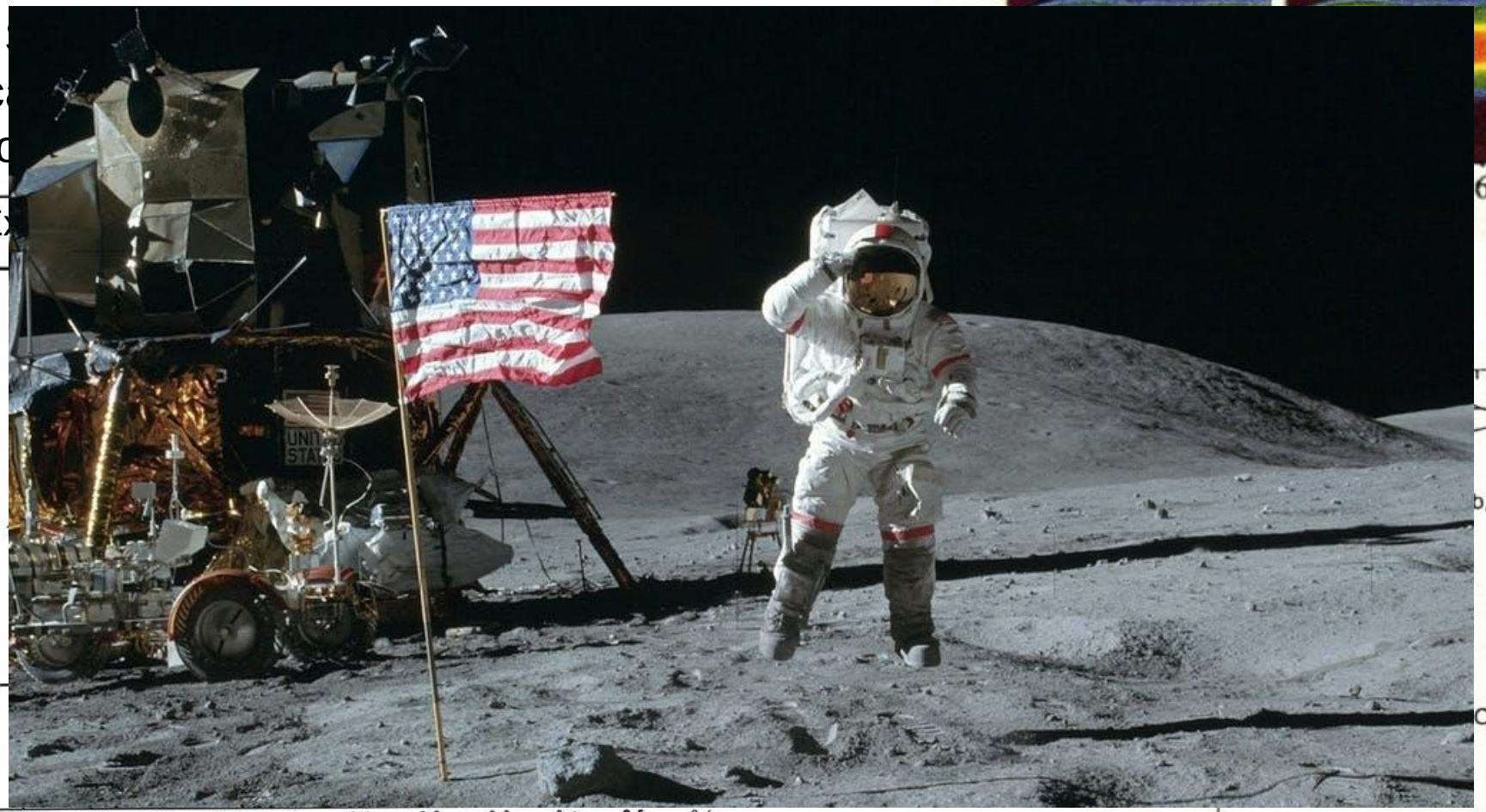
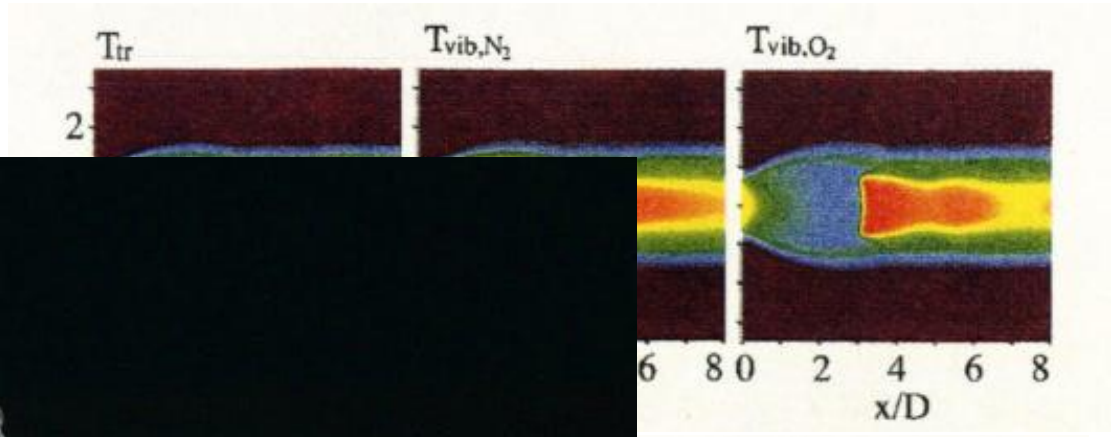


FIG. 7 STEADY-STATE T_{VIB} AND T_{TRANS} DISTRIBUTIONS FOR THE NONEQUILIBRIUM EXPANSION OF N_2; COMPARISON OF THE PRESENT TIME-DEPENDENT ANALYSIS WITH THE STEADY-FLOW ANALYSIS OF REFERENCE 7.

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



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

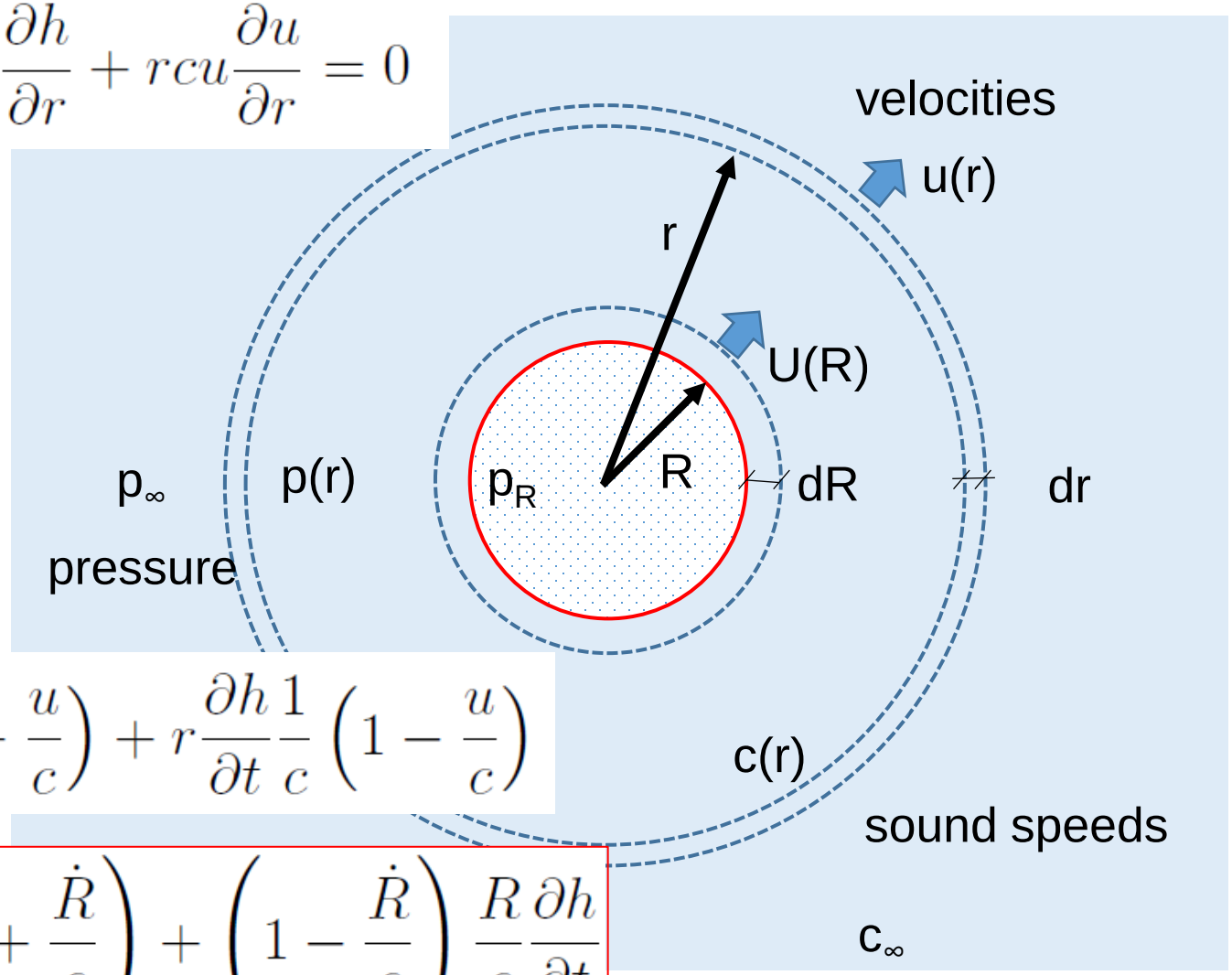
Solution for R(t) assuming a compressible liquid

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

with momentum and mass conservation

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

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



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

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

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

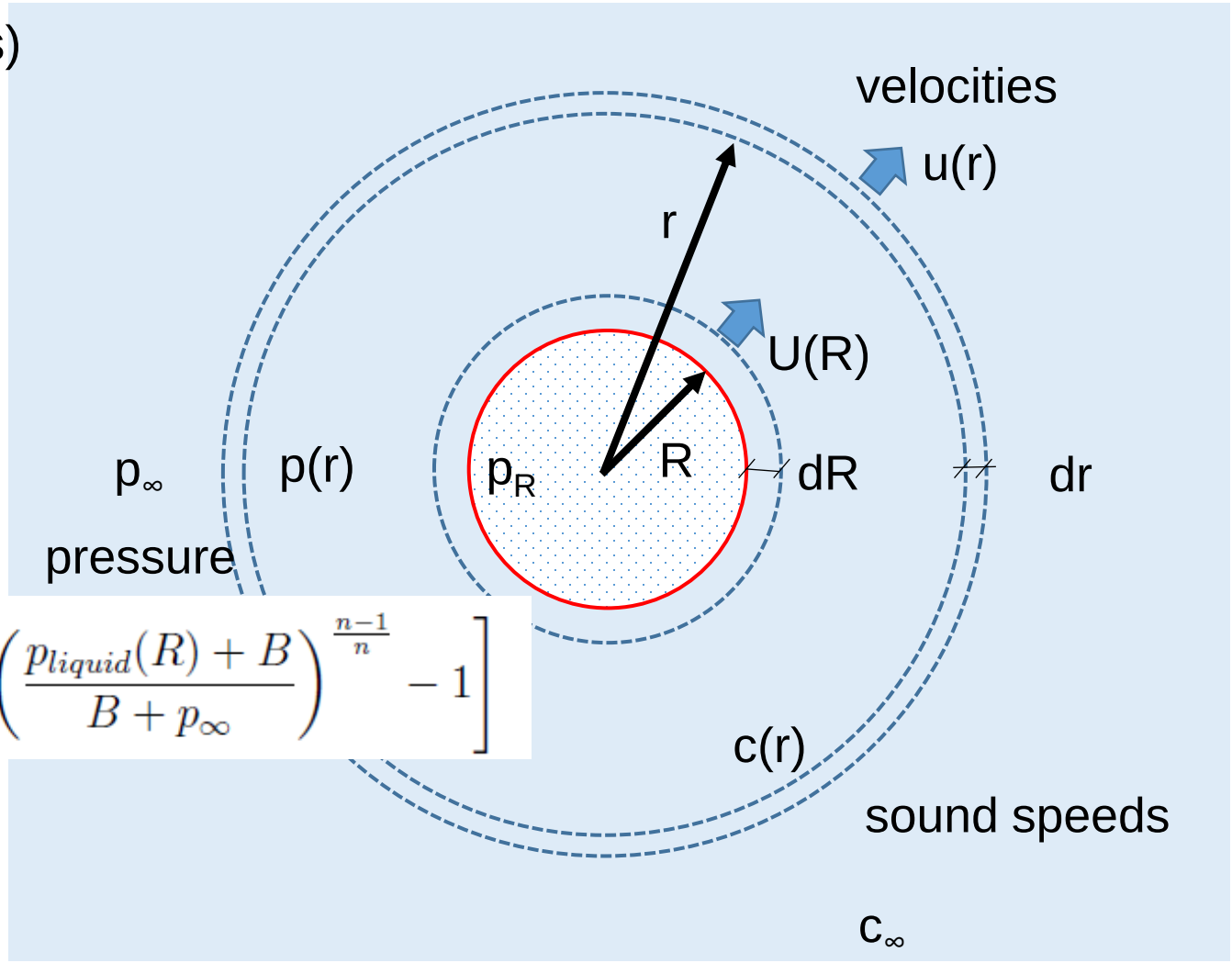
$$-\frac{\partial\phi}{\partial t} + \frac{1}{2}\vec{u}^2 = \int_{p_\infty}^{p(r)} -\frac{\mathrm{d}p}{\rho}$$

