GENERATION OF ANTIMICROBIAL NO_x BY TRANSIENT SPARK DISCHARGE

UNDERSTANDING & OPTIMIZATION

Mário JANDA

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Slovak grant agency VEGA 1/0419/18.

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OUTLINE

- **introduction to the Transient Spark (TS) discharge**
- TS applications = motivation
- TS diagnostic & modeling
- understanding of physics and chemistry behind TS
- optimization
- summary

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DC driven self-pulsing

frequency 1-10 kHz

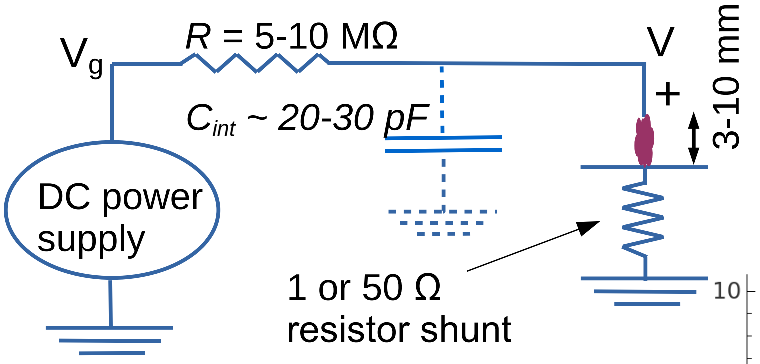
streamer-to-spark (short)

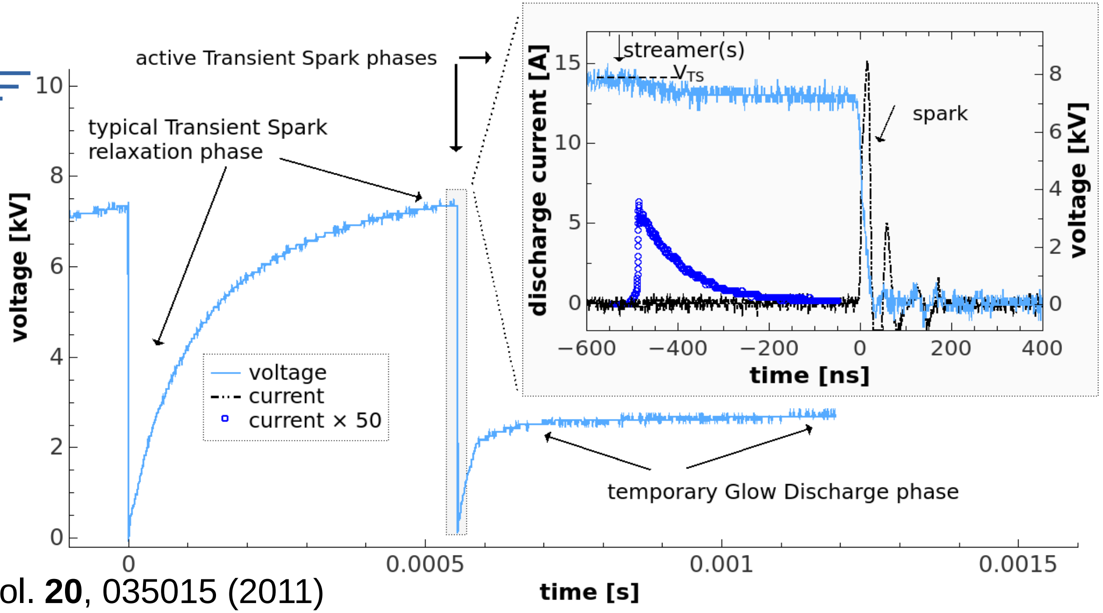
highly reactive non-equilibrium plasma

suitable for biomedical & environmental applications

TS – DC DRIVEN SELF-PULSING DISCHARGE

- streamer initiates breakdown and short spark
- repetitive (f ~ 1-10 kHz) charging and discharging of C_{int}





Janda M. et al., Plasma Sources Sci. Technol. **20**, 035015 (2011)

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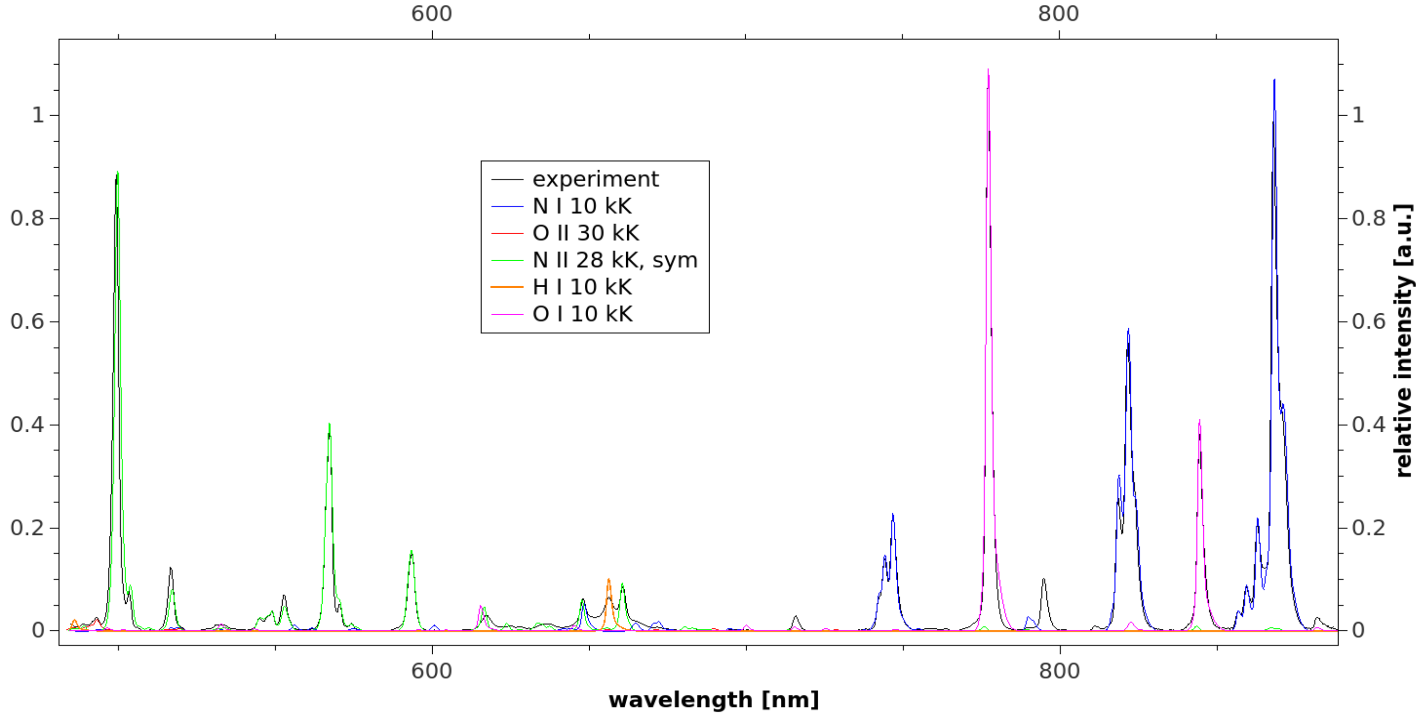
GENERATED PLASMA

- UV spectrum is dominated by N_2 SPS, and N II (O II) ionic lines
- Vis spectrum can be fitted by combining N I, N II, O I, O II and H lines
- T_{exc} ~ 30 kK (N II, O II), T_{exc} ~ 10 kK (N I, O I)



VOCs removal

CO_2 utilization

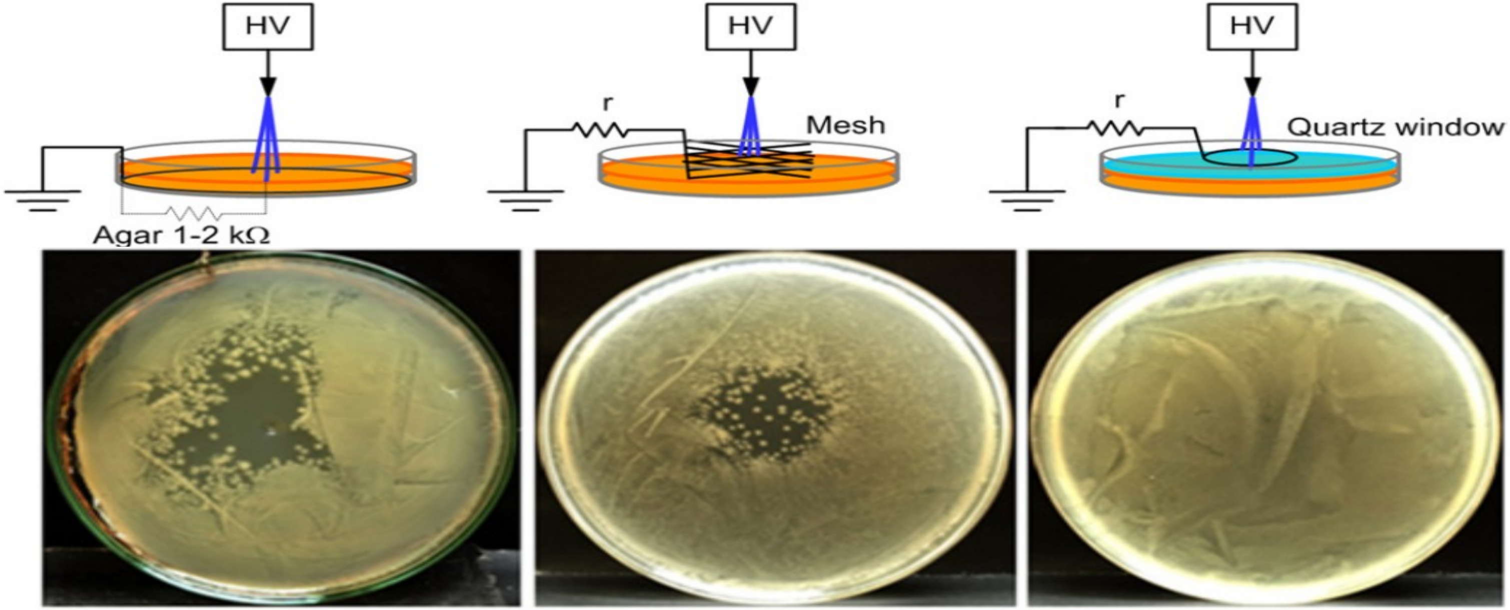
lean flame stabilization

bio-medical applications

disinfection of water and surfaces

BIO-DECONTAMINATION OF WATER AND SURFACES

- tested on various bacteria, yeasts, spores and biofilms
- antimicrobial agents in plasma - UV radiation, electric field, ions, neutrals
  - the effect of **reactive neutral species** dominates in TS



all agents UV, neutral species UV only

Machala Z. et al., J. Phys. D: Appl. Phys. **43**, 222001 (2010).

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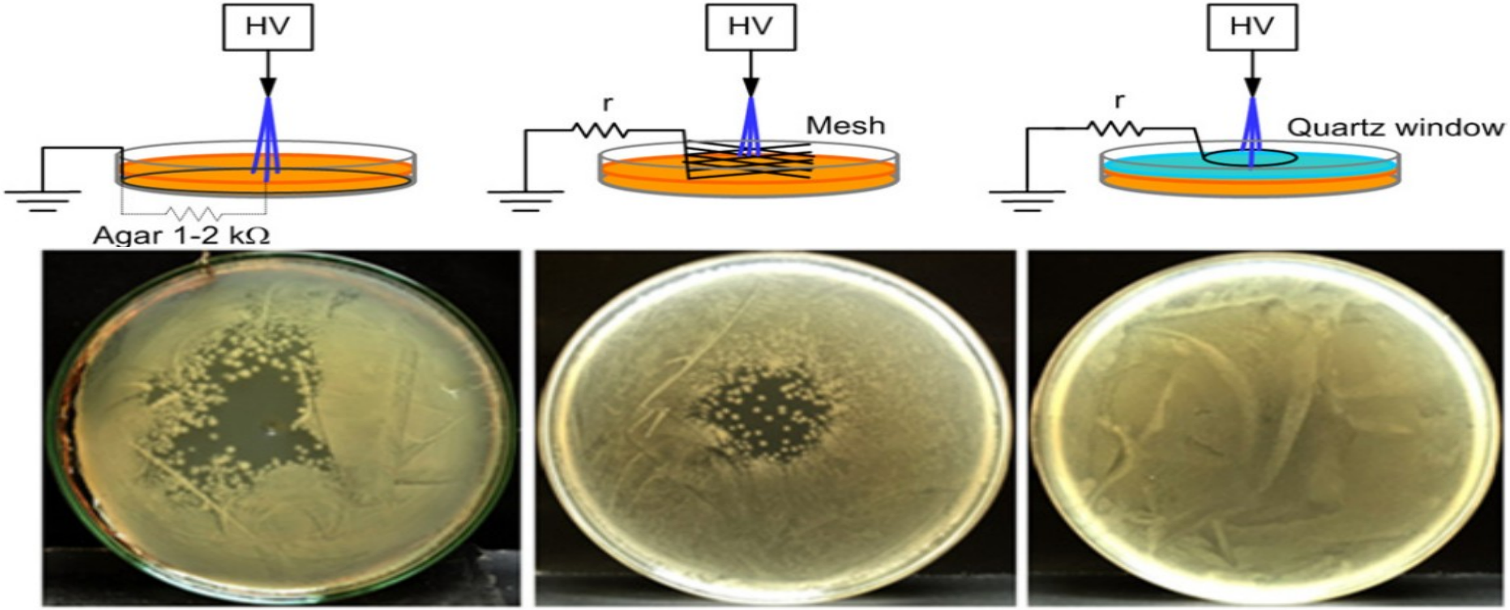

