NONEQUILIBRIUM PROCESSES DRIVEN BY ULTRA-SHORT PLASMA DISCHARGES

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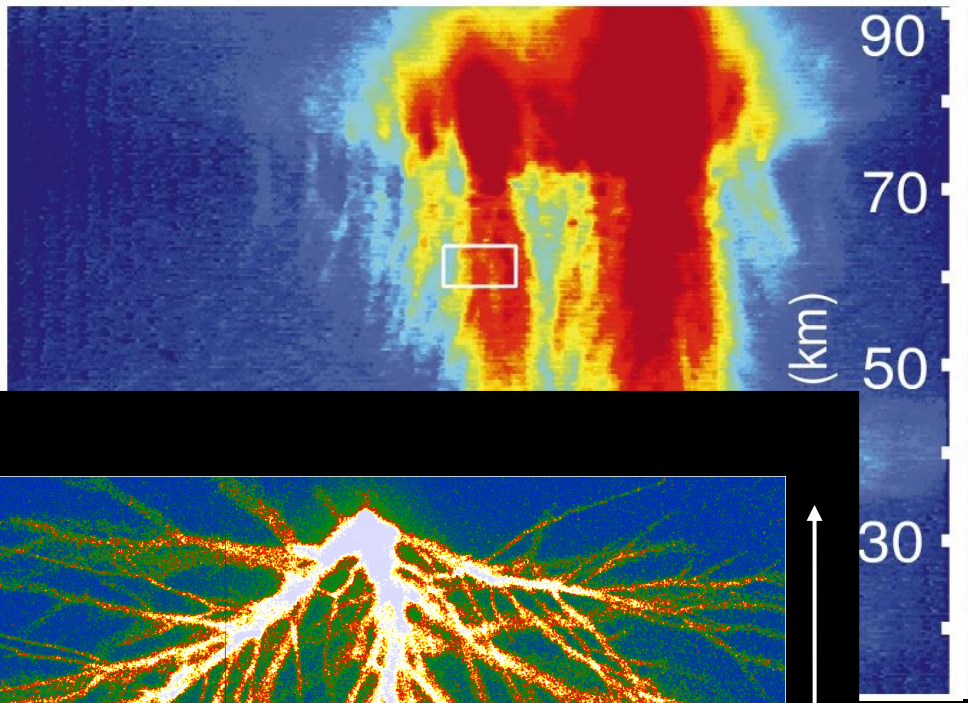
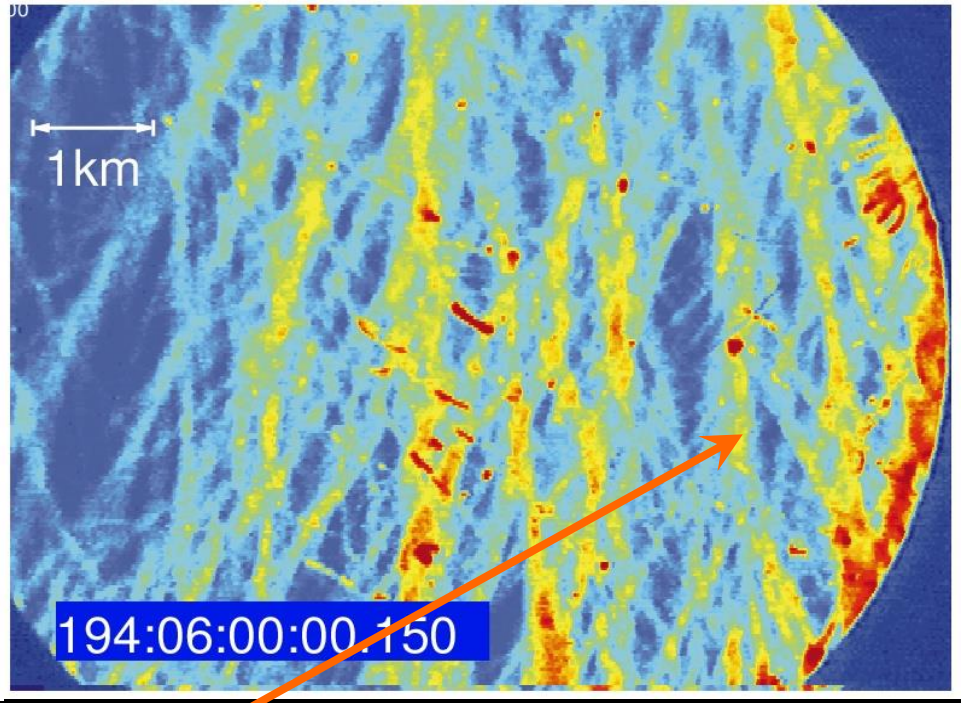
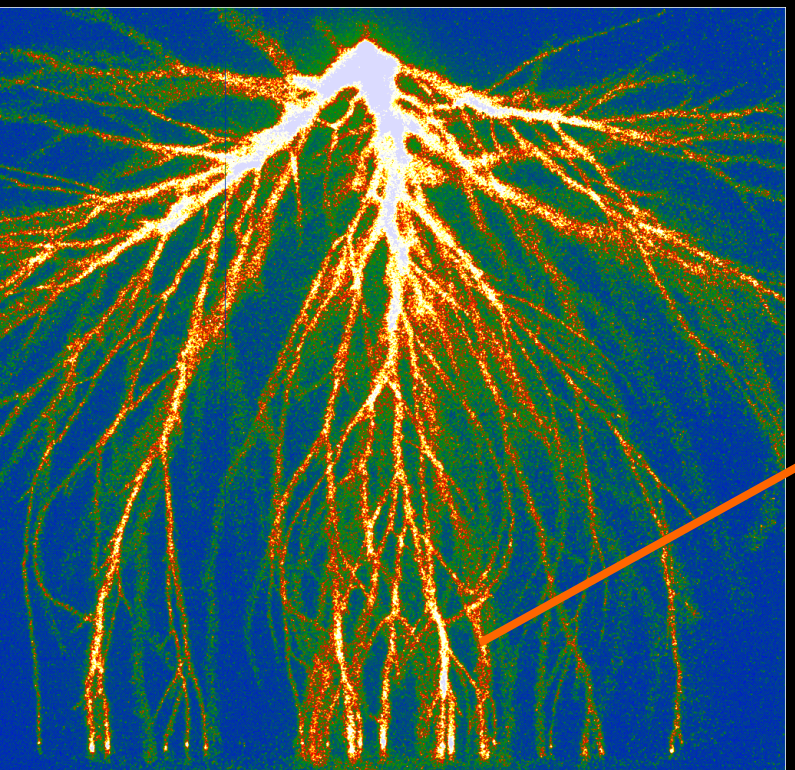
Frontiers of Plasma Science Town Meeting
July 1, 2015