definition enthalpy

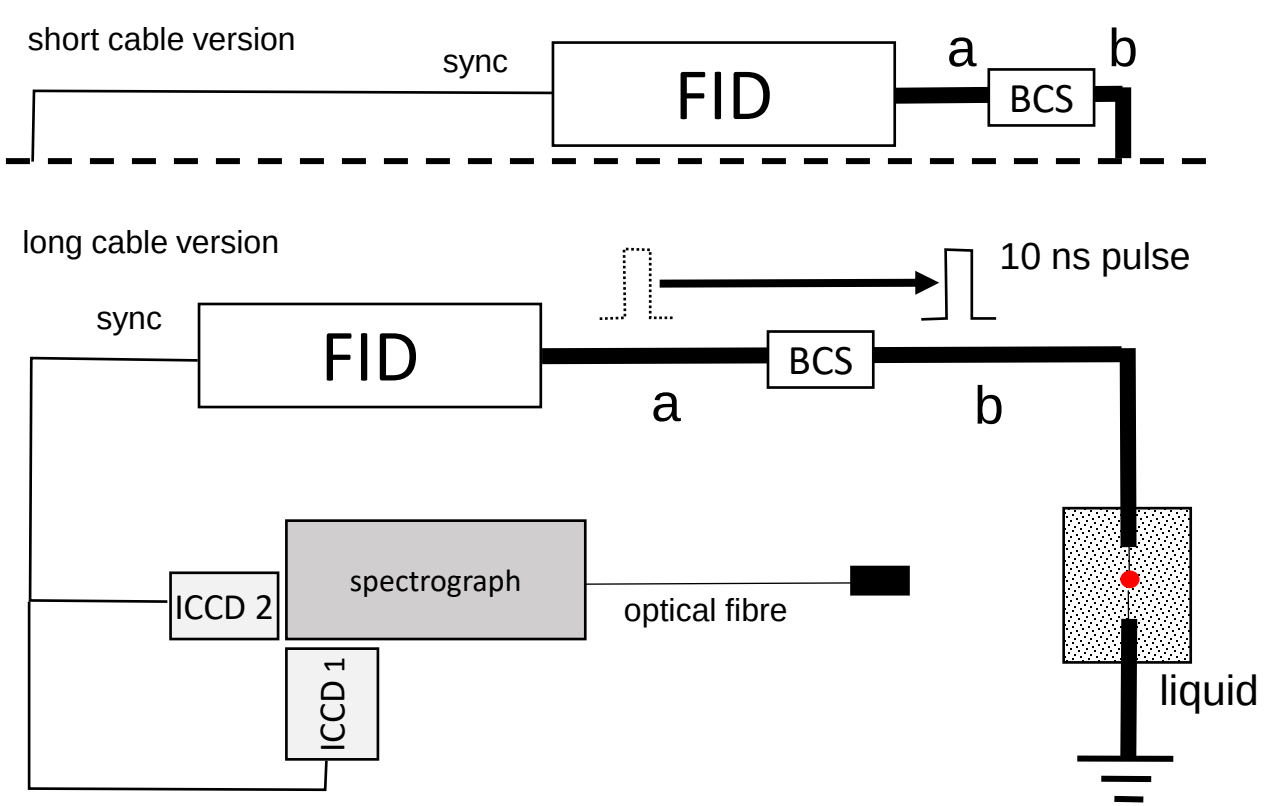
$$h = \int_{p_\infty}^{p(r)} -\frac{\mathrm{d}p}{\rho} \qquad h = \frac{n}{n-1}\frac{1}{\rho_0}(B+p_\infty)\left[\left(\frac{p_{liquid}(R)+B}{B+p_\infty}\right)^{\frac{n-1}{n}} - 1\right]$$

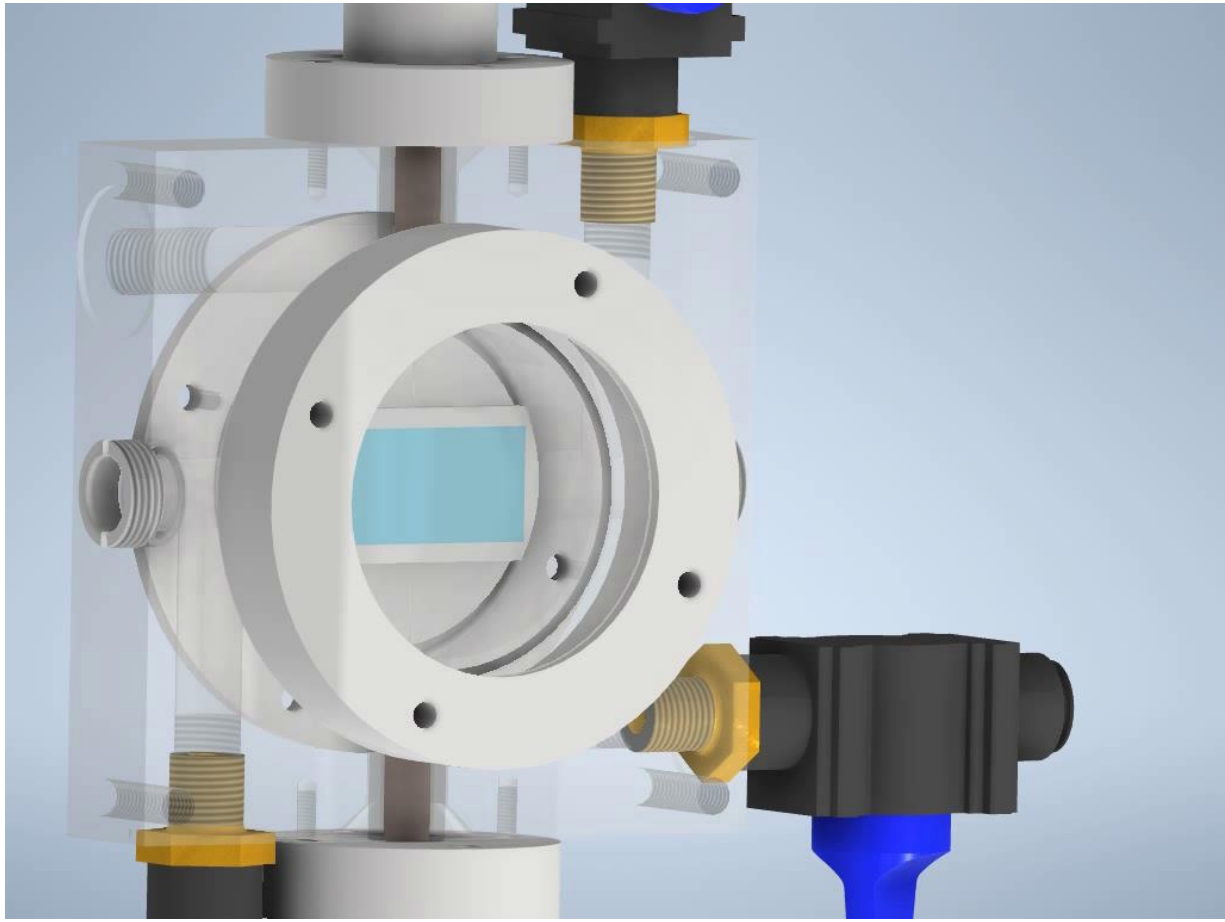
results in Bernoulli equation

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



Example 2: Plasma Chemistry in liquids – example H_2O_2 generation





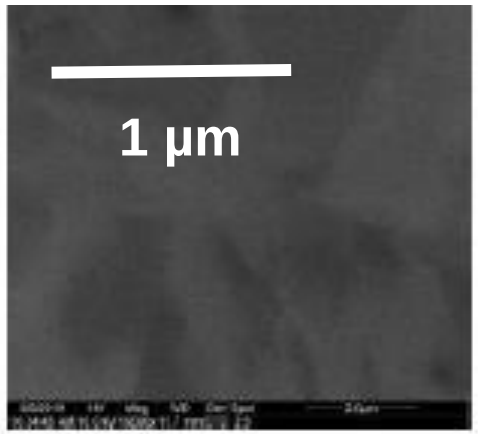
- 10 ns pulses, 14…30 kV, distilled water
- Shadowgraphy 2 ns … 70 ns gate widths
- Optical emission spectroscopy with 2ns and 30 ns gate time

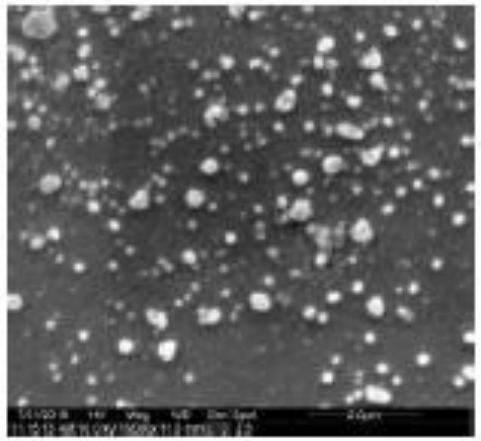
Nanosecond plasma based recovery of CuO nanocubes at copper electrodes

distilled water

dist. Water + 0.0035M KCl

20 kV

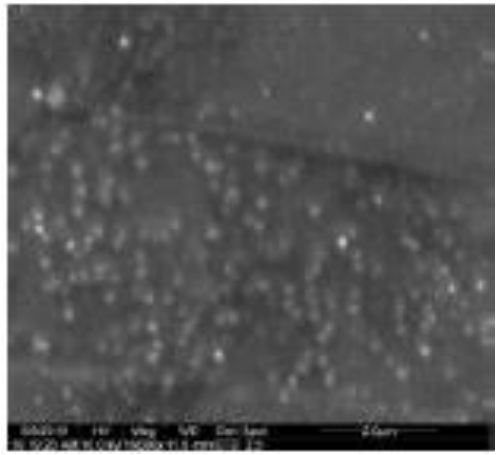


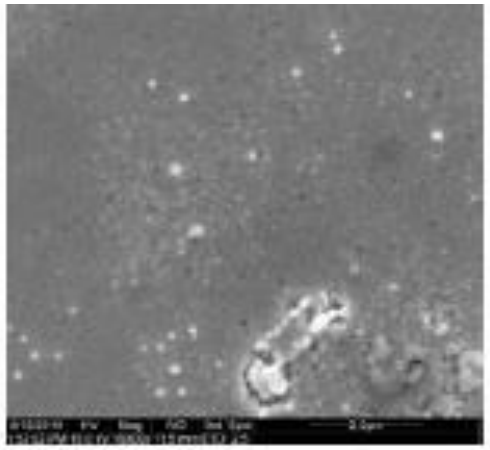


distilled water

dist. Water + 0.0035M KCl

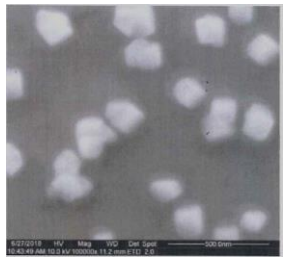
26 kV





Creation of Cu-nanocubes possible, if

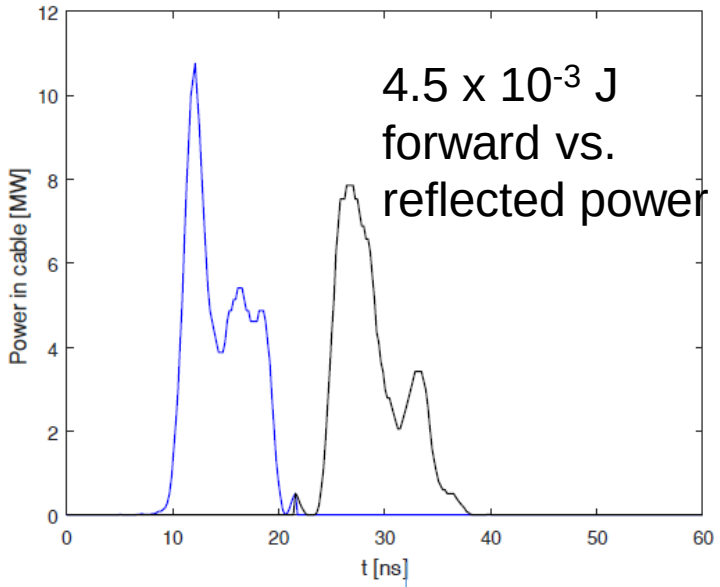
- no direct current to the sample, reduction of the oxide, plasma electrode distance to the sample important
- Cl necessary as nucleation sites
- Competition between oxidation due to H_2O_2, OH and reduction by H, e^-