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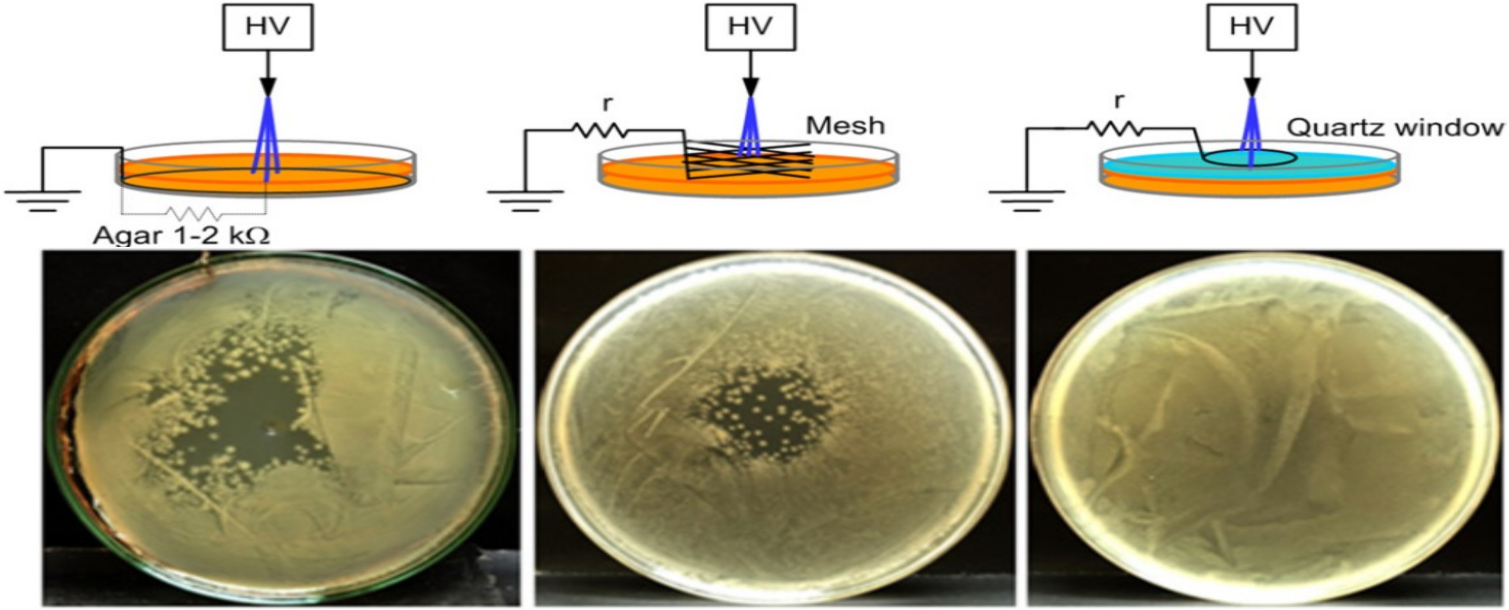

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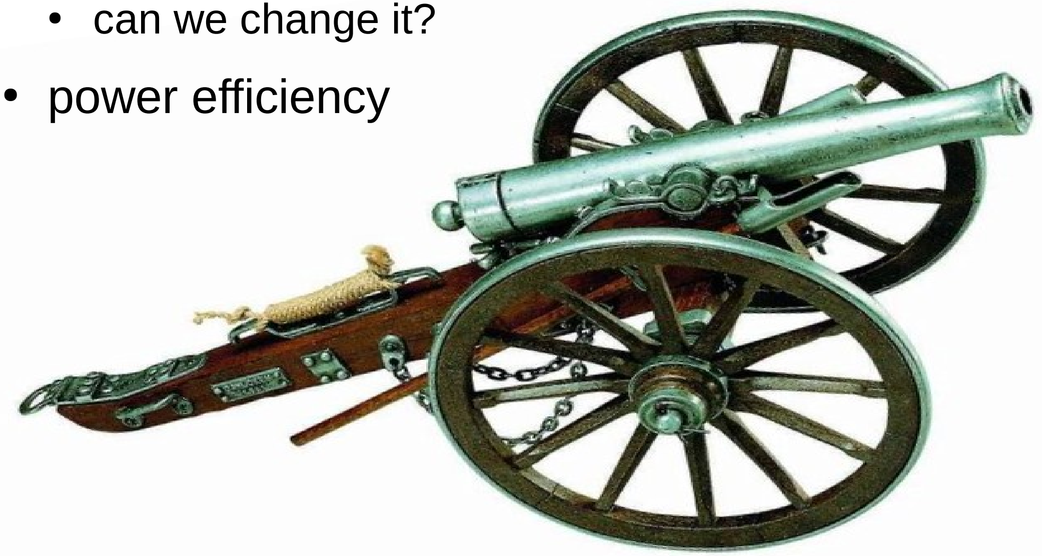
BASIC RESEARCH OF TS STILL NEEDED

- optimization of reactive species generation
  - optimal settings for generation of NO, NO_2 or O_3
- optimization of chemical selectivity
  - which gas phase products dominate in TS?
  - can we change it?
- power efficiency



electrical diagnostic

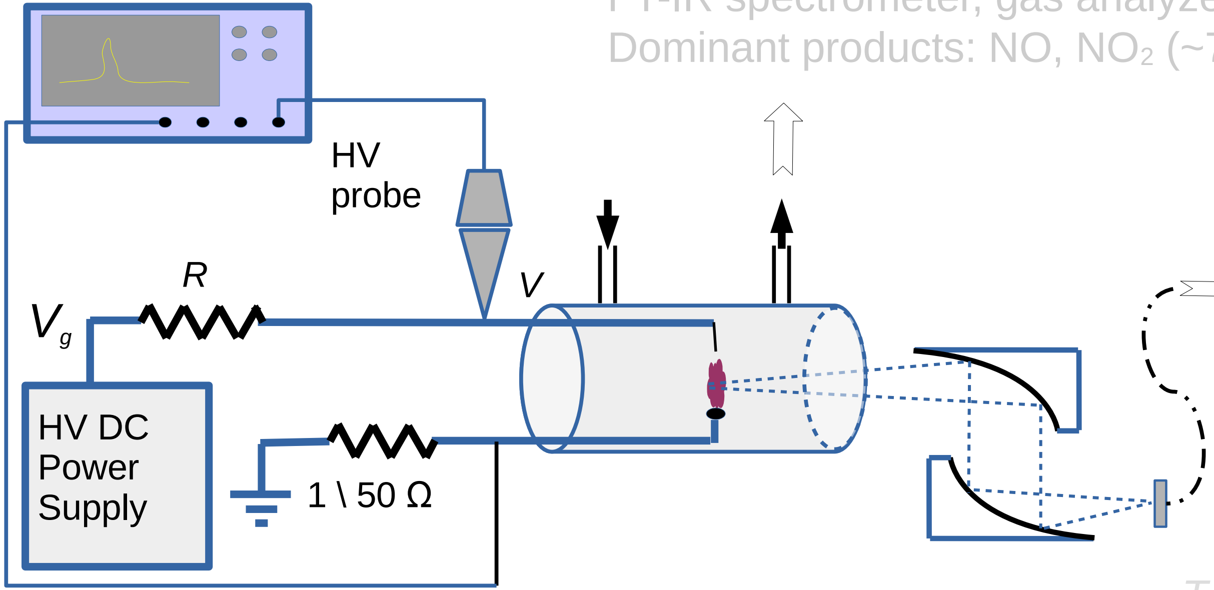
optical diagnostic

gaseous products

chemical modeling

EXPERIMENTAL SET-UP

FT-IR spectrometer, gas analyzer (NO_x, CO_x, HCs, O_3)
Dominant products: NO, NO_2 (~7×10^{16} molecules/J)



spectrometer
iCCD camera
photomultiplier
TC-SPC

T_g evolution (N_2 SPS)
n_e evolution (Stark)
E/N in streamer

oscilloscope
high voltage probe
current monitor
resistor shunts

V, I waveforms
repetition rate
energy per pulse
plasma resistance

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optical diagnostic
gaseous products
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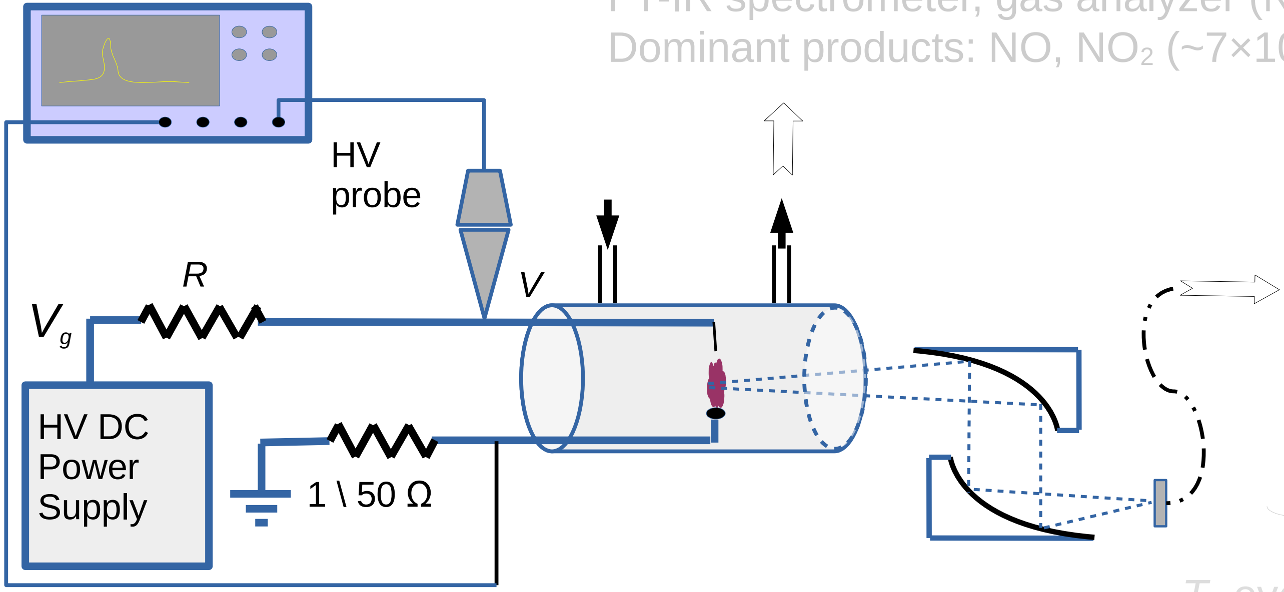

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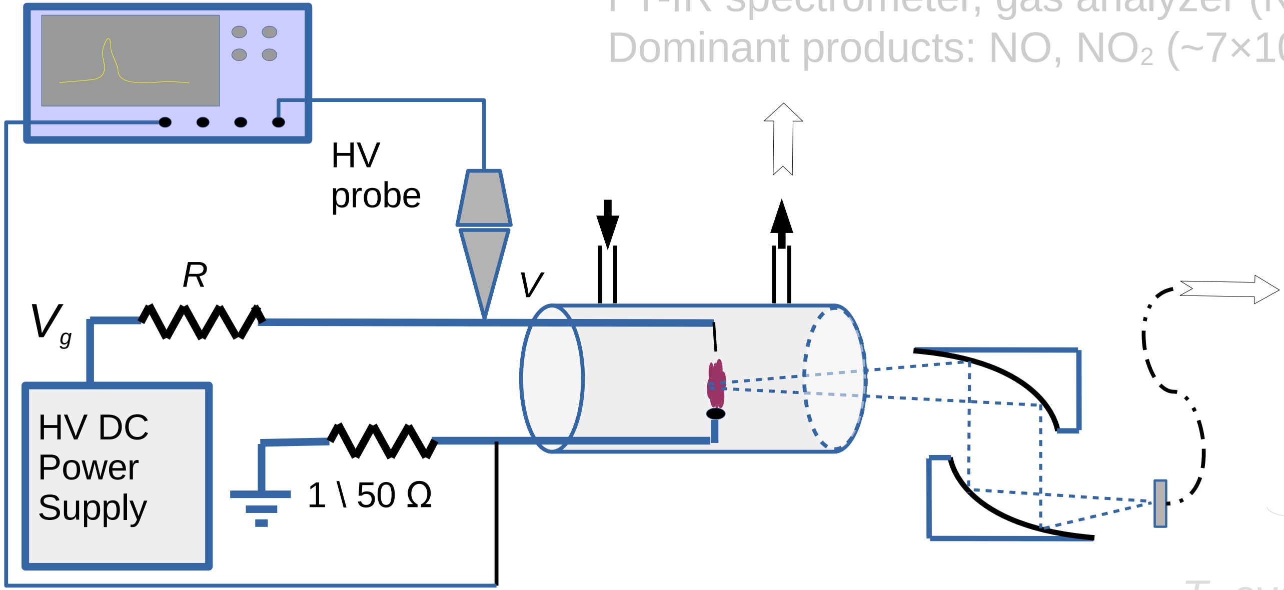