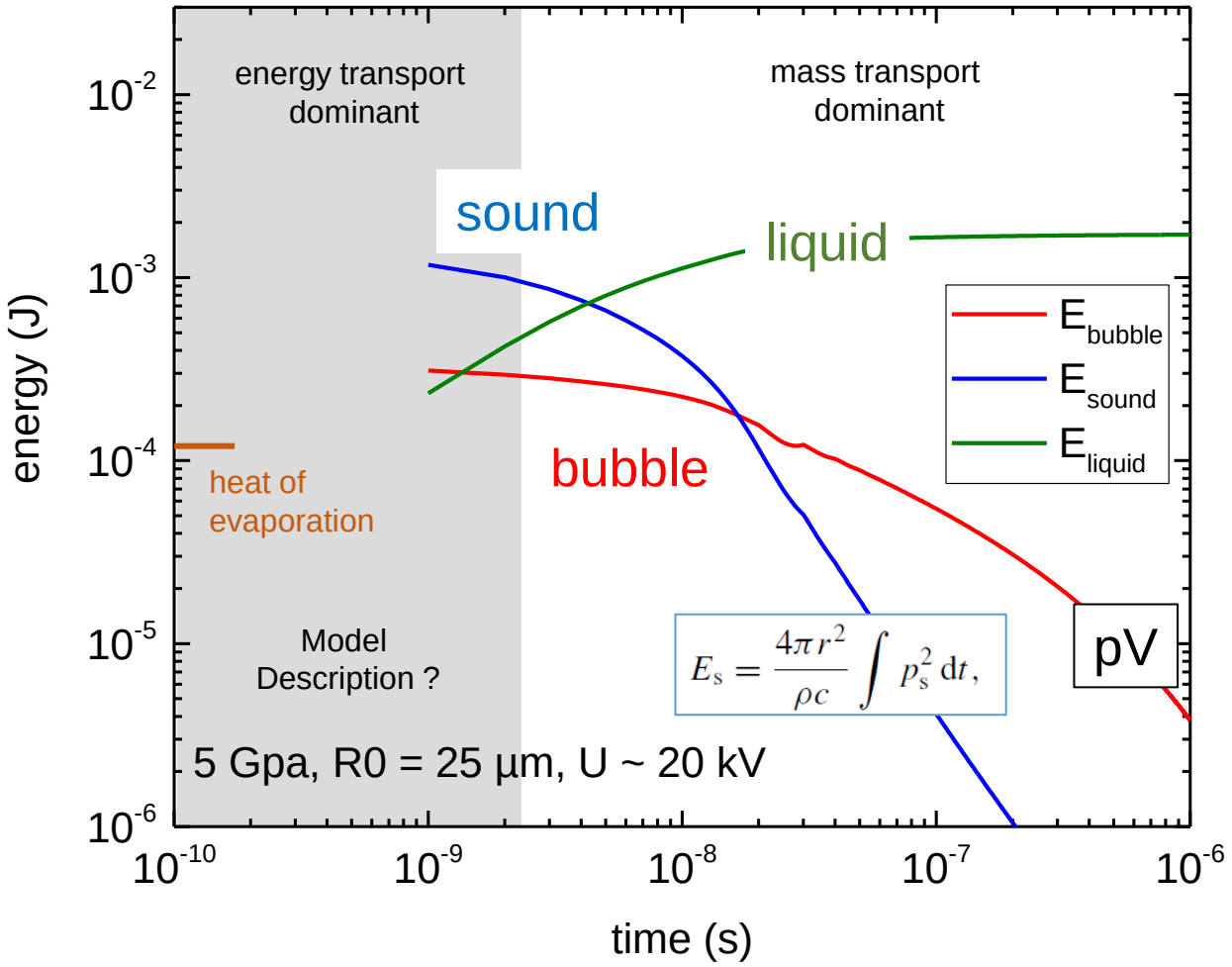
P. Grosse, B. Roldan et al.

Reference plasma based low pressure creation of CuO nanocubes

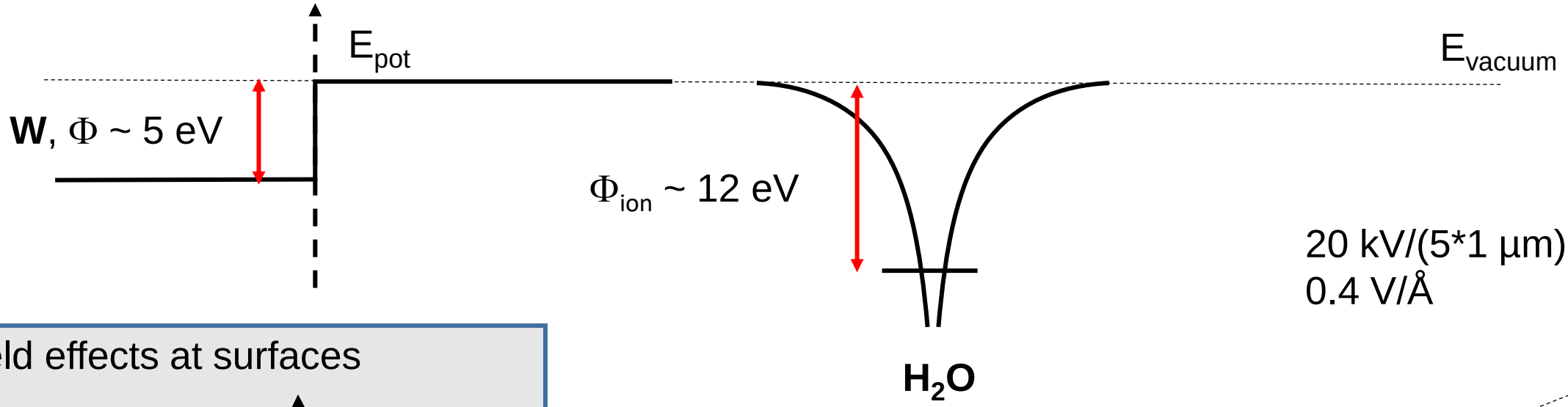
Dissipated energy during plasma ignition within the first 10 ns – comparison to experiments



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

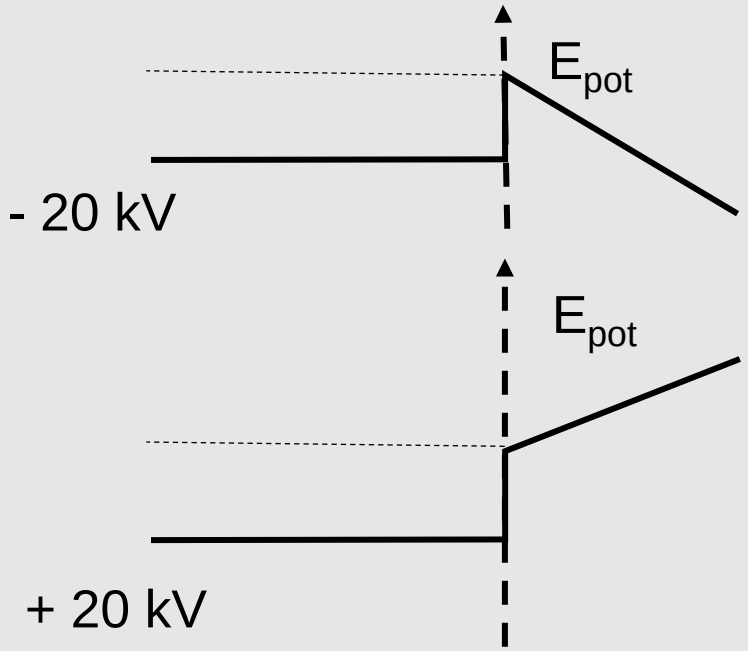


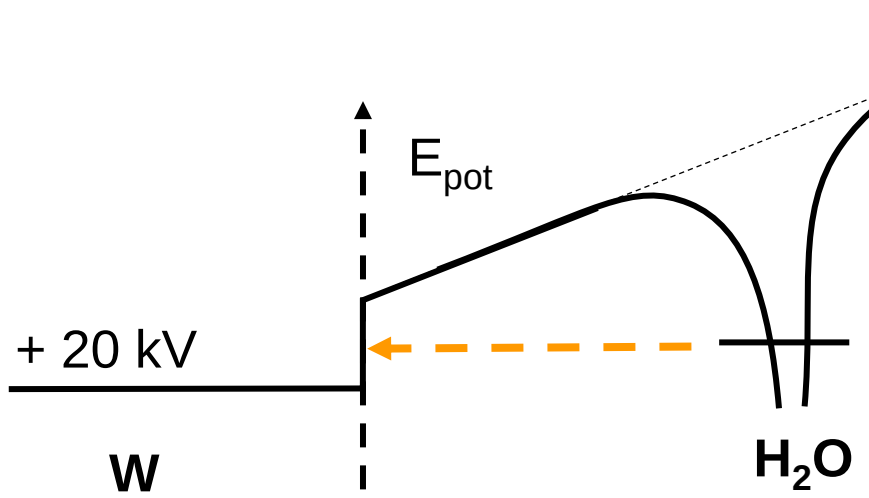
Field emission effects



20 kV/(5*1 µm) =
0.4 V/Å

Field effects at surfaces





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

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

Tunneling of e-

Streamer velocities in distilled water

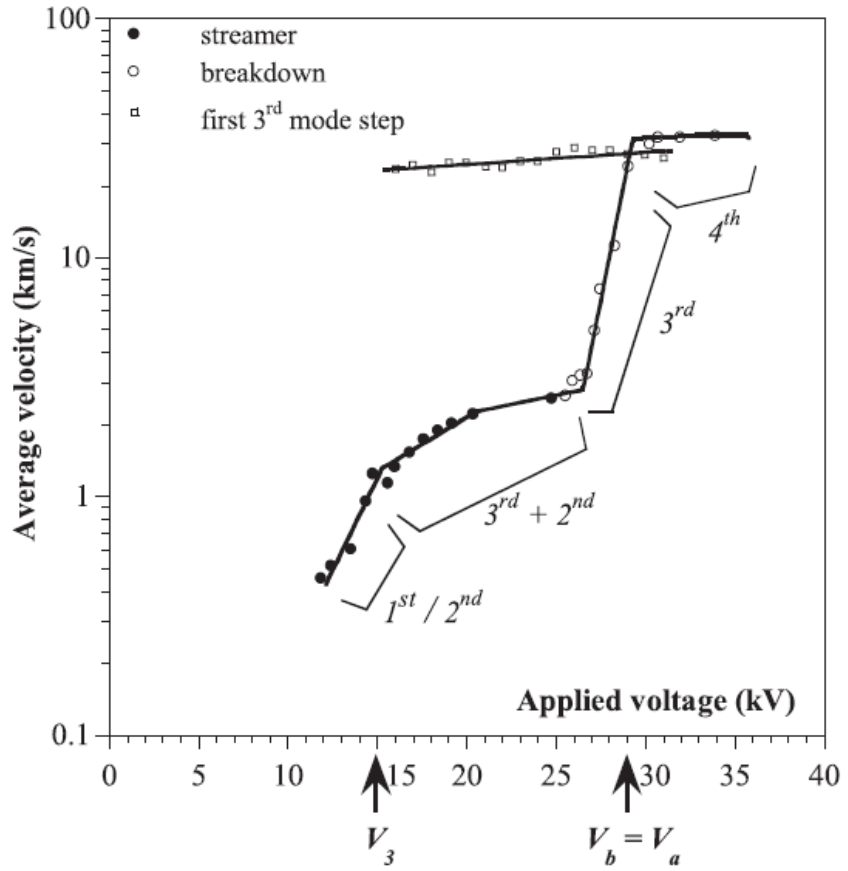
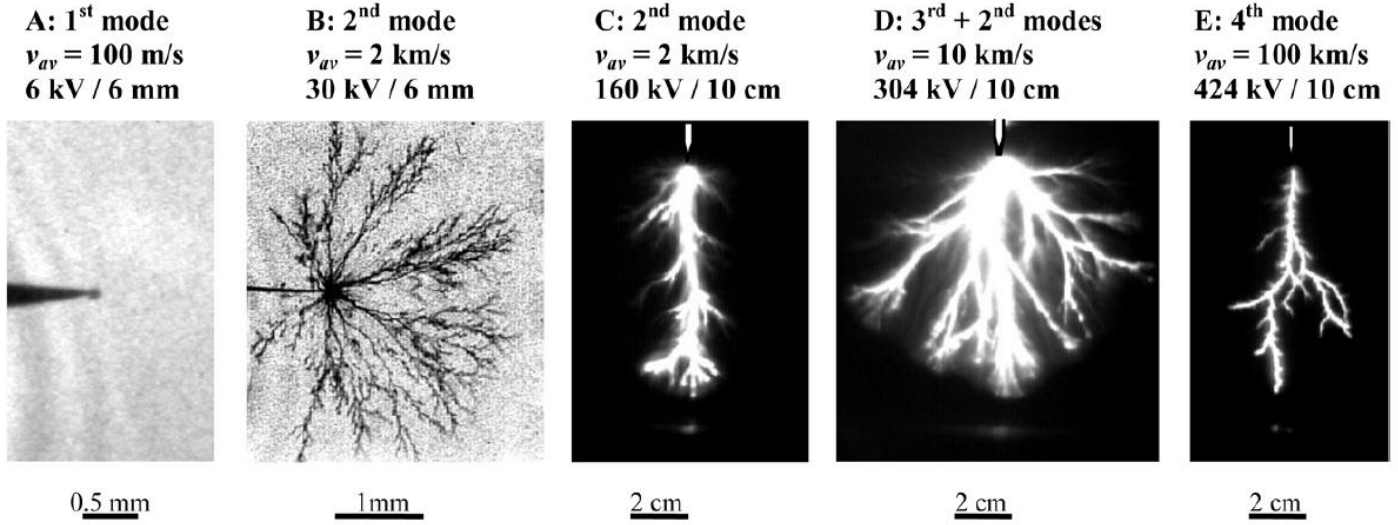
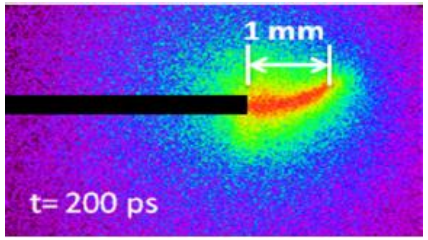


Figure 15. Average streamer propagation velocity v_{av} versus voltage in distilled water [52]. $d = 3$ cm, $r_p = 1$ μm.



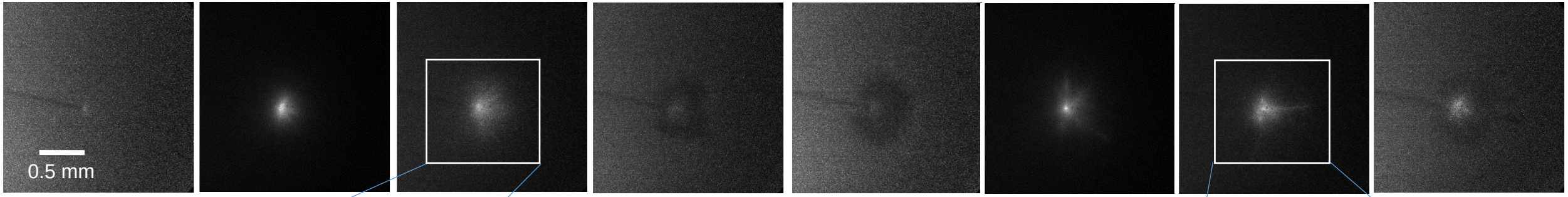
Propagation velocity of streamer in liquids (long pulses)
3 km/s … 100 km/s in 10 ns Δx = 3 µm … 0.1 mm
Propagation velocity of streamer in liquids (short pulses)
1000…5000 km/s in 10 ns Δx = 1 mm … 5 mm

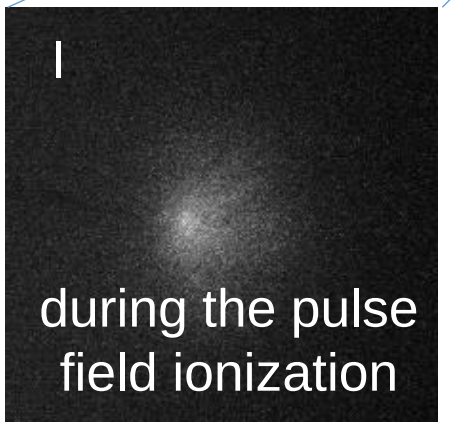


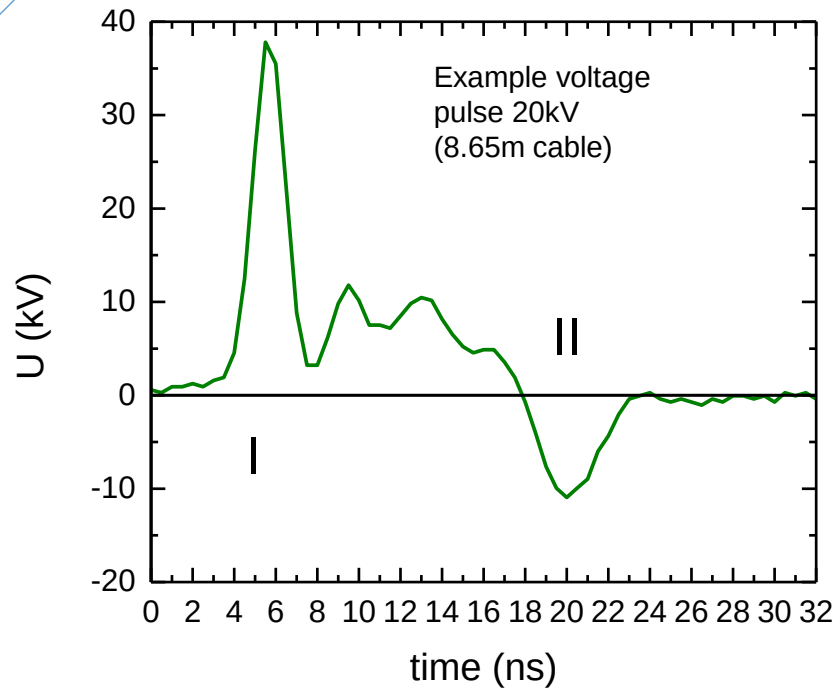
Comparison Streamer in air ~ 1000 km/s

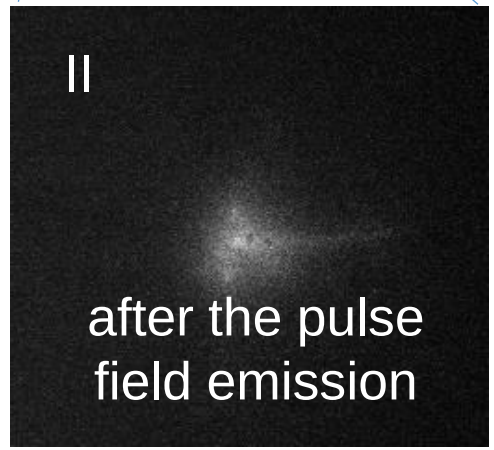
Lesaint et al. JPD 49 144001 (2016)
Starikovsky et al. PSST 20, 24003 (2011)

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



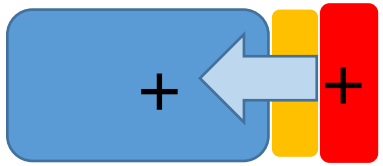






Start of the pulse water is polarized

Field ionization



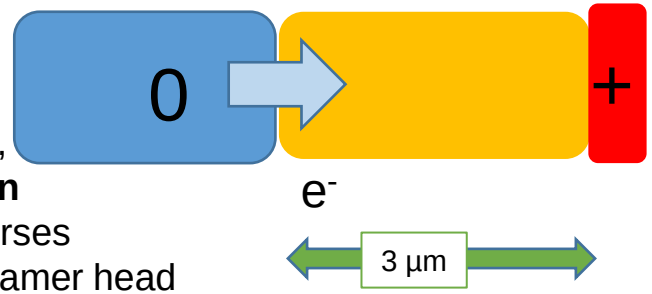
More directed discharge in field emission phase

Voltage stops,

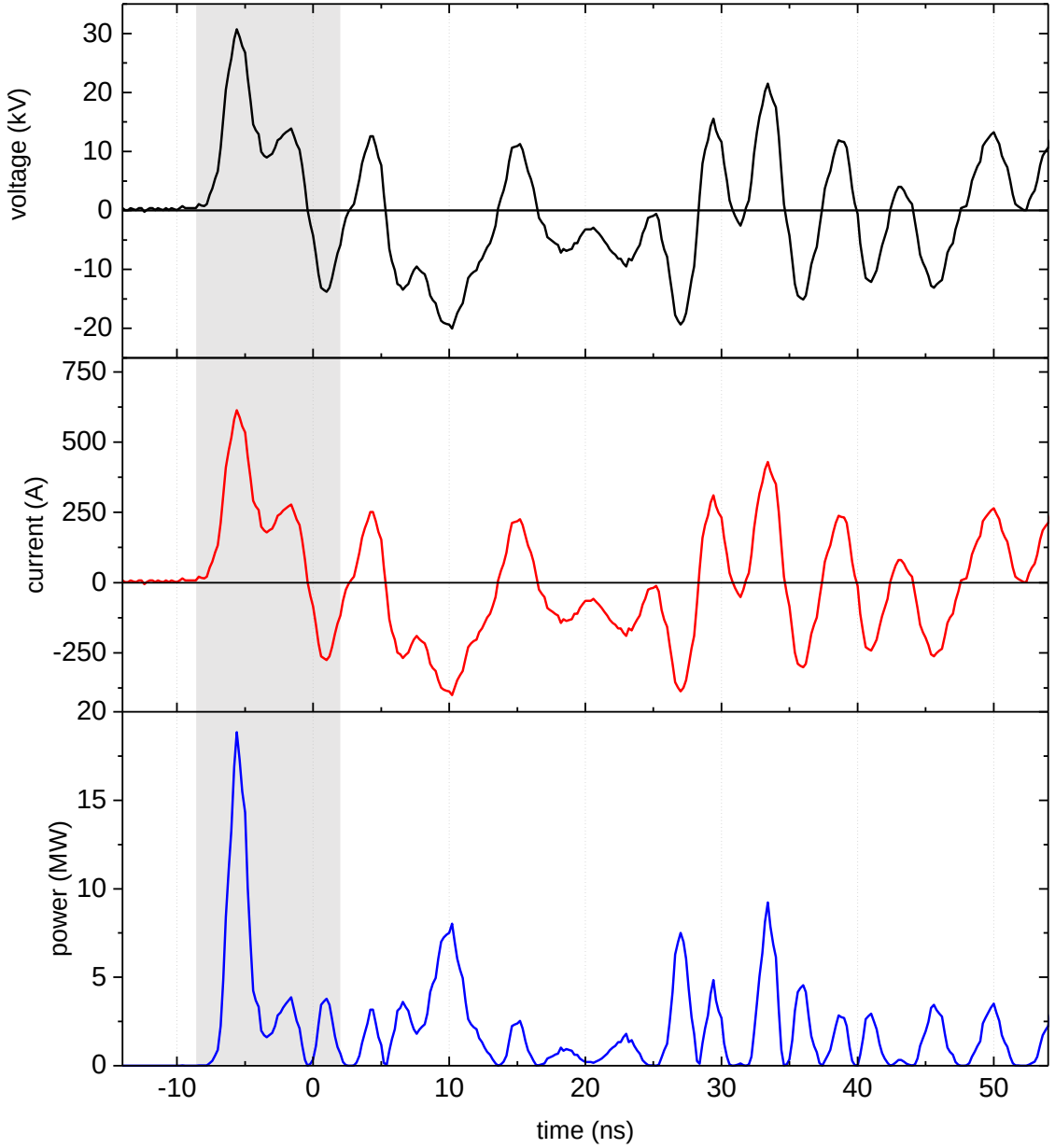
Field emission

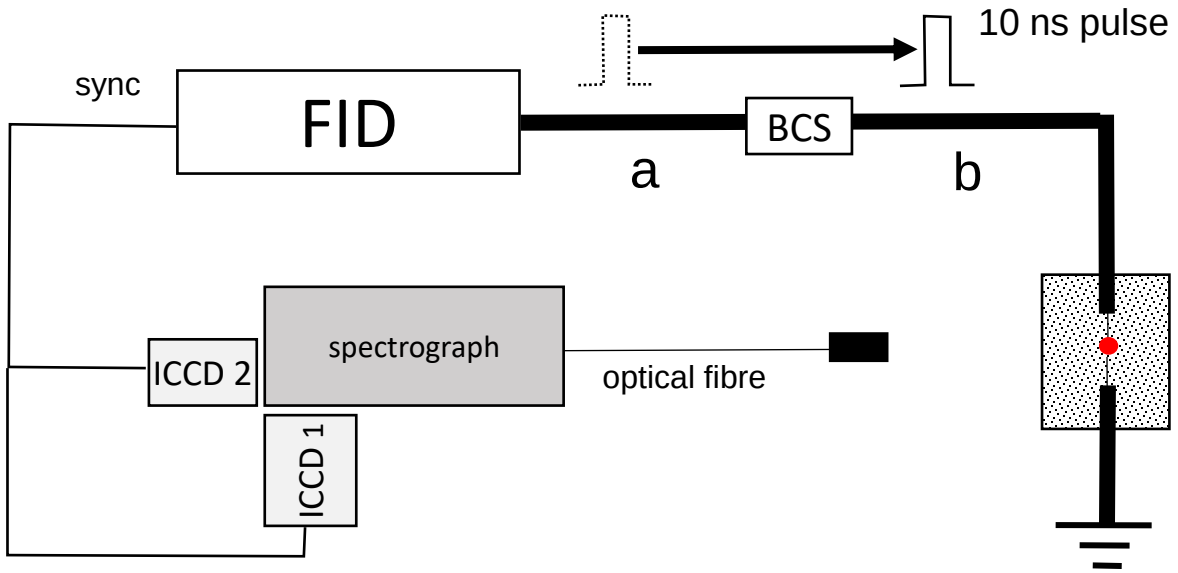
electron flow reverses

attracted to positive streamer head



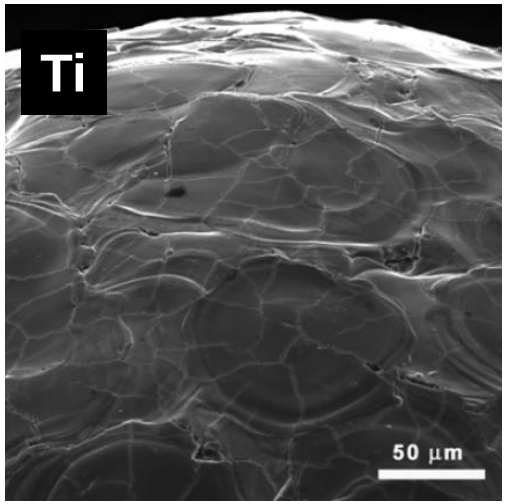
Current and Voltage signals for 10 ns 20 kV pulses using the 8.65 m cable

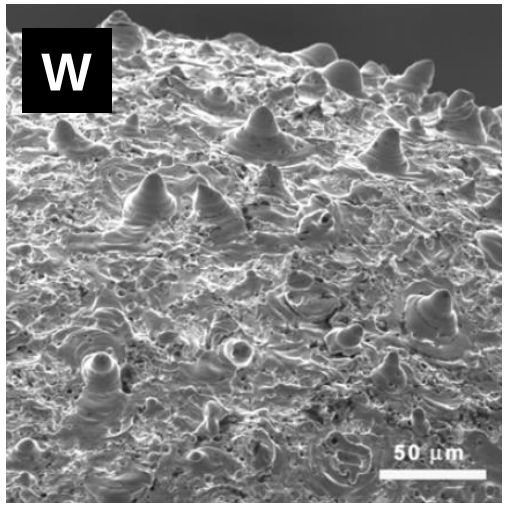


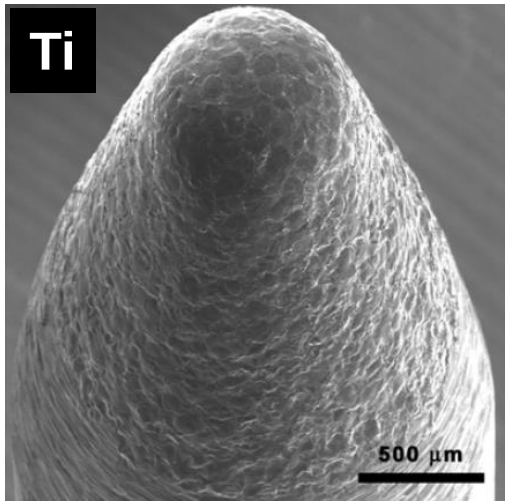


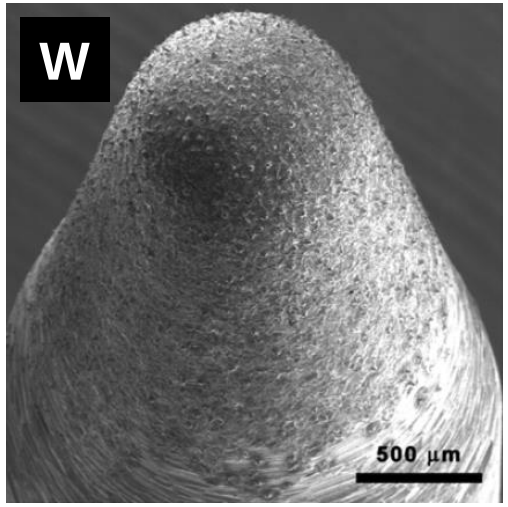
Tungsten vs. Titanium* tip (500 µm tip radius vs. 50 µm tip radius)

Spark 5..10 µs 3 J 1.5 x 10^7 J/m^2









- similar energy per m^2 dissipated
- Sequence of melting and solidification

thermal conductivity @ 1000 ºC
melting temp.