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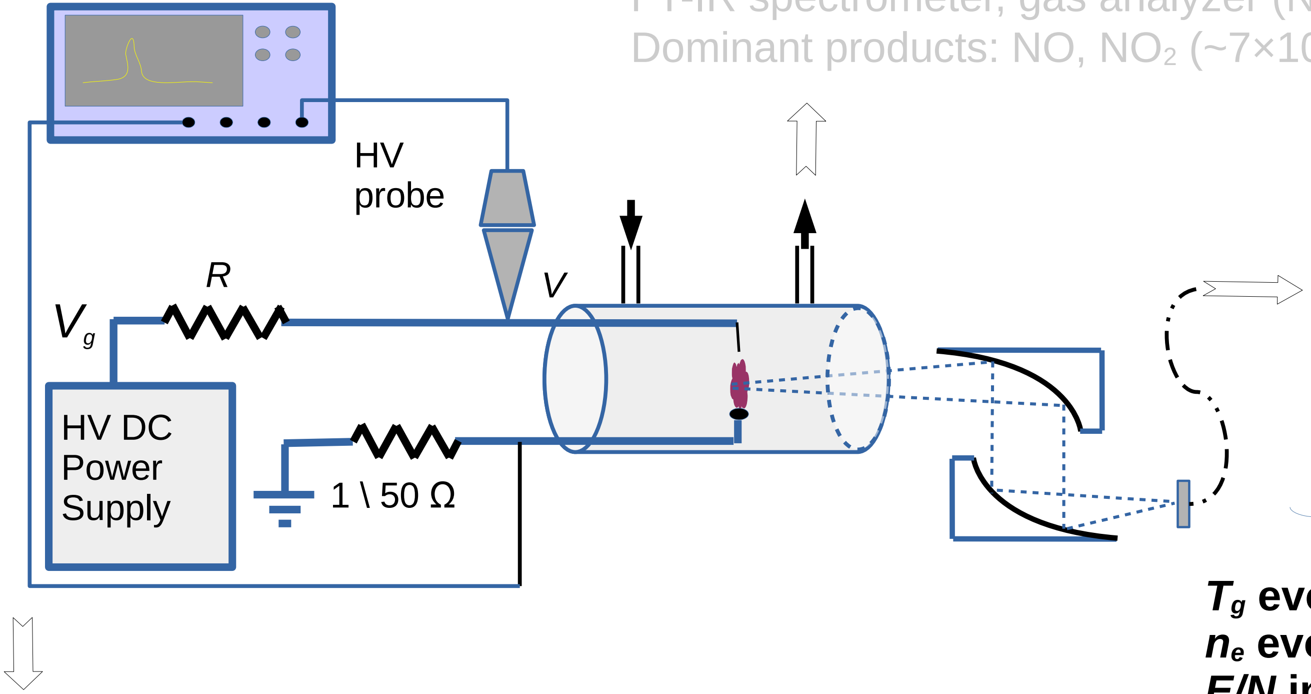

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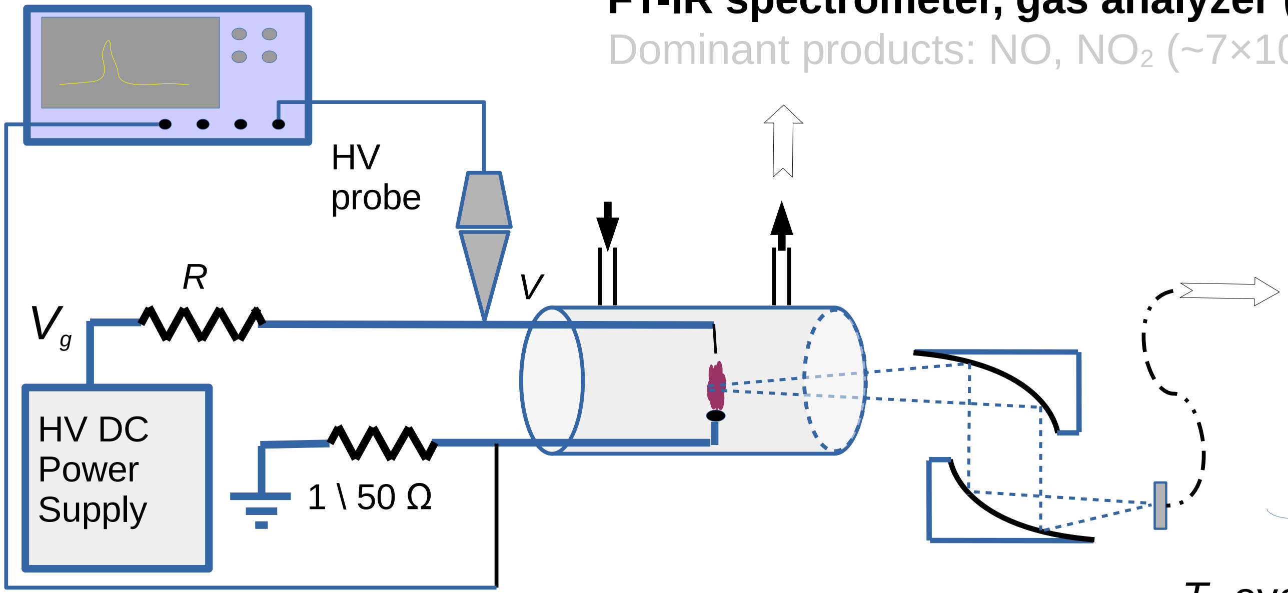

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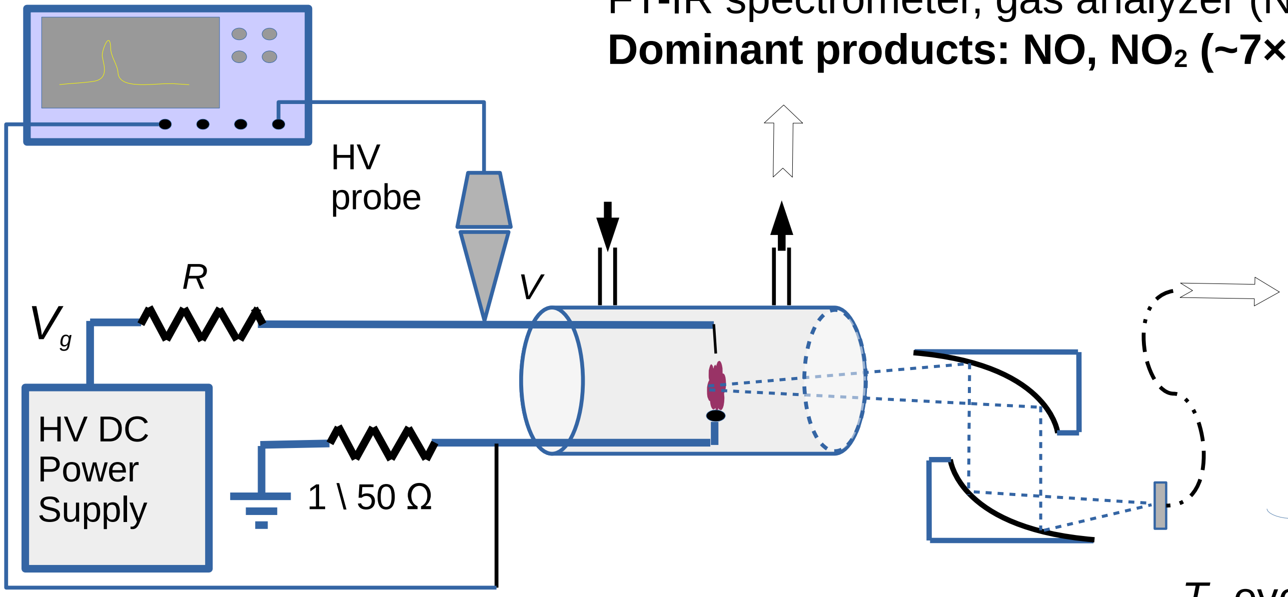

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CHEMICAL KINETIC MODEL – ZDPlasKin [1]

```
ELEMENTS
e Ar
END

SPECIES
e Ar Ar^+
END

BOLSIG
Ar
END

REACTIONS
e + Ar => e + e + Ar^+    ! Bolsig Ar->Ar^+
e + Ar^+ + Ar => Ar + Ar ! 1.0d-25
END
```

list of elements, species and reactions → preprocessor → ZDPlasKin Fortran90 Module

Bolsig+ solver — numerical solver of Boltzmann equation [2]

+

DVODE library — numerical solver for system of ordinary differential equations

+

ZDPlasKin Fortran90 Module

+

module provided by user (Fortran)

compilation → executable program → output data

+

Cross-sections database

Our major task: physical model of Transient Spark → module provided by user (Fortran)

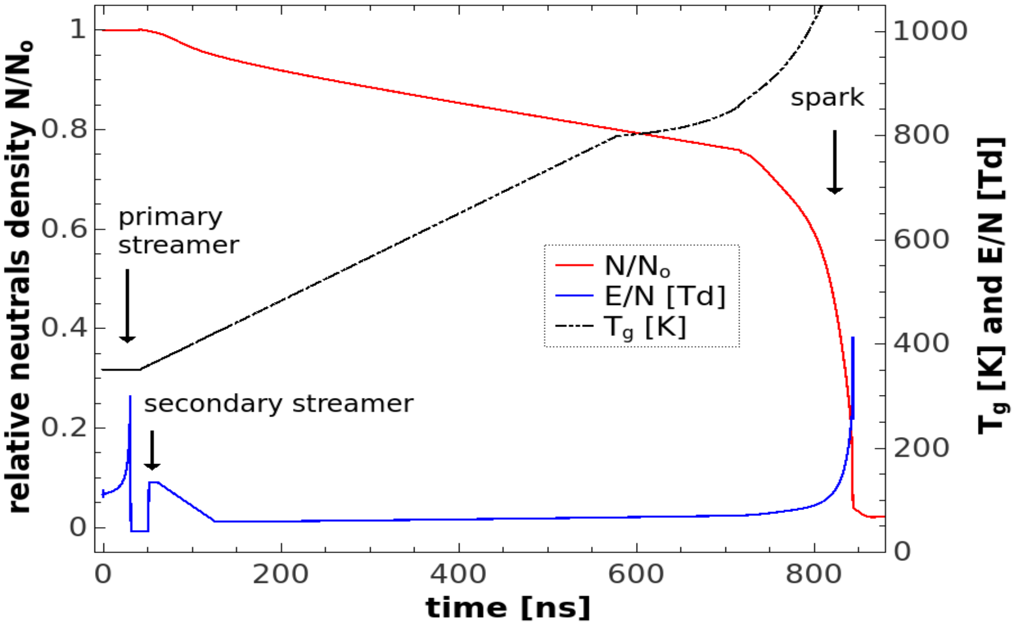
describes evolution of *Tg*, *E/N*, ...

[1] www.zdplaskin.laplace.univ-tlse.fr
[2] www.bolsig.laplace.univ-tlse.fr

STREAMER-TO-SPARK TRANSITION

- *E/N(t)* during streamer based on literature and our experimental data [1]
- *N* evolution from Naidis [2], T_g from N_2 SPS, *E(t)* calculated (discharging of C_{int}) [3]
- hydrodynamic expansion breakdown mechanism

$\uparrow T_g \rightarrow \uparrow p \rightarrow$ hydrodynamic expansion $\rightarrow \downarrow N \rightarrow \uparrow E/N \rightarrow$ ionization $\rightarrow$ breakdown



[1] Janda M et al. (2018) J. Phys. D: Appl. Phys. **51**, 334002
[2] Naidis GV, (2009) Eur. Phys. J. Appl. Phys. **47**, 22803
[3] Dvonč L., Janda M (2015) IEEE Trans. Plasma Phys. **43**, 2562-2570

electrical diagnostic
↓
liquid phase products
↓
optical diagnostic
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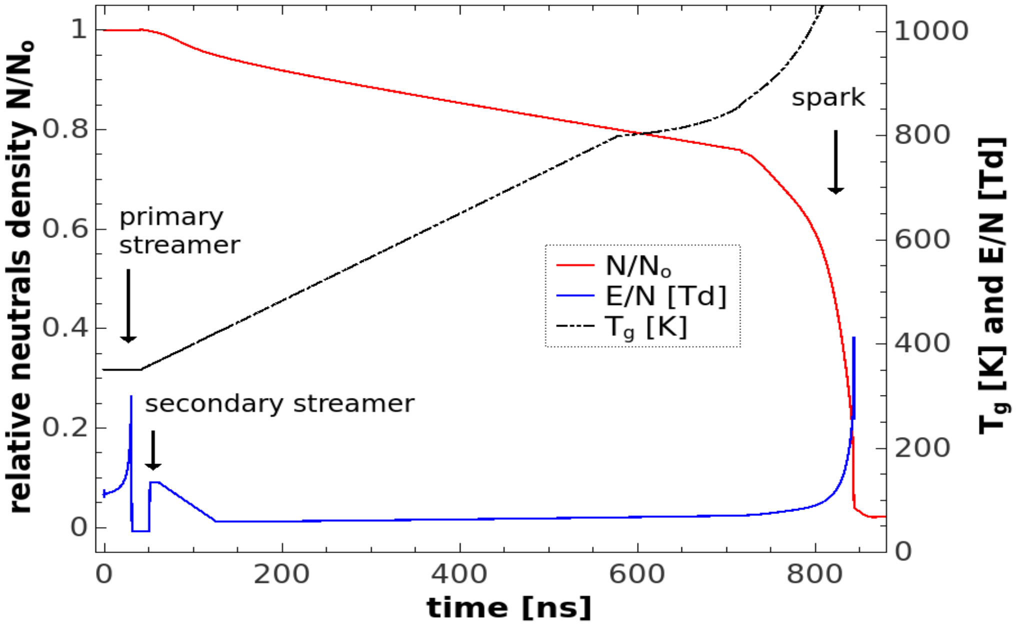