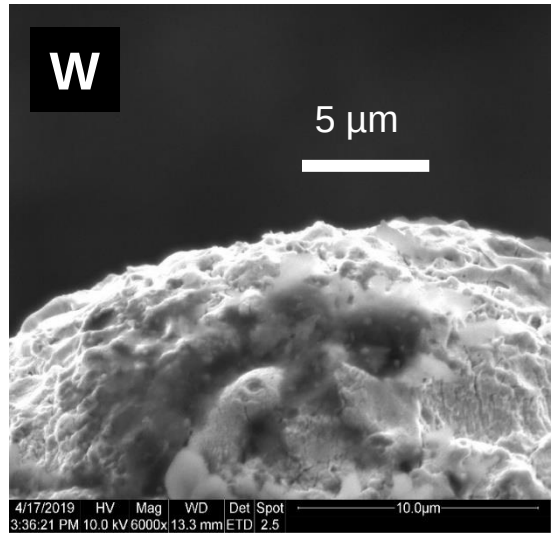
- Ti – 22 W/m K, 2000 K
- W – 115 W/m K, 3700 K
- Pt – 82 W/m K, 2500 K

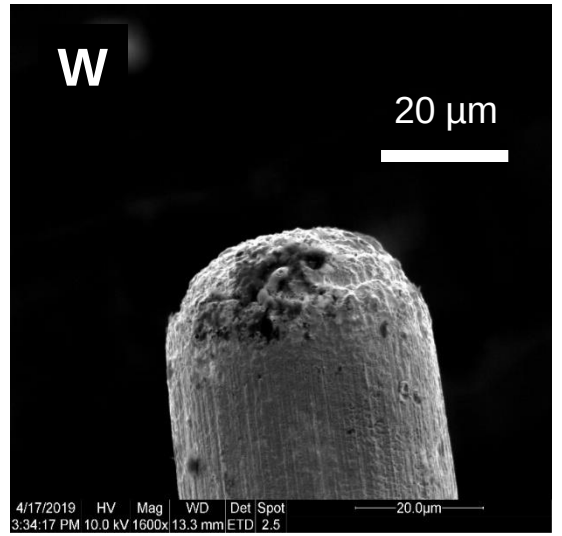
- In case of W only small melting tips (for Pt, T, larger molten areas)

- similar to cathode spot in lamps

ns pulse 10 ns

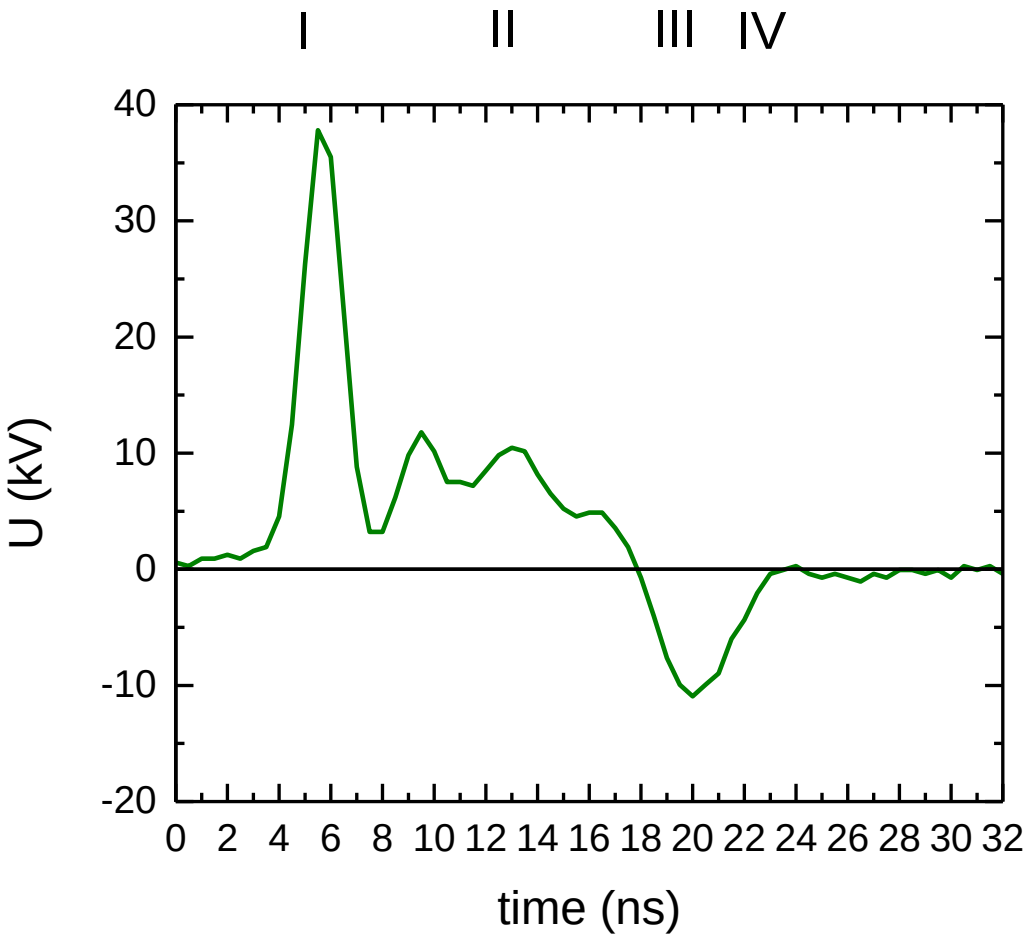
0.03 J 1.5 x 10^7 J/m^2



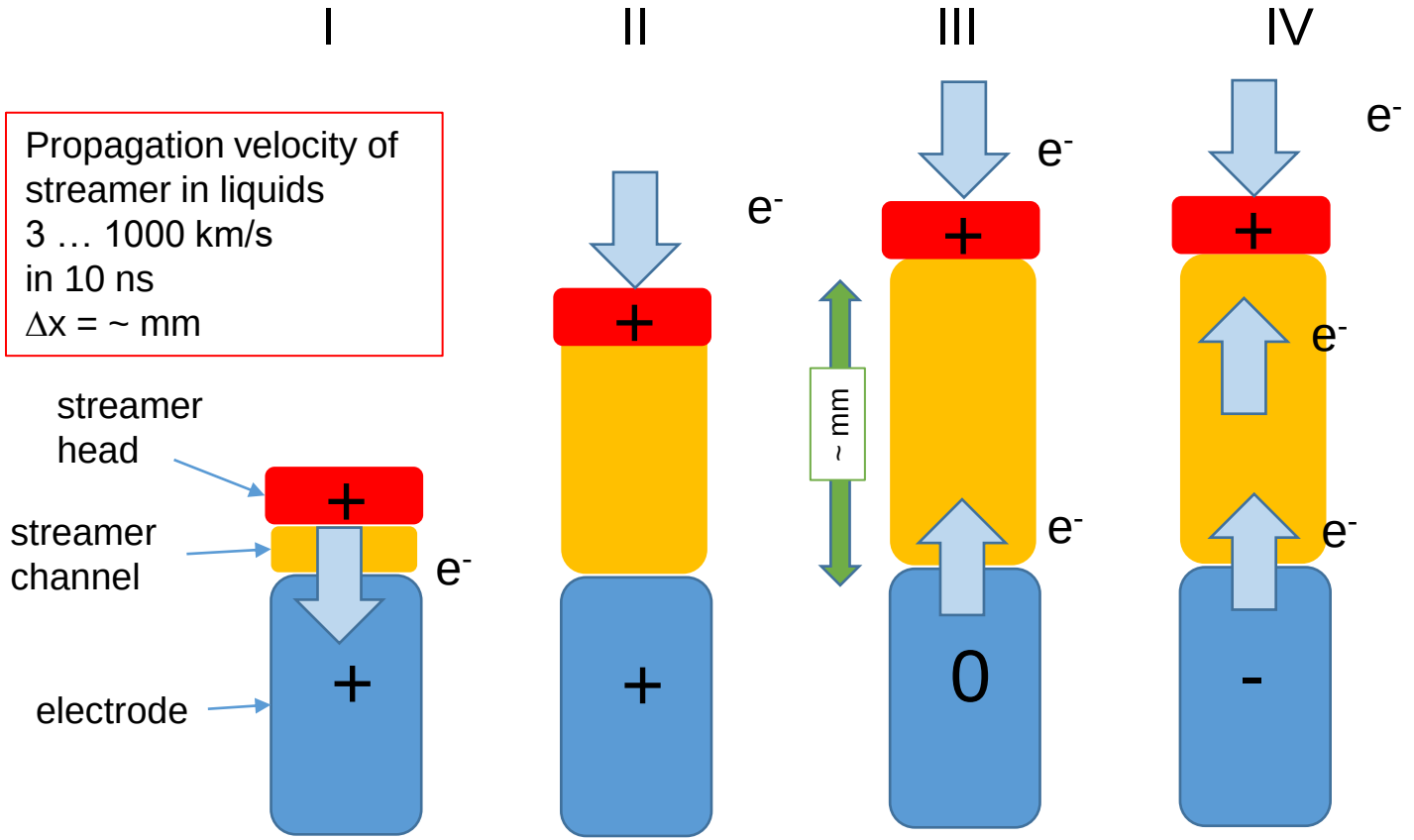


*P. Lukes et al. PSST 20, 3401 (2011)

Sequence of the propagating discharge



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



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

Streamer Propagates, electrons are collected from channel voltage drops

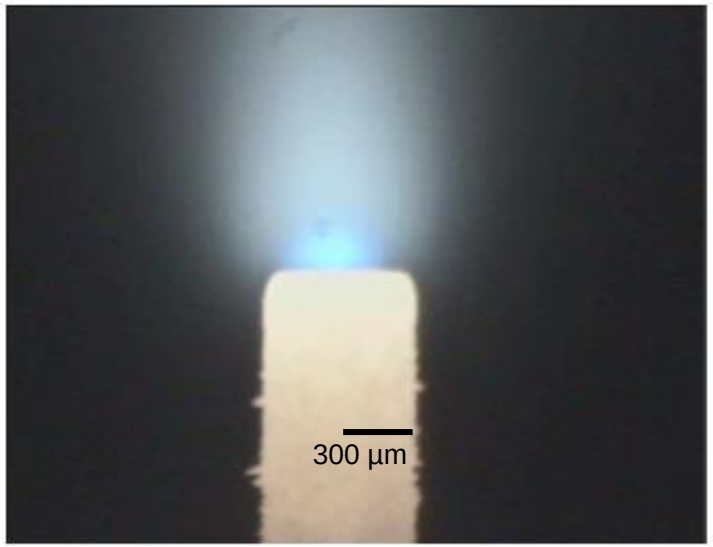
Voltage stops, **Field emission** electron flow reverses attracted to positive streamer head

thermal emission leads to change of polarity

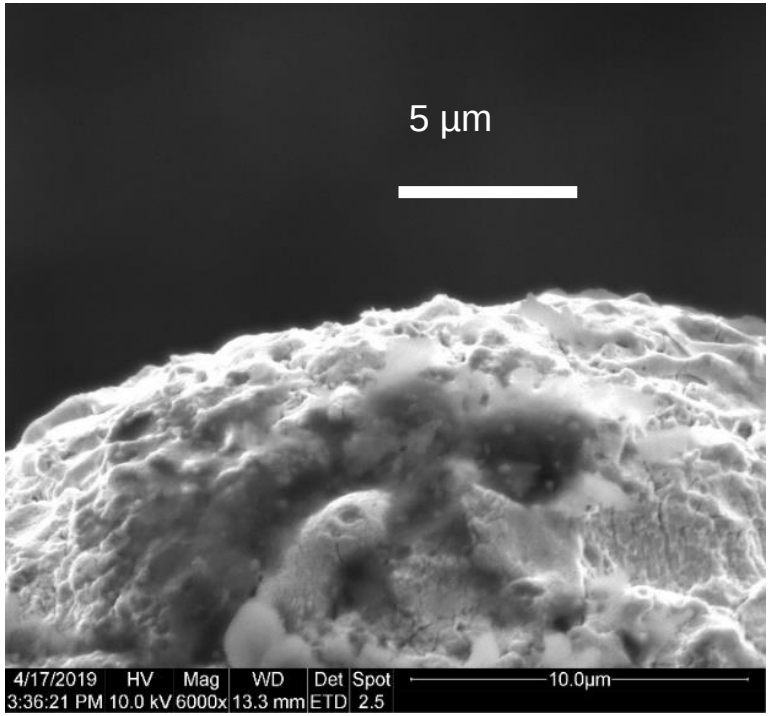
Comparison to cathode spots at high pressure lamps