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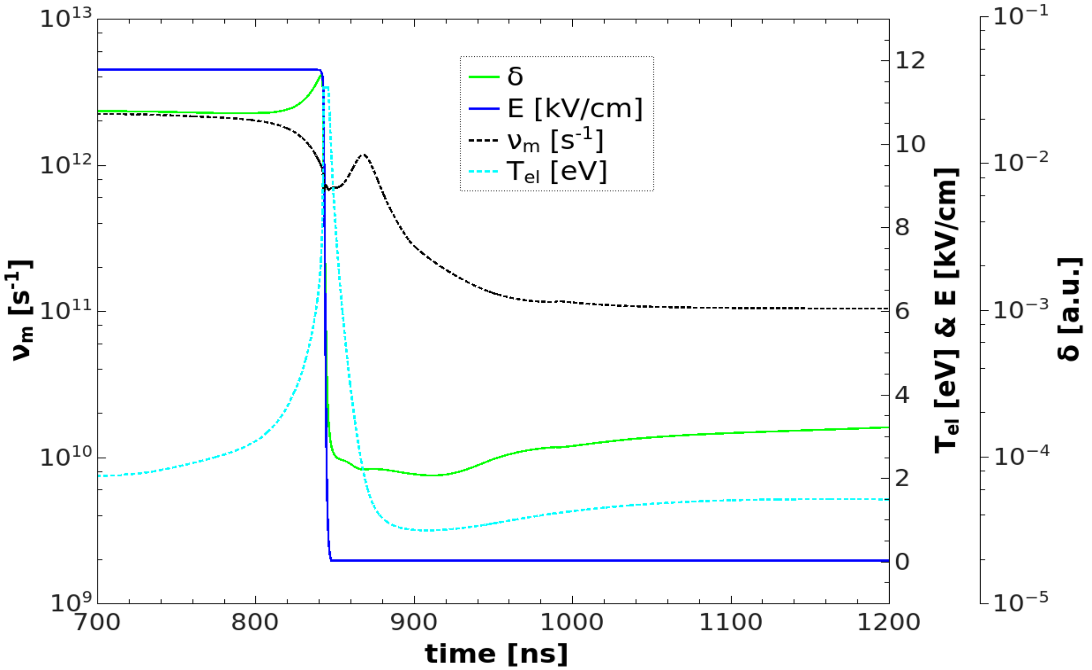
SHORT SPARK PHASE

- starts when ionization degree reaches 2×10^{-2}, duration 400 ns
- $E(t)$ calculated (discharging of C_{int}), T_{el} evolution calculated

$$\frac{d\varepsilon}{dt} = \frac{e^2 E^2}{m_e \nu_m} - \delta\left(\varepsilon - \frac{3}{2} k T_g\right)\nu_m$$



ν_m – collision frequency of electrons
ε – electron mean energy
T_g – gas temperature
δ – relative energy lost per collision, taking into account both elastic and inelastic processes

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RELAXATION PHASE – work in progress

D_p^{spark} = 50 μm
D_p^{max} = 500-1000 μm
τ_{exp} = 3-30 μs

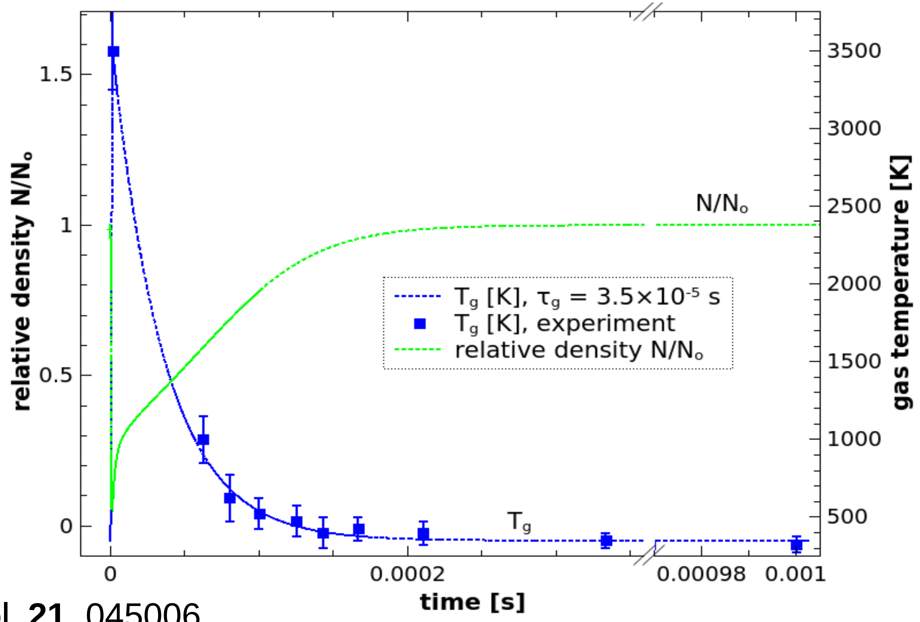
- plasma channel expansion [1]

$$D_p(t) = D_p^{spark} + \left(D_p^{max} - D_p^{spark}\right)\left\{1 - \exp\left(-t/\tau_{\exp}\right)\right\}$$

- temperature changes [2] $T_g(t) = T_g^o + \left(T_g^{max} - T_g^o\right)\exp\left(-t/\tau_g\right)$
  - from measured 'steady-state' temperature $T_g^o(f)$
- mixing with ambient air
  - inflow ($J^+_{N_2/O_2}$) of N_2 and O_2
  - several models tested

$$J^+_{N_2/O_2}(t) \propto \Delta n_{N_2/O_2}(t)$$

$$J^+_{N_2/O_2}(t) \propto \Delta p(t)$$



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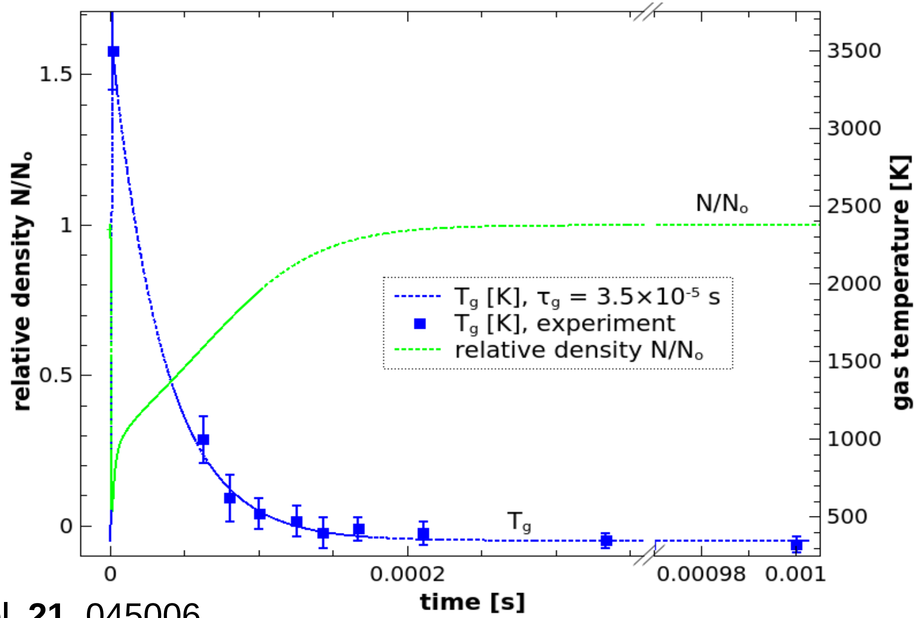

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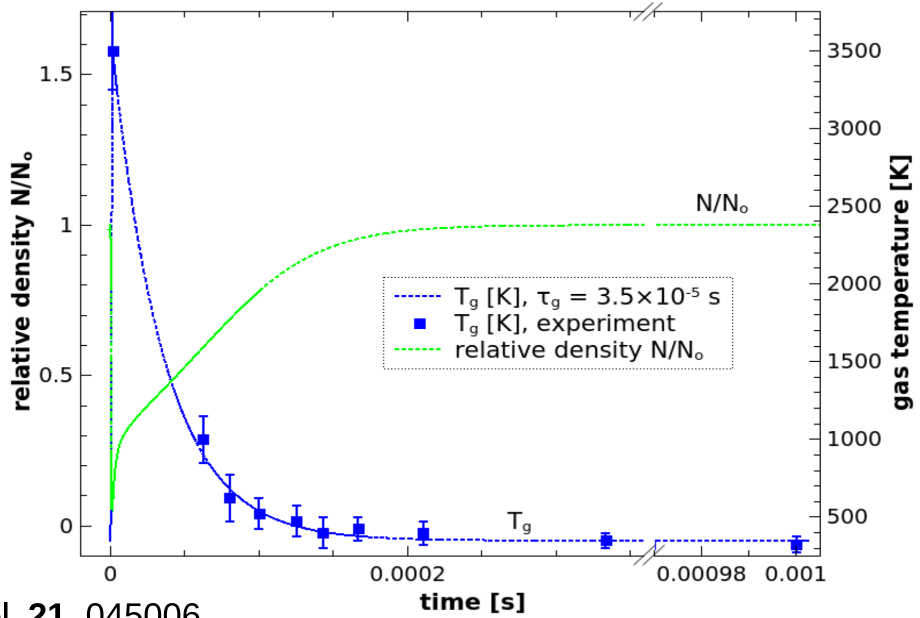

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electrical diagnostic

liquid phase products

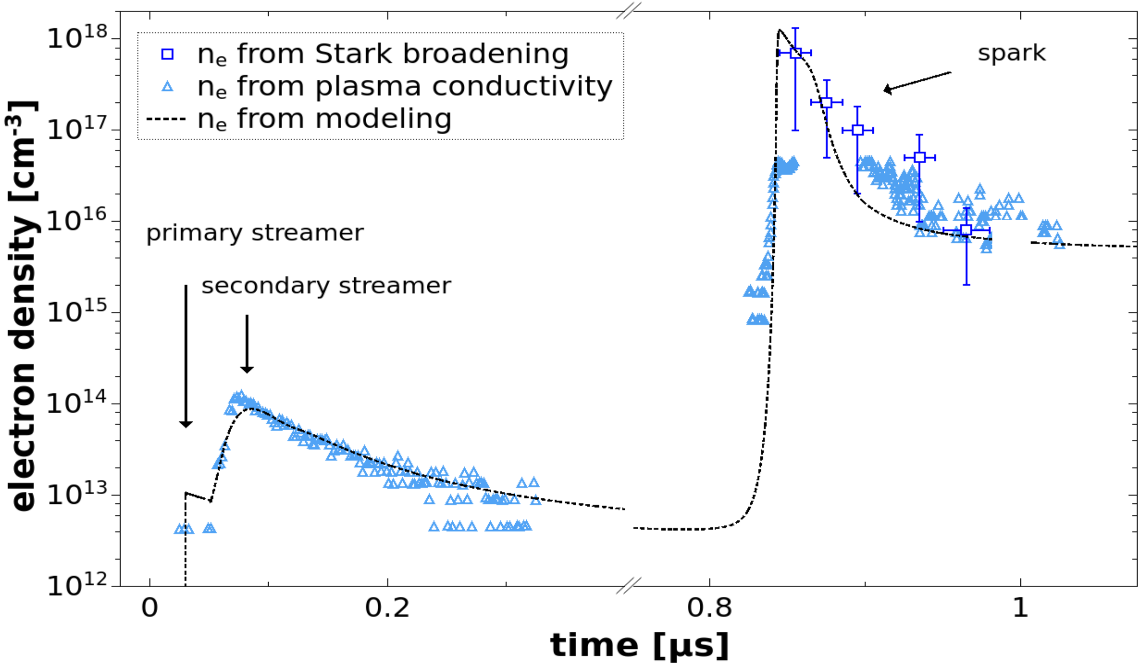
optical diagnostic

gaseous products

chemical modeling

MODEL VERIFICATION

- voltage temporal evolution – good agreement
- electron density – reasonable agreement
- suitable for study of RONS generation mechanisms



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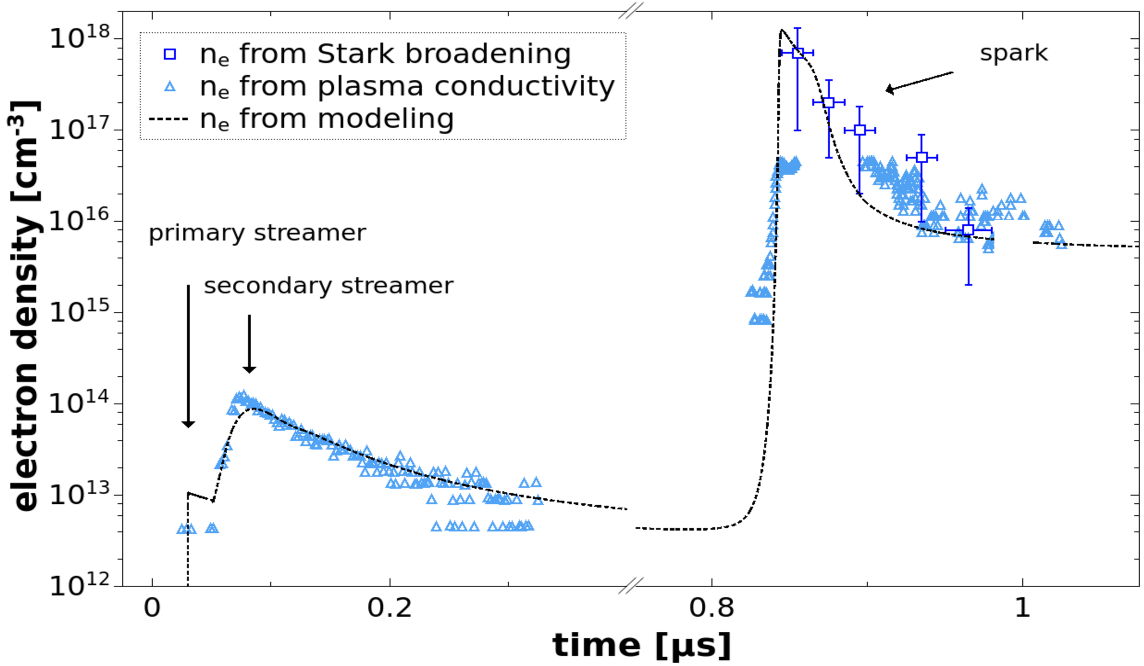

RONS – reactive oxygen and nitrogen species

O atoms by streamer

ionization & atomization by spark

more N atoms during spark

NO shortly after spark

NO_2/O_3 in relaxation phase

RONS DURING ACTIVE DISCHARGE PHASE

- streamer produces mostly N_2* and O atoms
- strong degree of ionization and atomization
- more N than O atoms indicates different final products

- generation of some NO shortly after the spark

$$e + N \overset{T_{el}}{\longleftrightarrow} e + e + N^+$$
$$N^+ + O_2 \rightarrow NO + O^+$$

NO, NO_2 and O_3 are mostly produced in relaxation phase !

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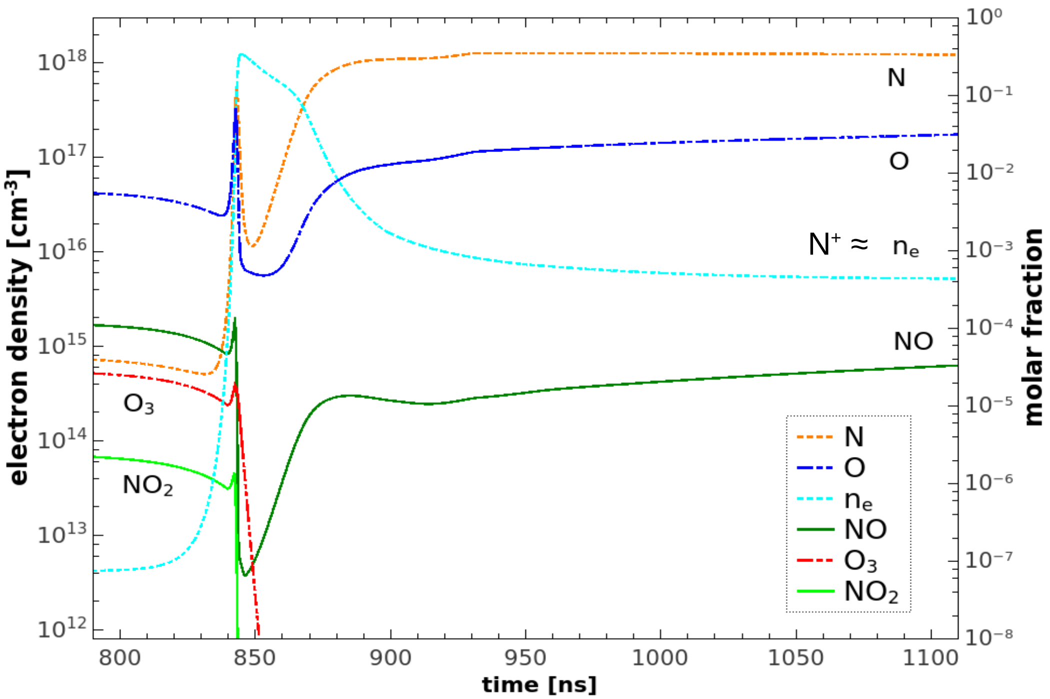

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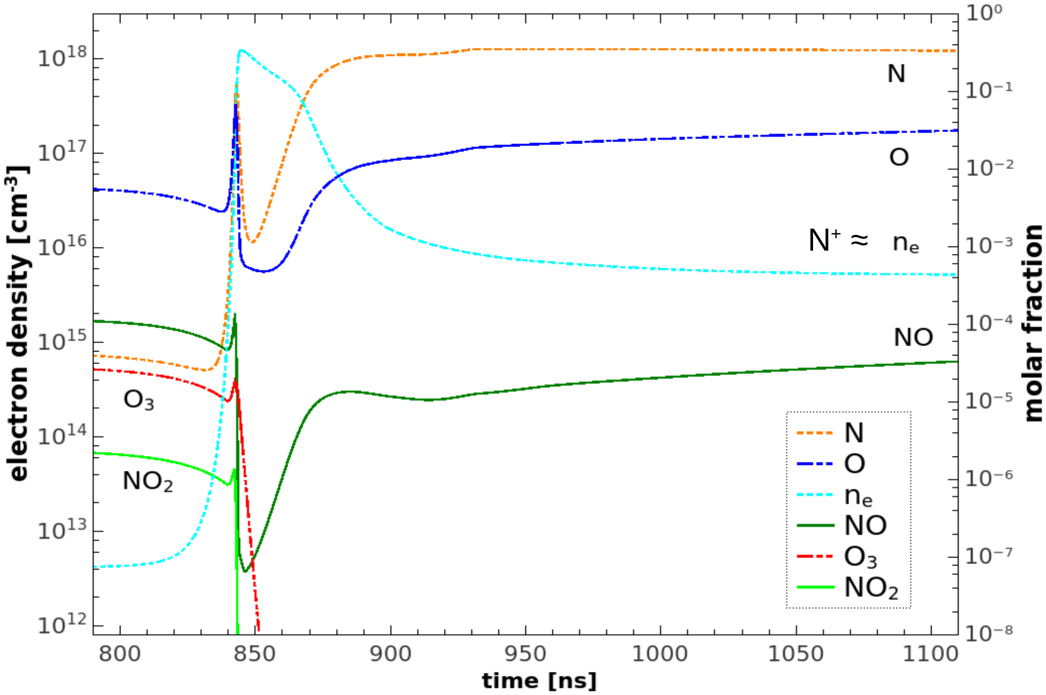

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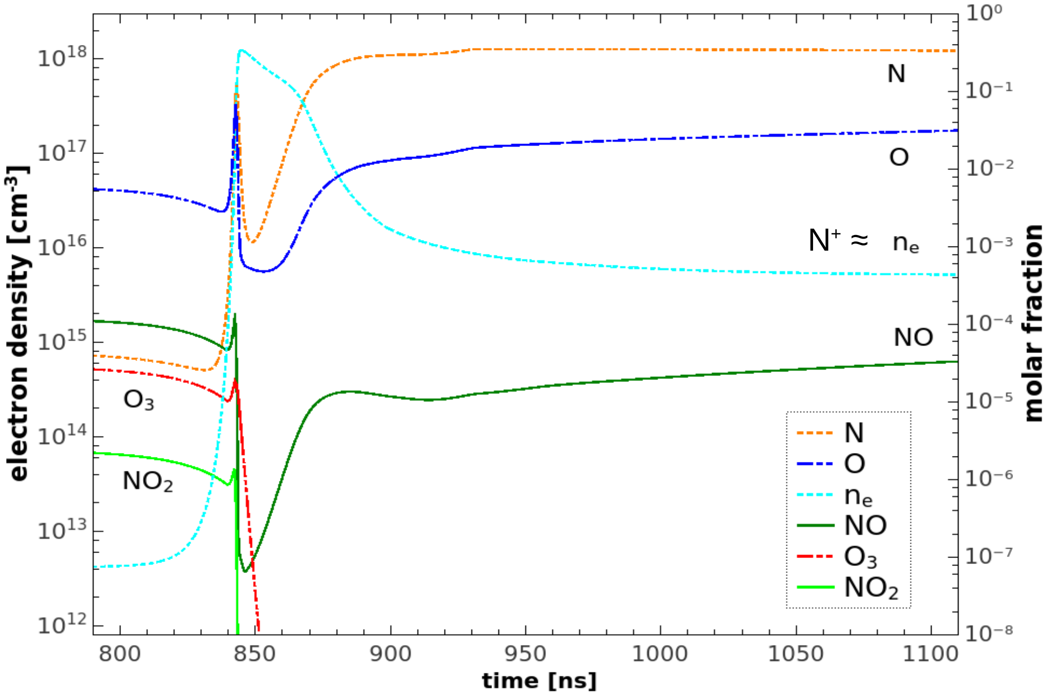

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ionization & atomization by spark

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more N atoms during spark

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NO shortly after spark

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NO_2/O_3 in relaxation phase

NO, NO_2 and O_3 GENERATION MECHANISMS

- NO generated by modified Zeldovich mechanism (fast, high T_g)

$O_2 + M \rightarrow O + O + M$ (thermal decomposition, relatively slow, high T_g)

$O + N_2(v\geq0) \rightarrow N + NO$ (rate limiting slow reaction)

$N/N^* + O_2(v\geq0) \rightarrow O + NO$

- NO_2 generation/removal (relatively fast, elevated T_g)

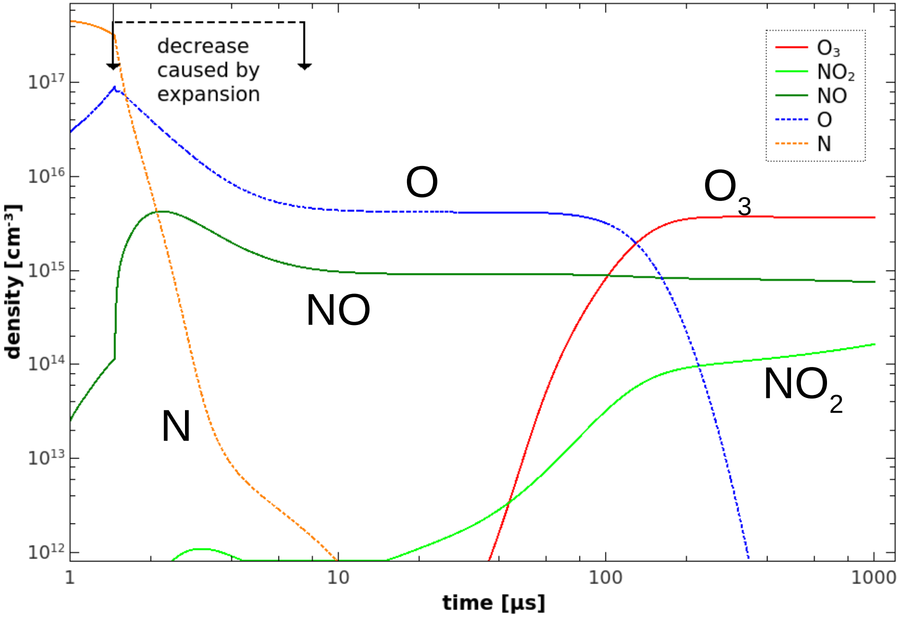
$$\left.\begin{array}{l} O + NO + M \rightarrow NO_2 + M \\ O + NO_2 \rightarrow O_2 + NO \end{array}\right\} O \downarrow$$

- O_3 generation (slower, low T_g)

$O + O_2 + M \rightarrow O_3 + M$

- NO_2 generation (slow, low T_g)

$NO + O_3 \rightarrow NO_2 + O_2$



O atoms by streamer

⇩

ionization & atomization by spark

⇩

more N atoms during spark

⇩

NO shortly after spark

⇩

NO_2/O_3 in relaxation phase

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- NO_2 generation/removal (relatively fast, elevated T_g)