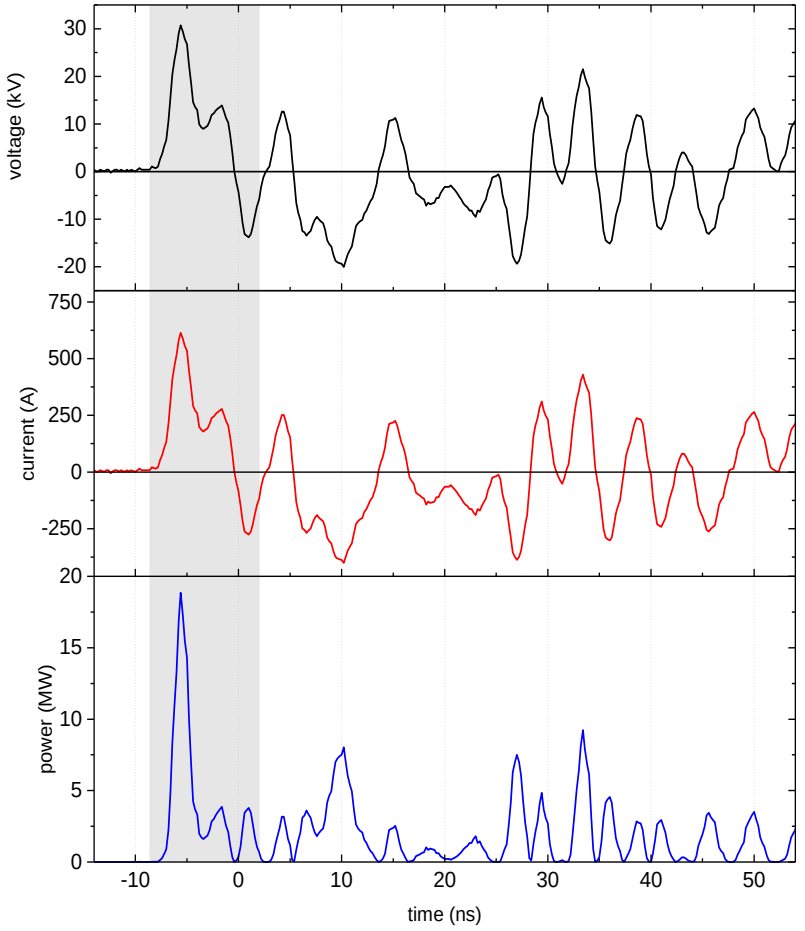
@500 A on a 2 µm radius spot
= magnetic field pressure of 1 Gpa

Pinch effects at W tips



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



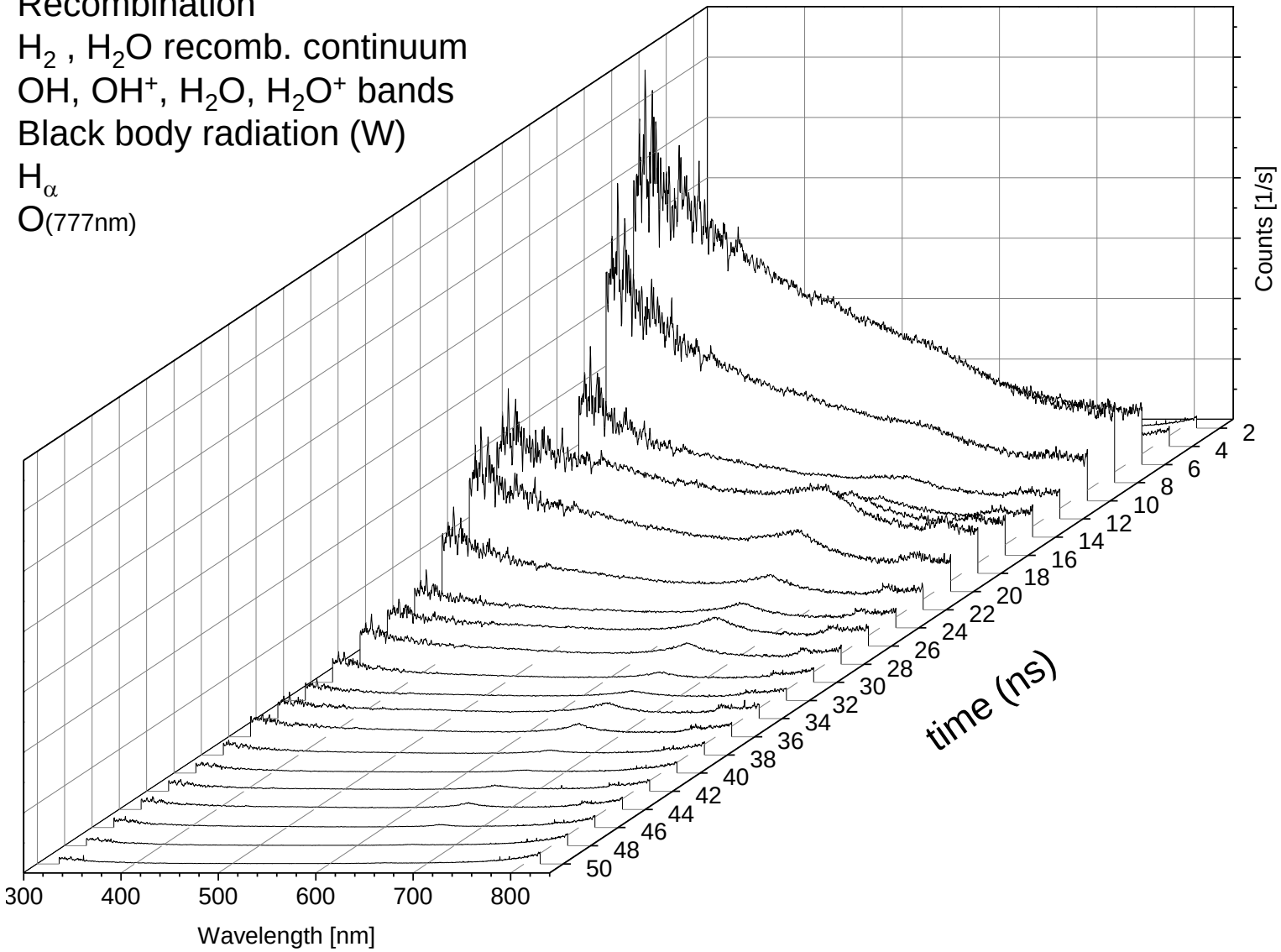


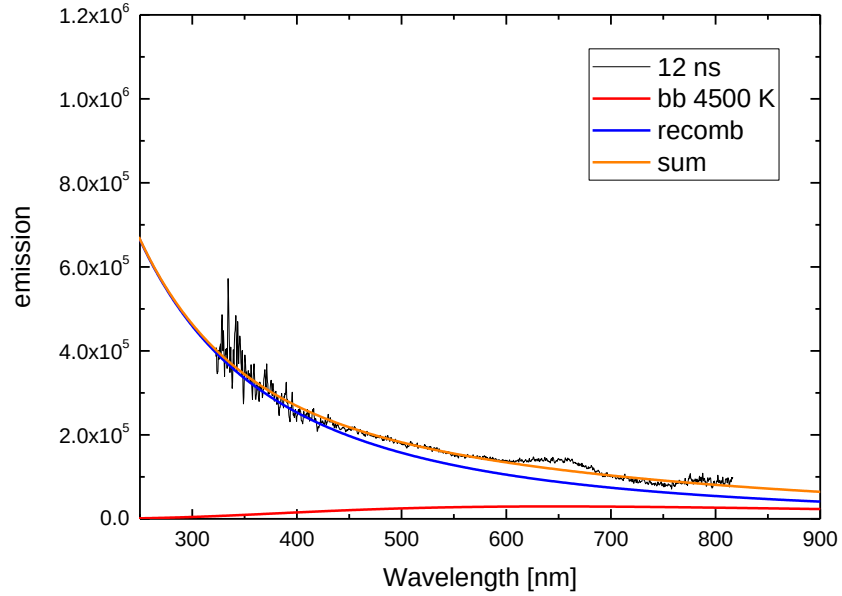
A. Bergner et al. PSST 23, 054005 (2014)

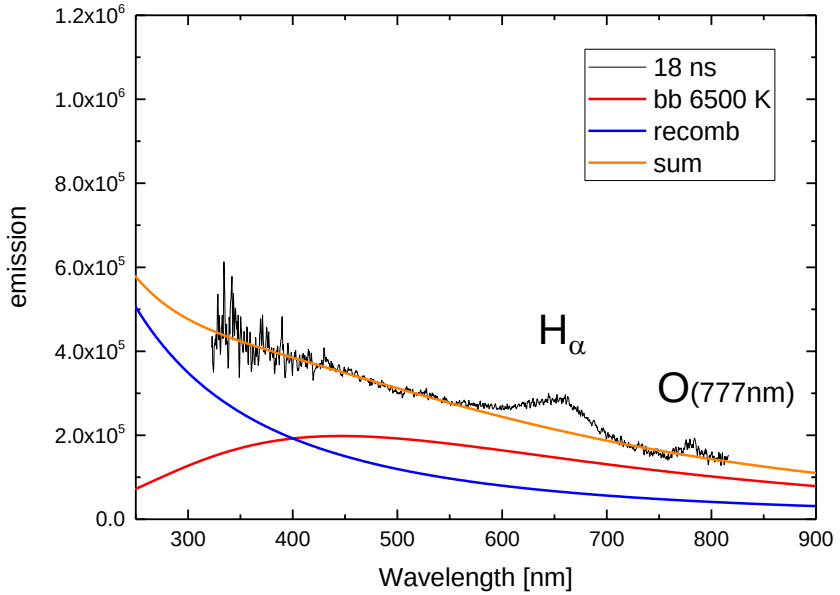
Temperatures from emission spectra of the plasma

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)





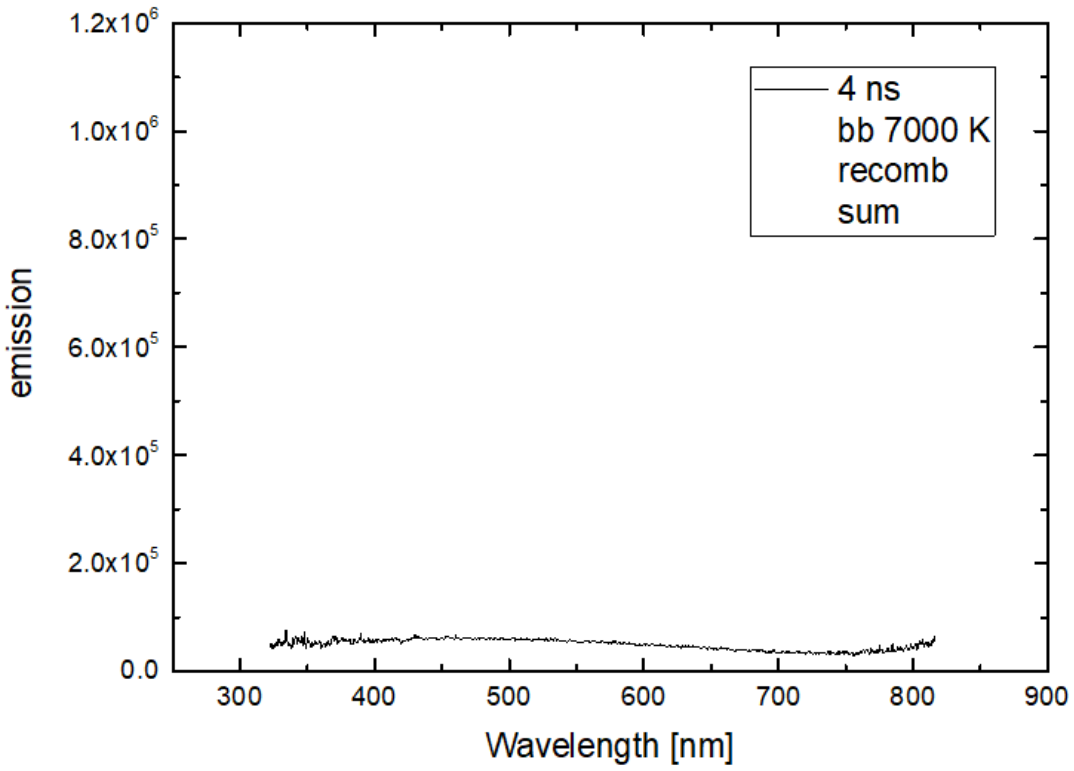


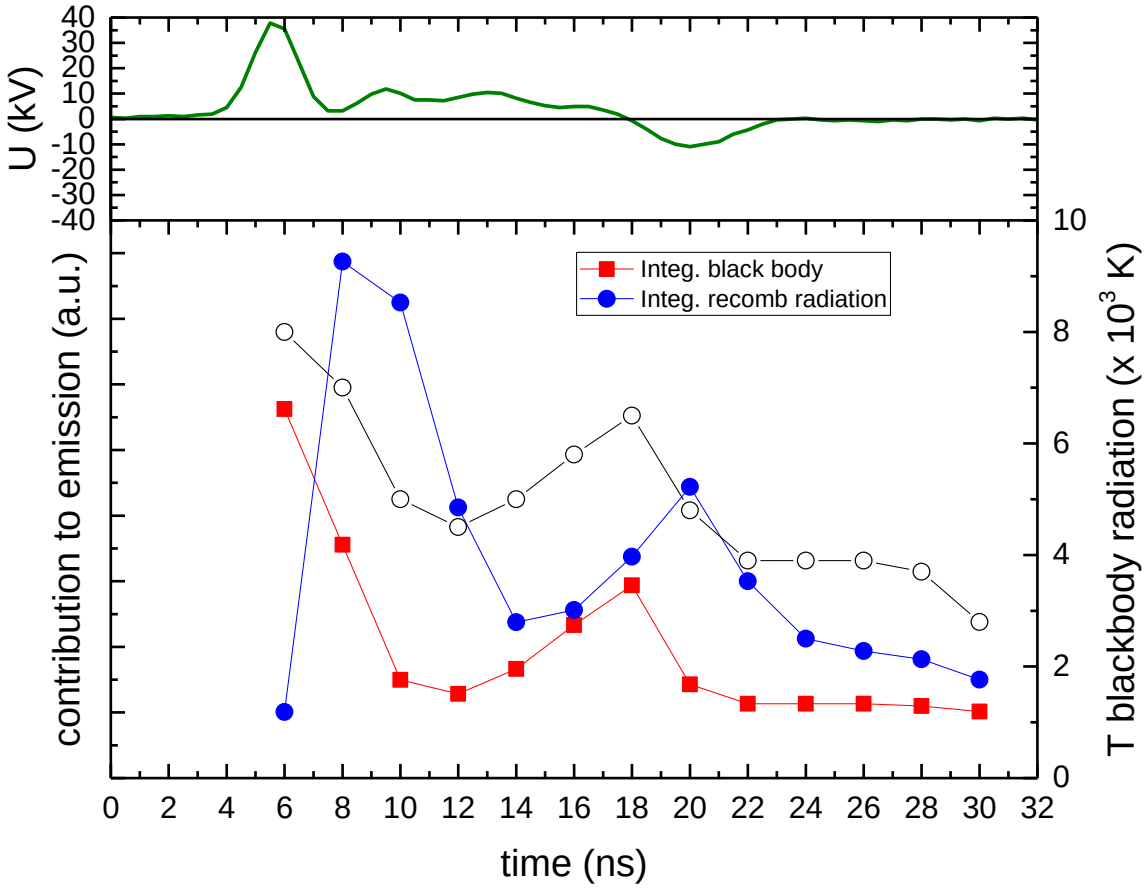
Temperatures from emission spectra of the plasma