$O + NO + M \rightarrow NO_2 + M$

$O + NO_2 \rightarrow O_2 + NO$

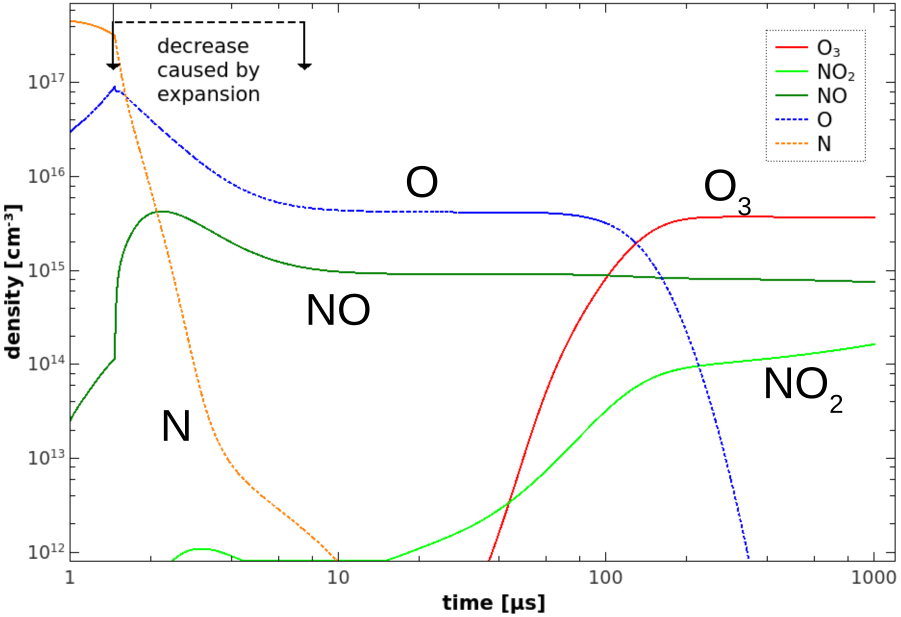
O ↓

- O_3 generation (slower, low T_g)

$O + O_2 + M \rightarrow O_3 + M$

- NO_2 generation (slow, low T_g)

$NO + O_3 \rightarrow NO_2 + O_2$



⇓

O atoms by streamer

⇓

ionization & atomization by spark

⇓

more N atoms during spark

⇓

NO shortly after spark

⇓

NO_2/O_3 in relaxation phase

NO, NO_2 and O_3 GENERATION MECHANISMS

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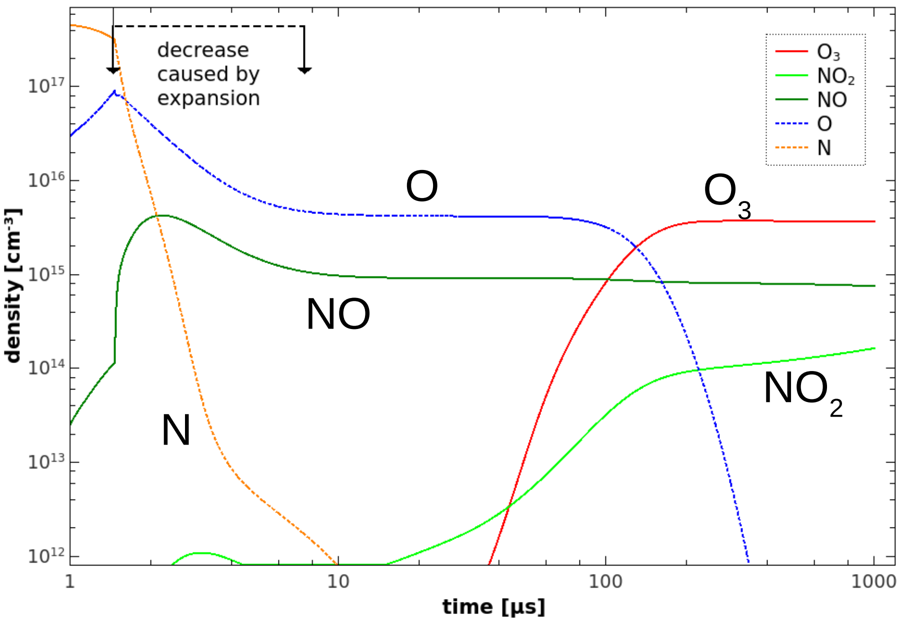

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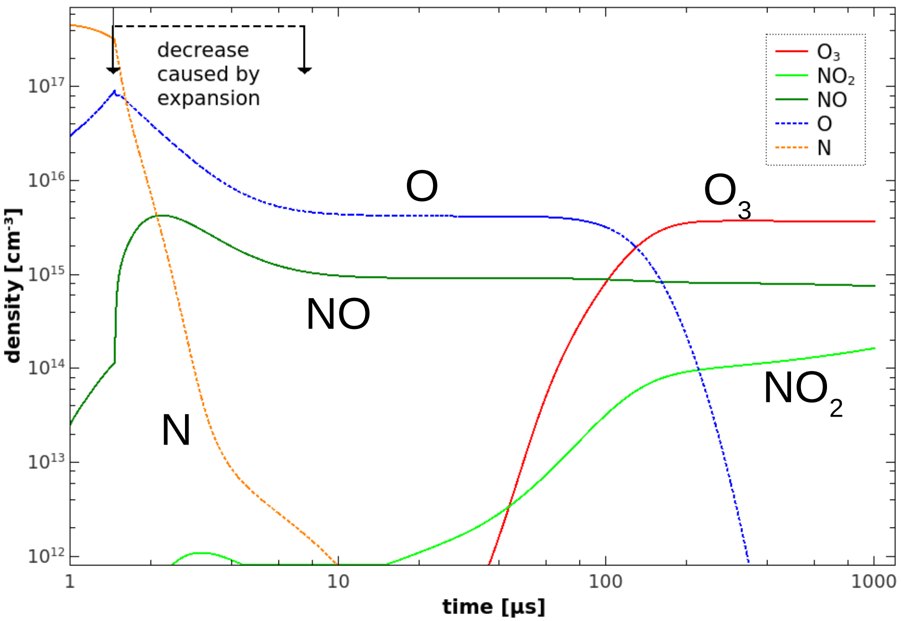

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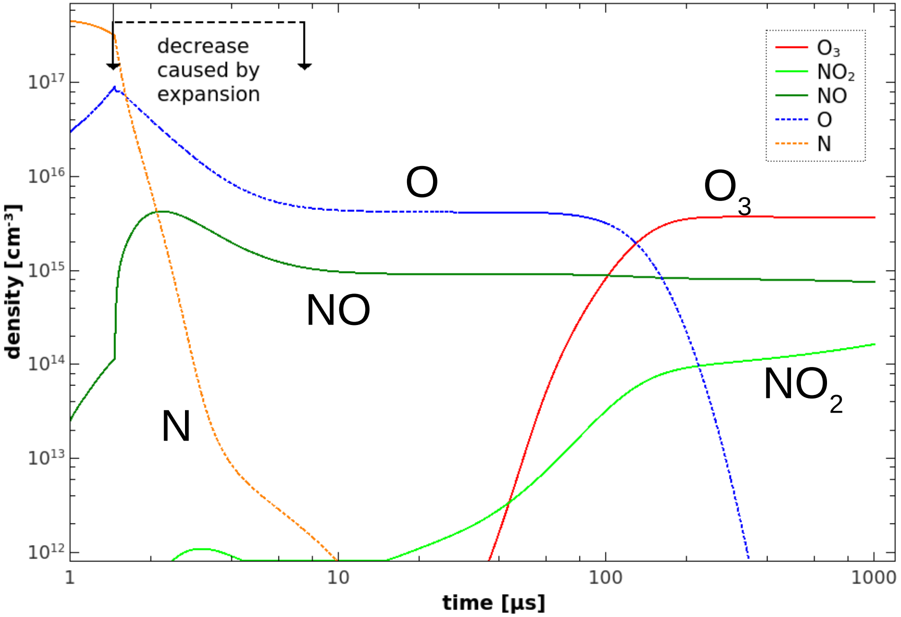

NO GENERATION ENHANCEMENT

- NO generated by N^+ and by modified Zeldovich mechanism (fast, high T_g)
- how to increase the NO production according to model?
  - stronger spark pulses
    - more N and N^+
  - slow cooling (or higher T_g^{max})
    - more time for Zeldovich mechanism reactions
  - fast inflow of O_2/N_2 to hot plasma channel
    - more reactants for Zeldovich mechanism reactions
- how to do it in praxis ?
  - circuit modifications

optimization criteria
electric circuit modifications
additional resistor
external capacitor
smaller limiting resistor

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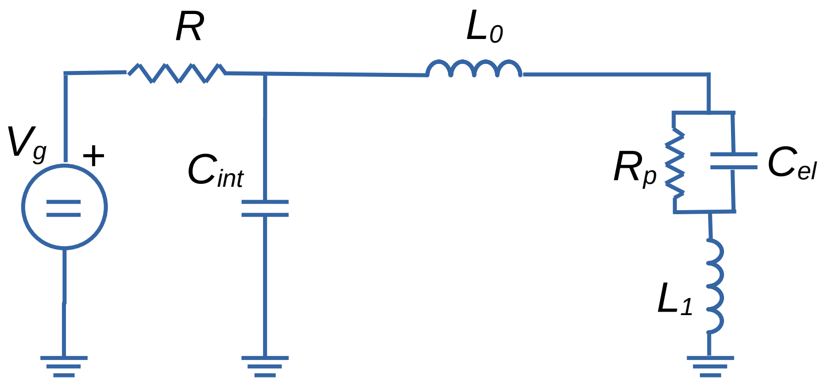
ELECTRIC CIRCUIT FOR TS GENERATION

- additional resistor r (0.1-30 kΩ) to divide C_{int} (C_0 ~ 20 pF, C_1 ~ 10 pF)



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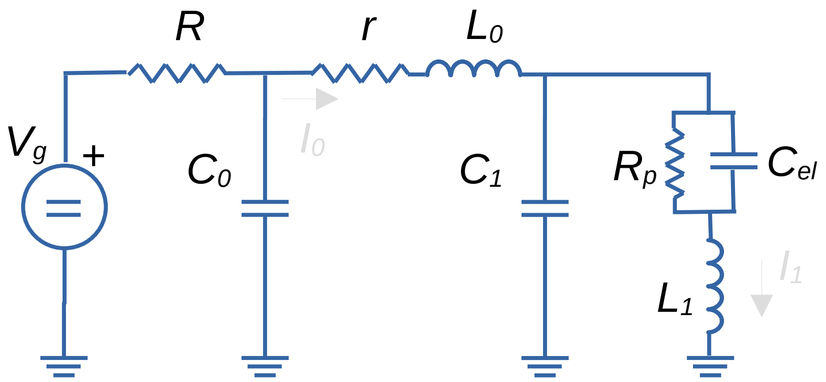

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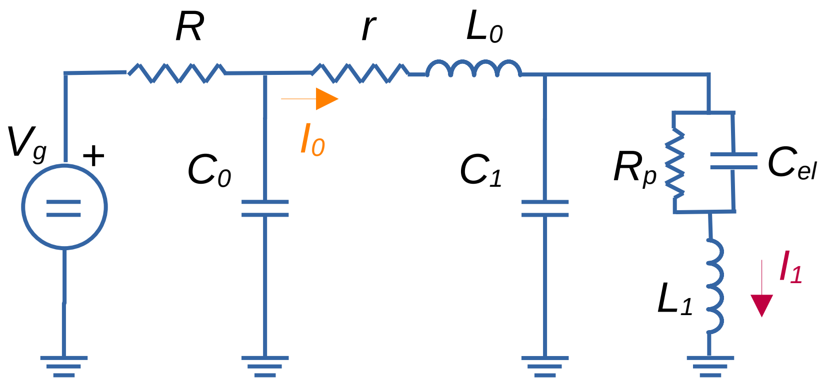

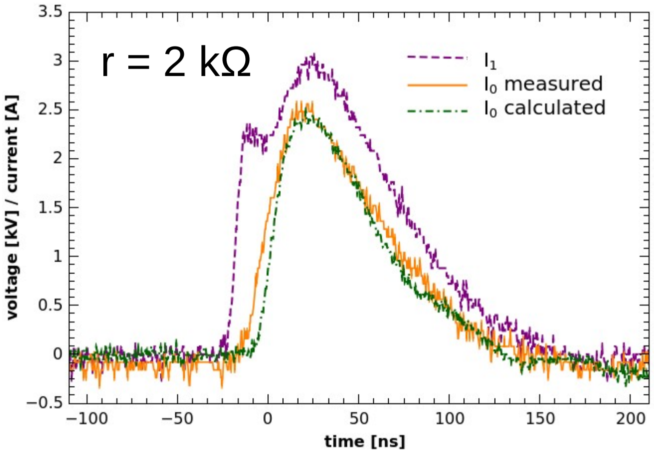

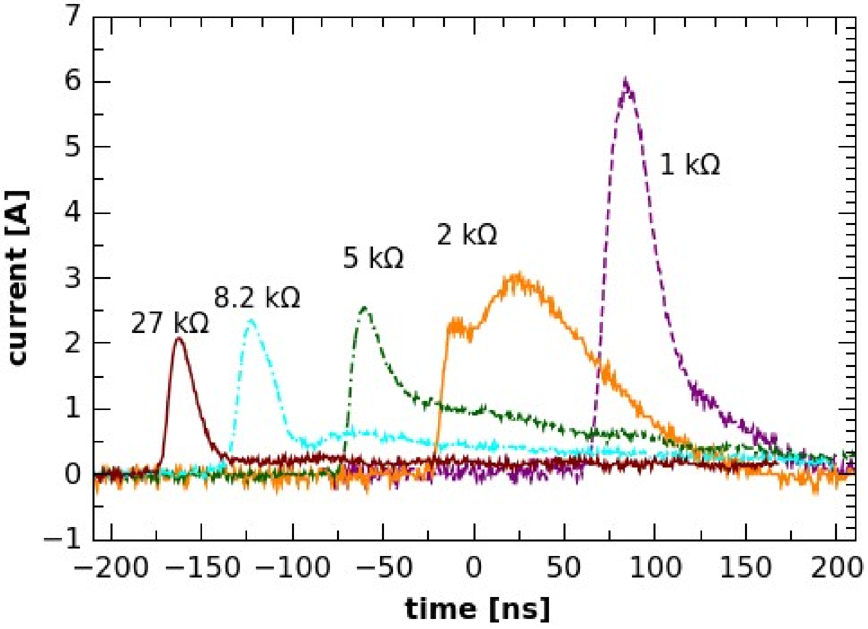

Janda M. et al., Plasma Sources Sci. Technol. **20**, 035015 (2011)

optimization criteria

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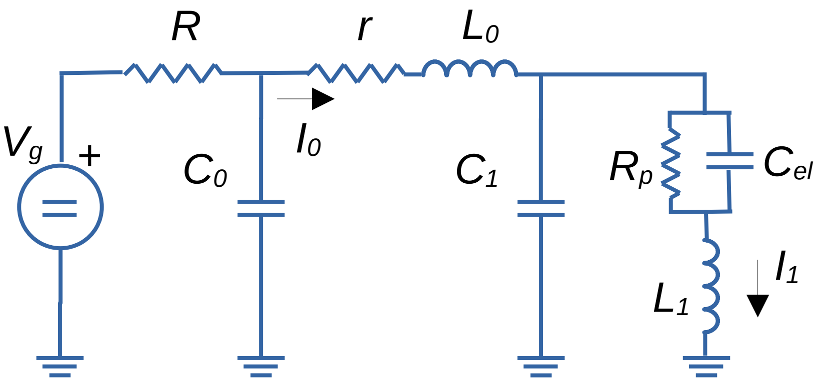
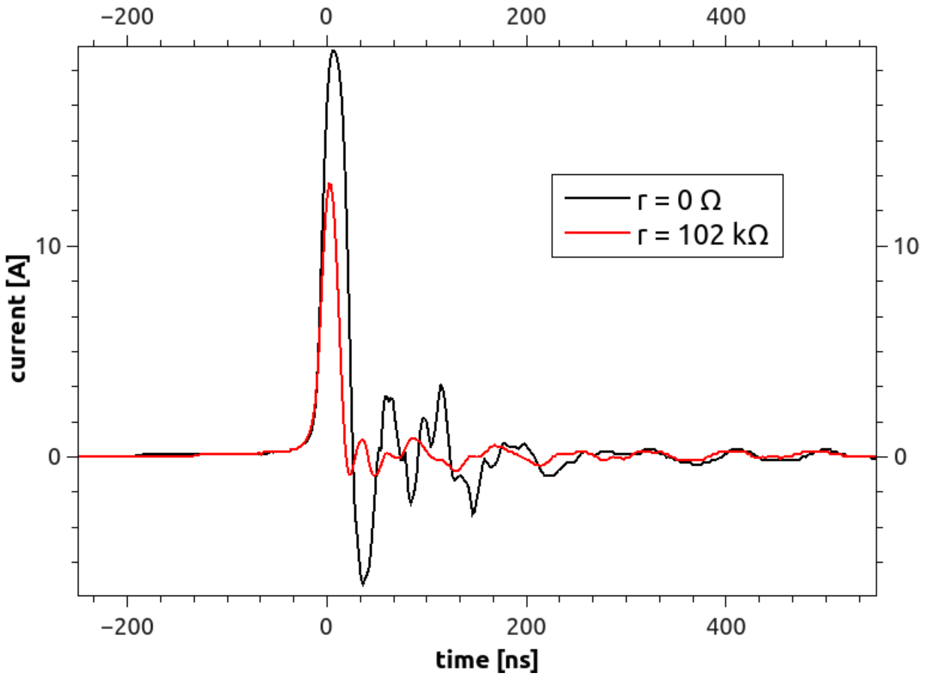
ELECTRIC CIRCUIT FOR TS GENERATION

- increased C_{int} (C_0 ~ 15-30 pF, C_1 ~ 20 pF), r = 0-470 kΩ





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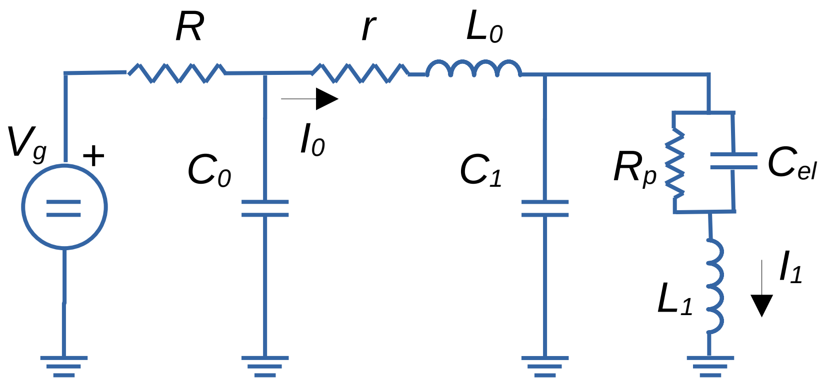
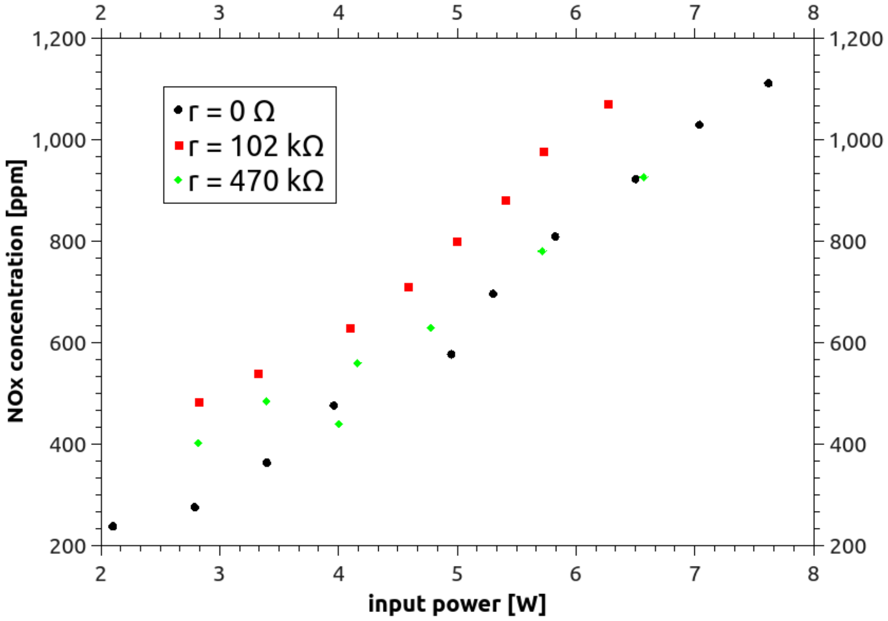
INFLUENCE OF *r* ON NOx GENERATION

- strongest effect for C_0 ~ 15 pF, r = 102 kΩ (C_1 ~ 20 pF)





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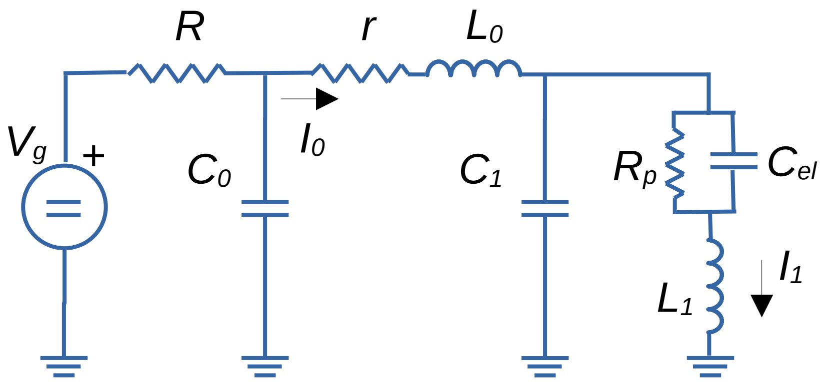

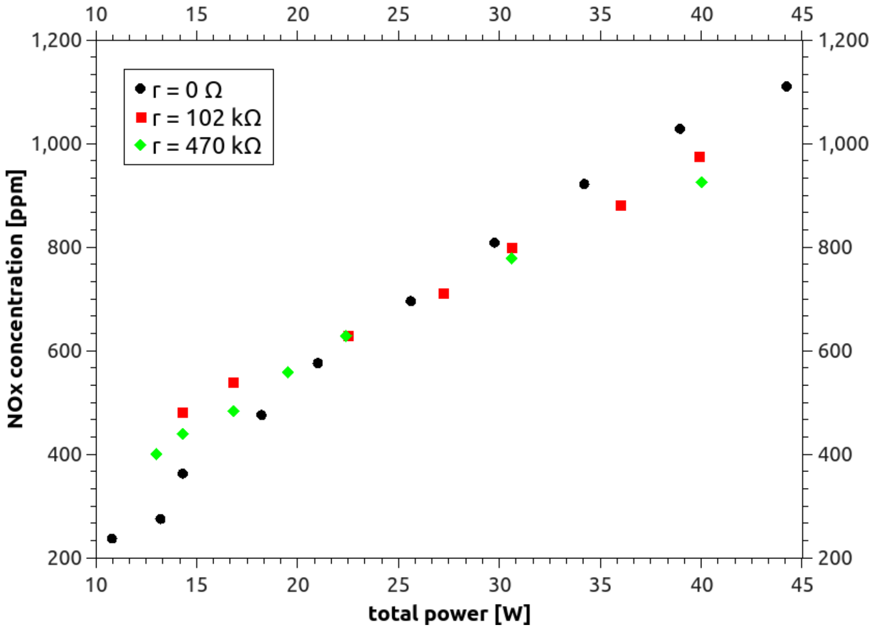

- additional energy losses on *r*
- increase of C_0 above ~15 pF by cable prolongation is not efficient

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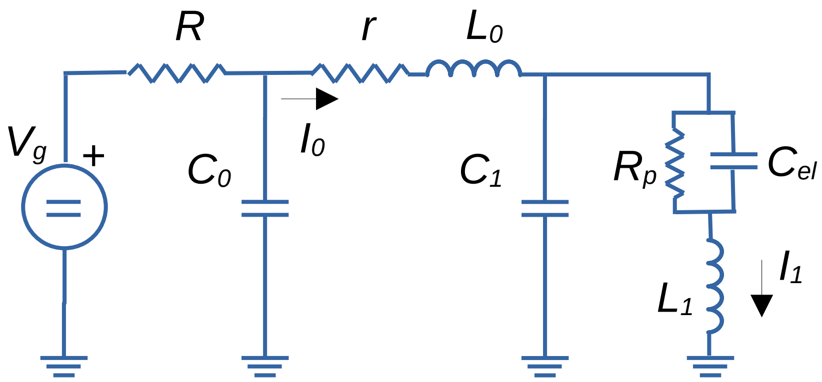