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

For 20 kV Experiment

T_0 < 8000 K @ 0 ns

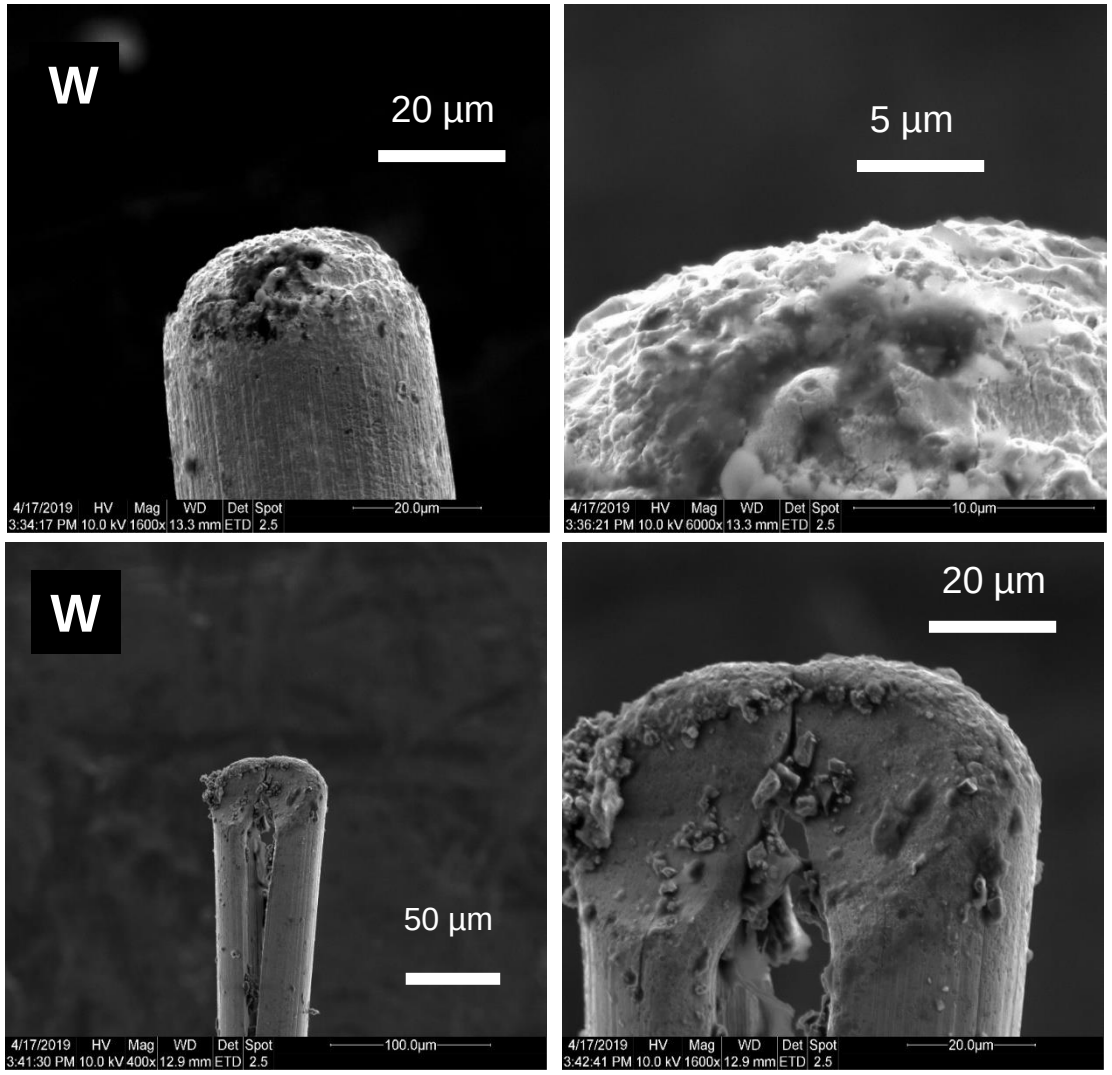


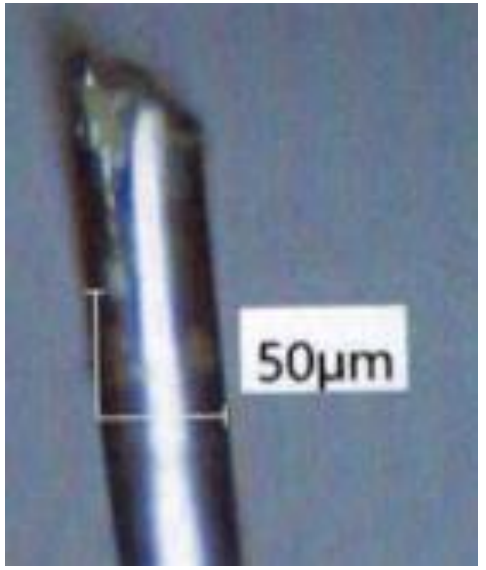


RUHR UNIVERSITÄT BOCHUM RUB

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



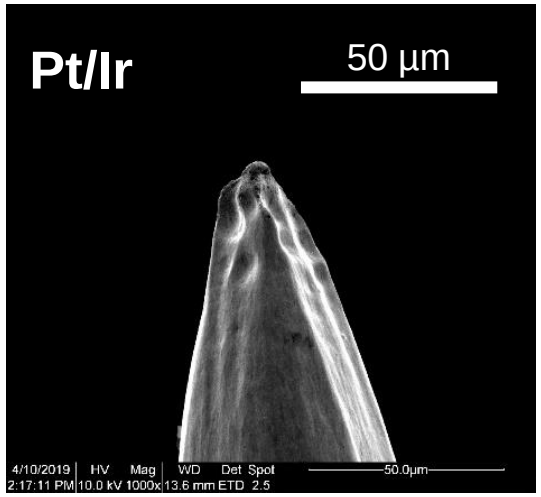


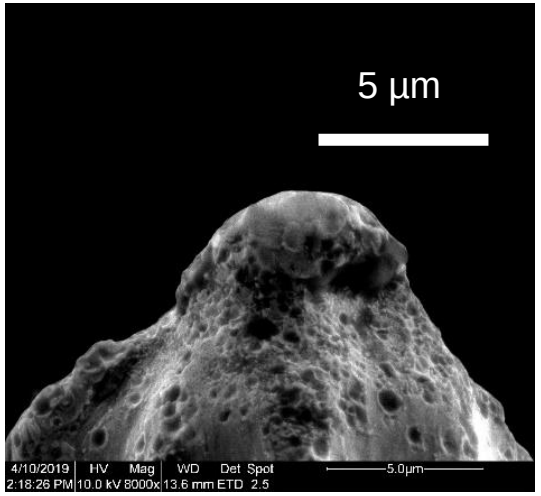
Short term use, < 7 h

long term use, ~ 30 h

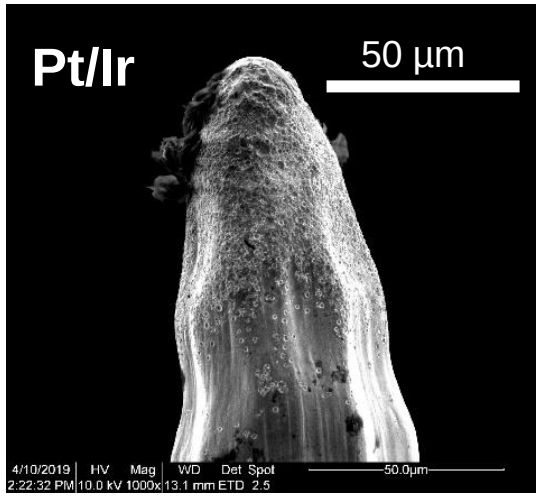
Platinum / Iridium tip (from AFM/SEM microscopes with 5..10 nm tip radius)

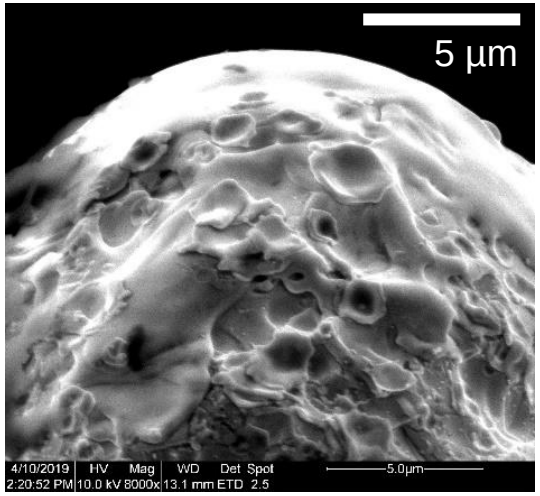
- Only short term operation possible
- After 1 h no plasma ignition possible anymore
- Pt melting temperature 2100 K
- Pt thermal conduct. 82 W/ m K
- Ir melting temperature 2700 K
- only Ir oxidizes





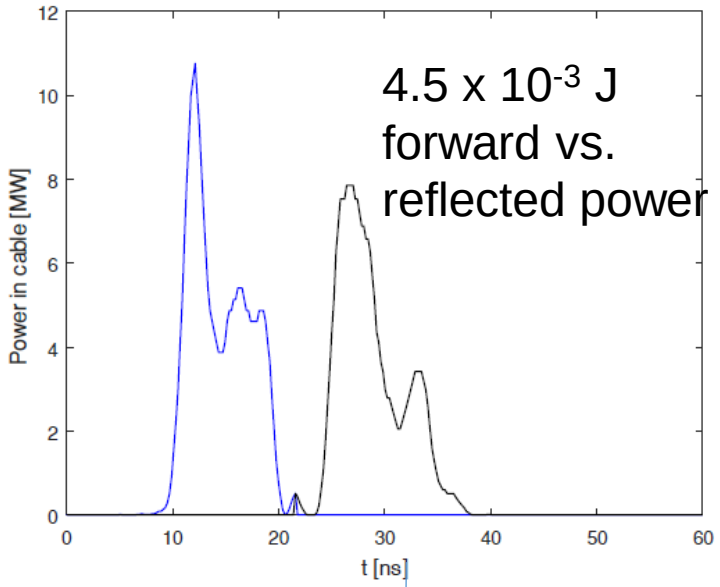
Short term use, 2 min



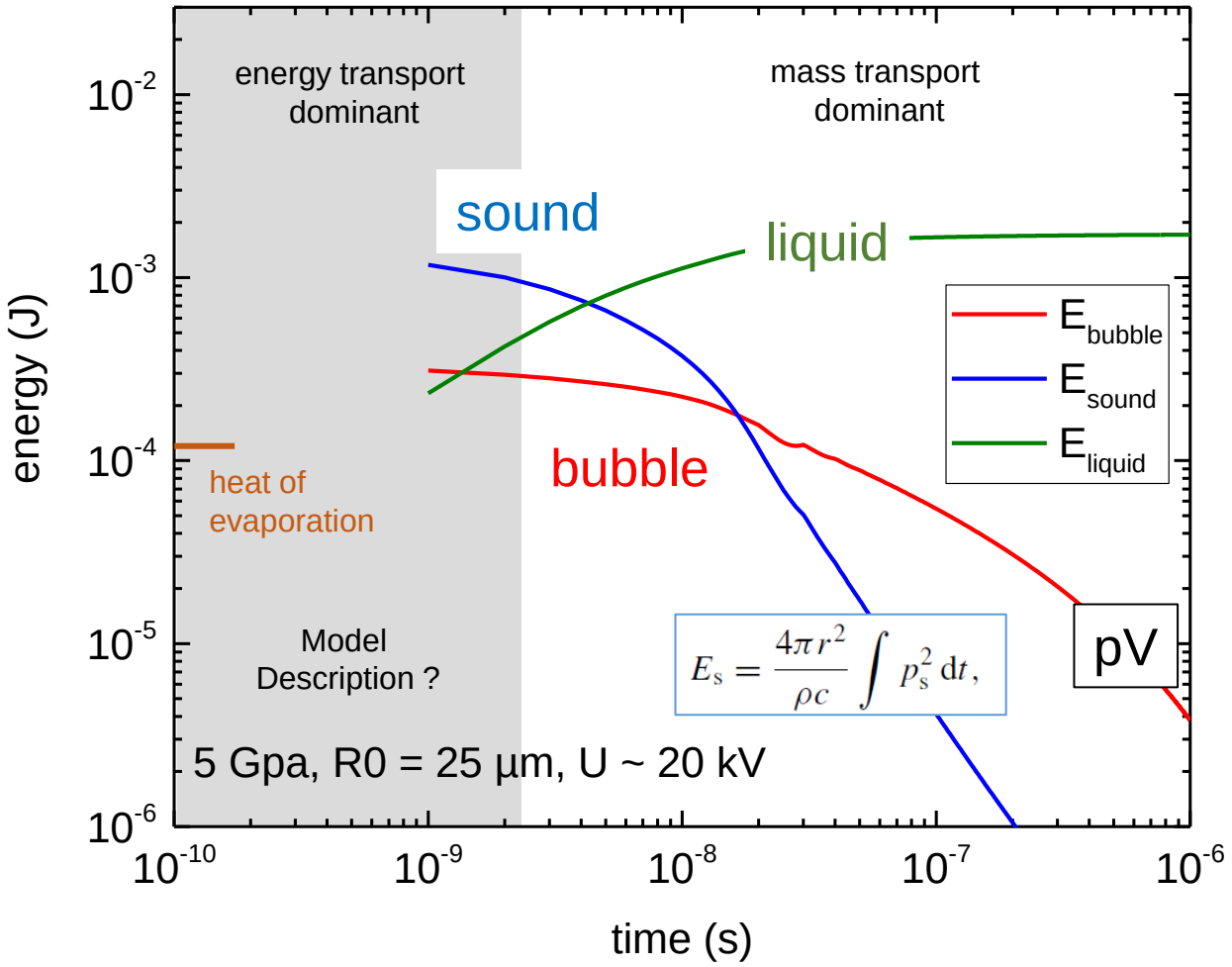


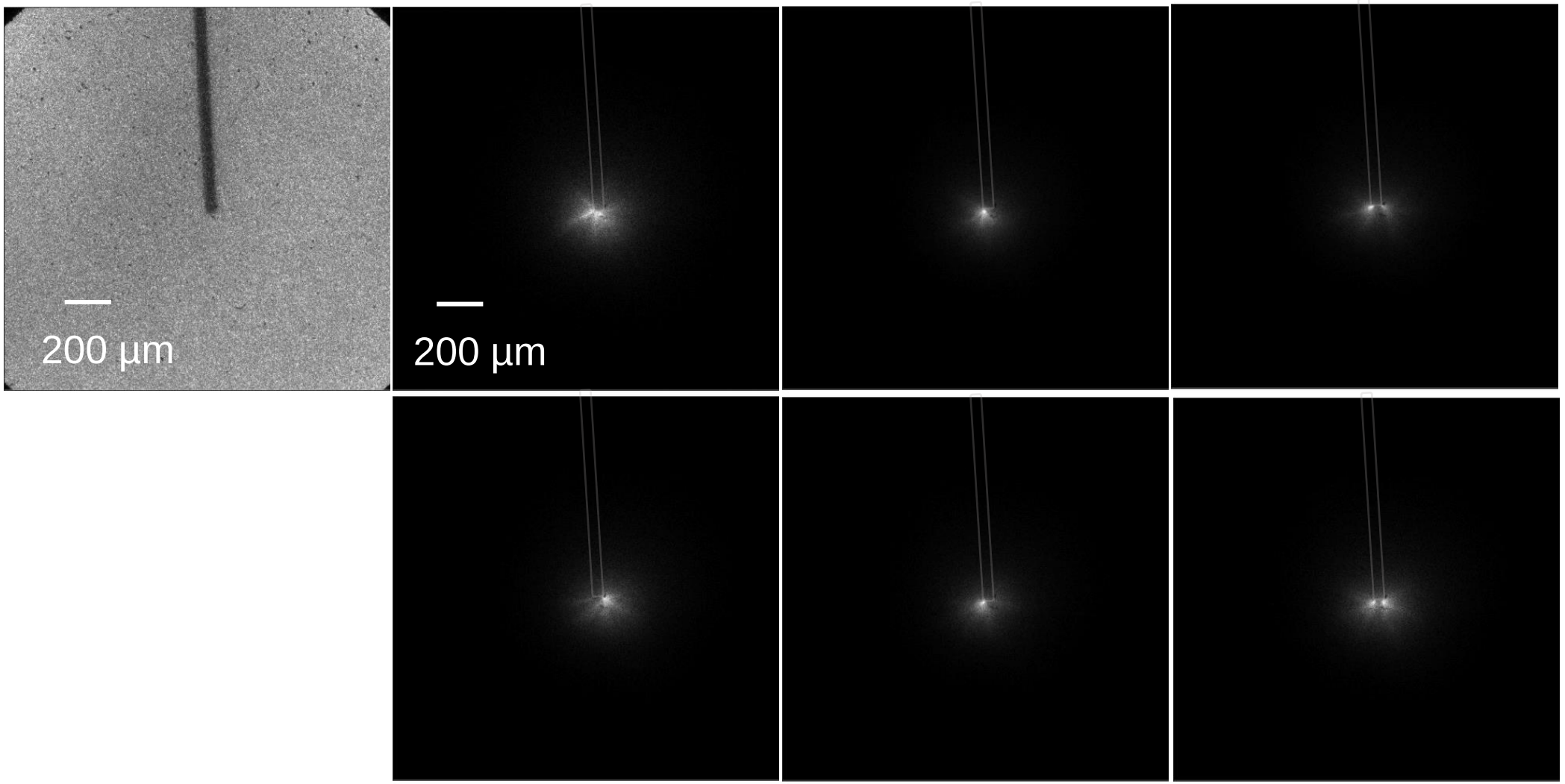
long term use, ~ 1 h

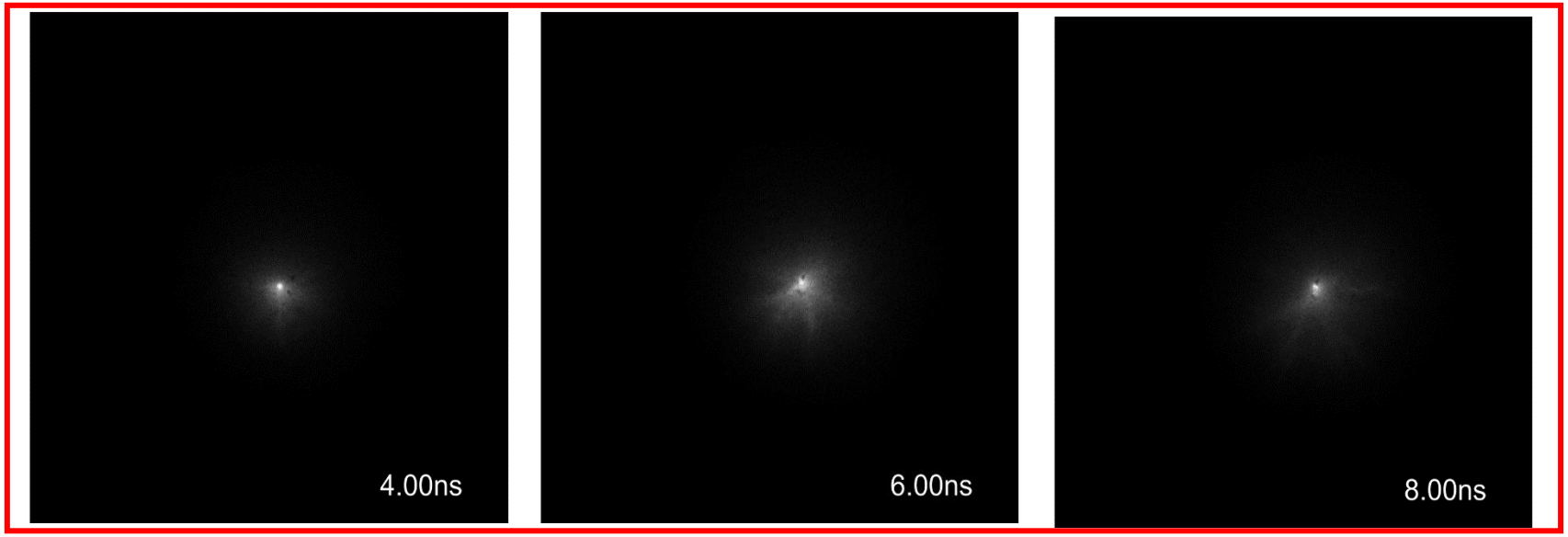
Dissipated energy during plasma ignition within the first 10 ns – comparison to experiments

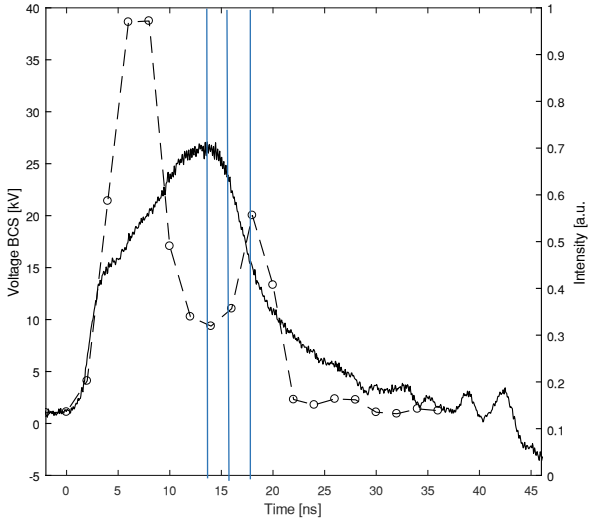


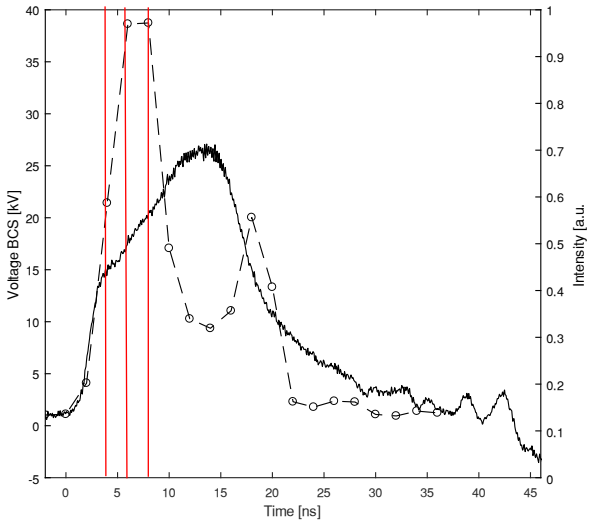
In ns plasmas at very high initial pressure, most of the energy is transferred to the sound wave

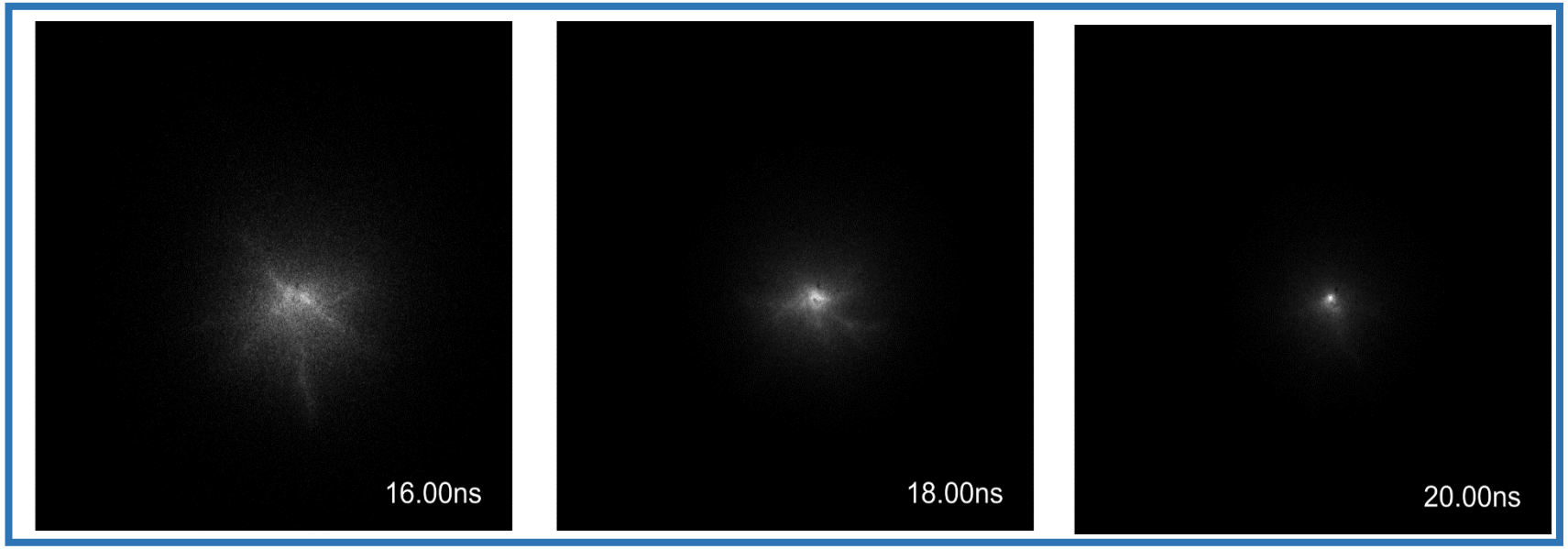












Nature of the 1/λ^x background in emission – cathode spots on the tungsten electrode