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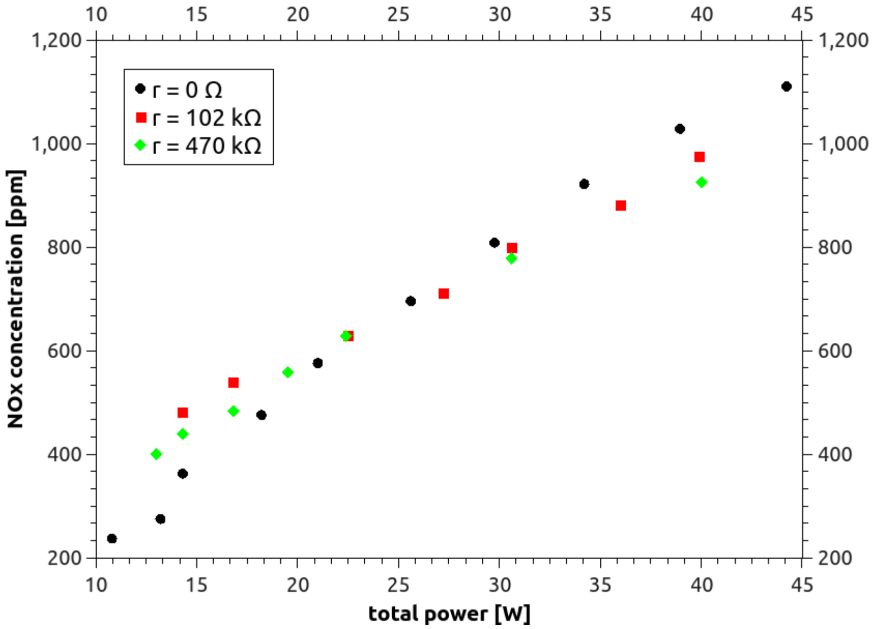

optimization criteria
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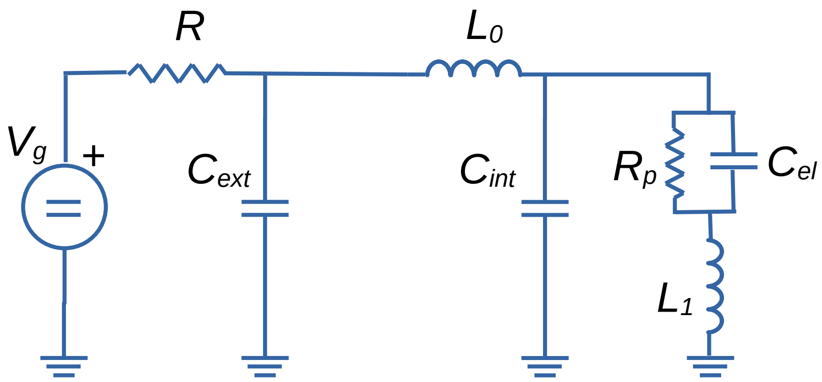
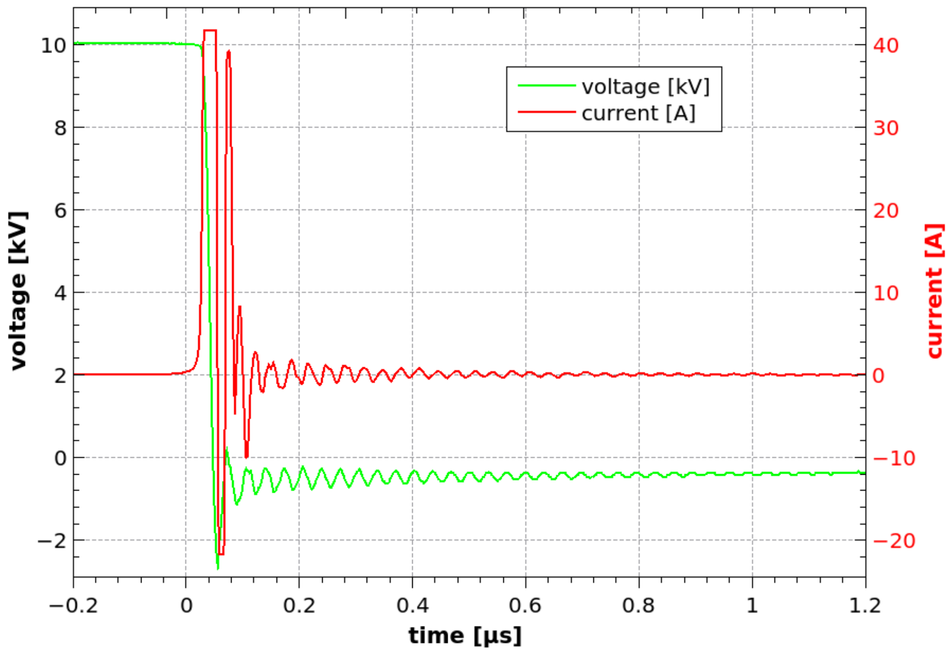
INFLUENCE OF C_{ext} ON NOx GENERATION

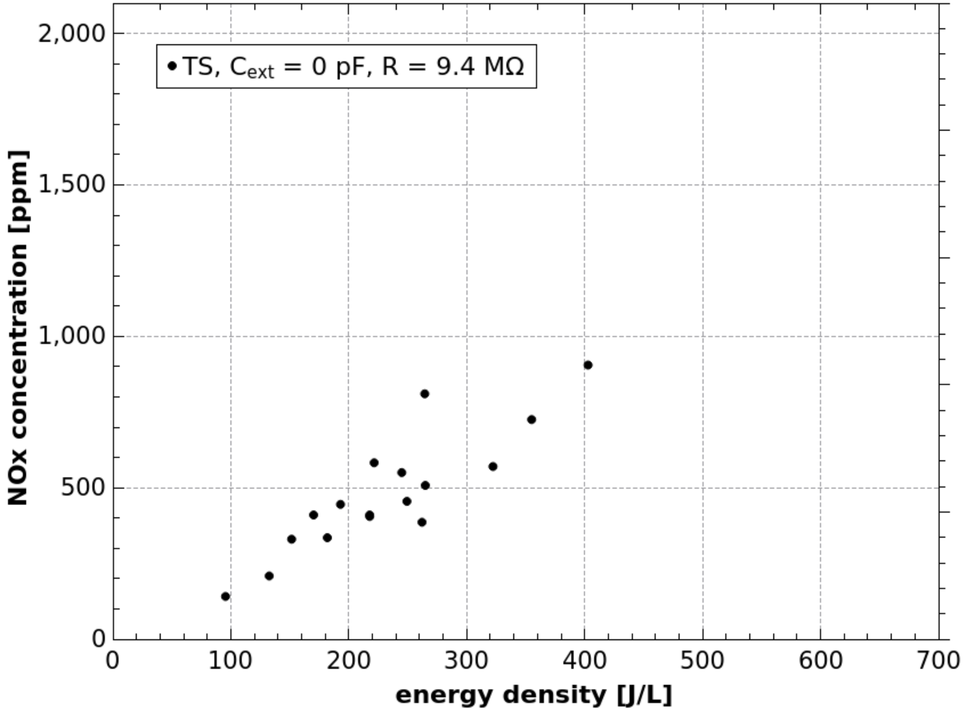
- additional external capacitor C_{ext} = 50-500 pF, C_{int} ~ 20 pF





INFLUENCE OF C_{ext} ON NOx GENERATION

- external capacitor C_{ext} = 50 pF, C_{int} ~ 20 pF, R = 9.4 MΩ or 3.2 MΩ
- C_{ext} > 100 pF not suitable (low TS frequency)



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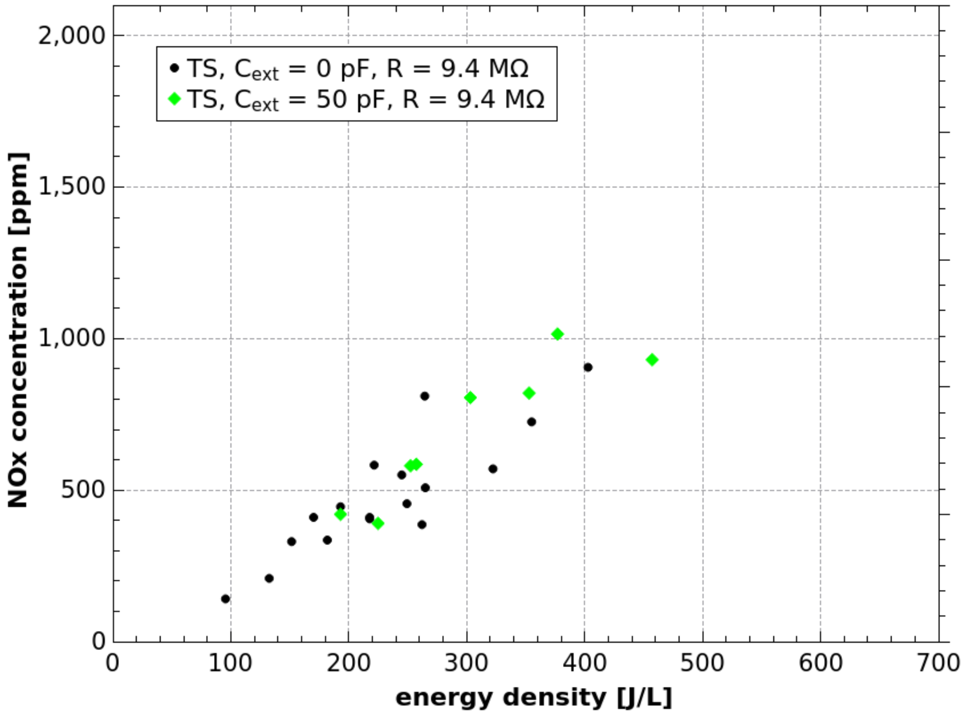

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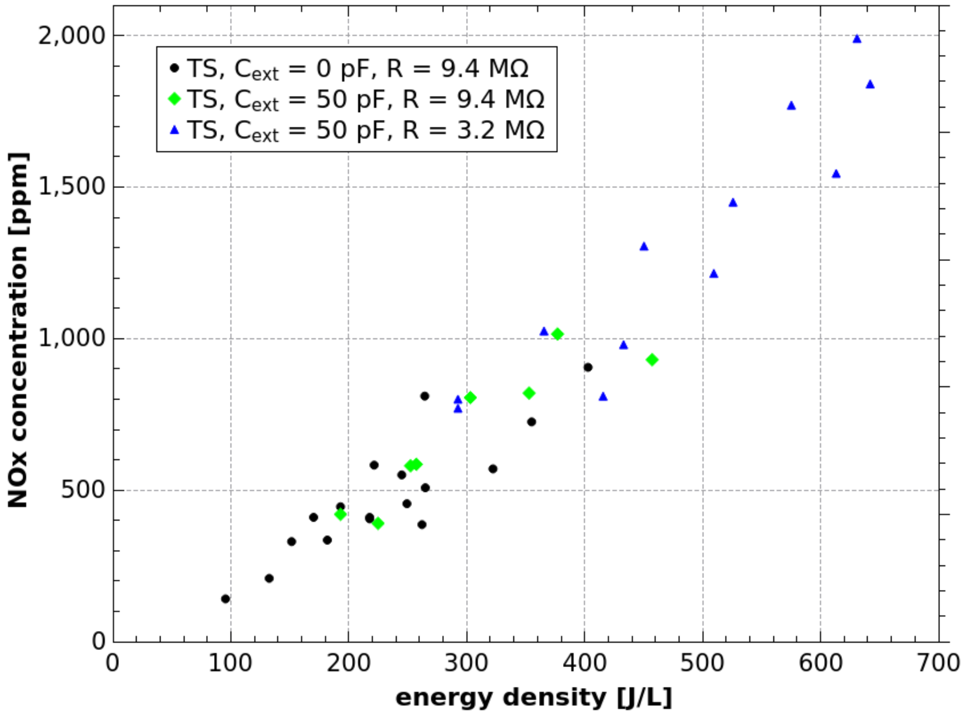
- higher NOx concentration can be achieved



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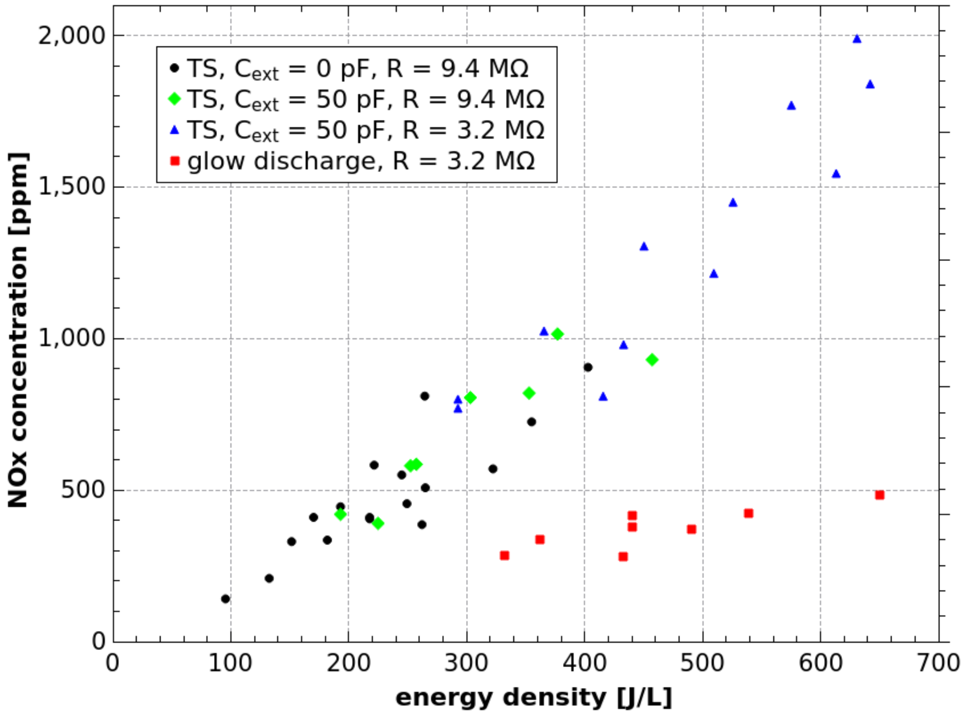
- transition to glow discharge without C_{ext} when R = 3.2 MΩ



SUMMARY

- TS - relatively simple source of highly reactive non-thermal plasma
  - streamer phase – excited nitrogen species generation mainly
  - short spark phase – significant source of O and N atoms
- NO_x - dominant gas phase products for TS in air
  - higher temperature and high degree of ionization during spark phase
- higher efficiency of NOx generation still possible
  - electric circuit modifications
    - NOx production enhancement with division of capacity
    - external capacity enables higher energy density and more NOx