Telescopic images of sprite discharges

[Gerken et al., Geophys. Res. Lett. 2000]





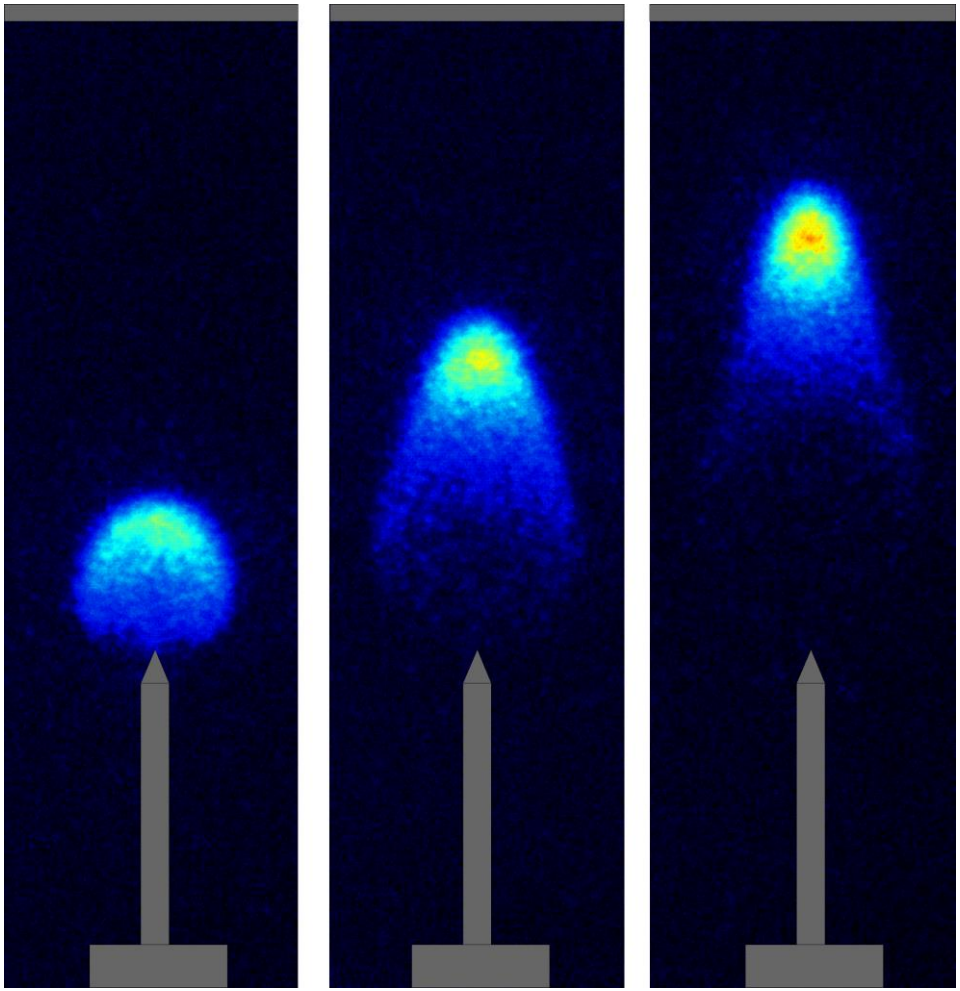


4 cm

Similarity law:
1 bar versus 10^{-5} bar … even 30 bar in lamps and spark plugs!

Streamers, sprites, leaders, lightning: from micro- to macroscales. 2007. Ute Ebert

Streamer Head Image

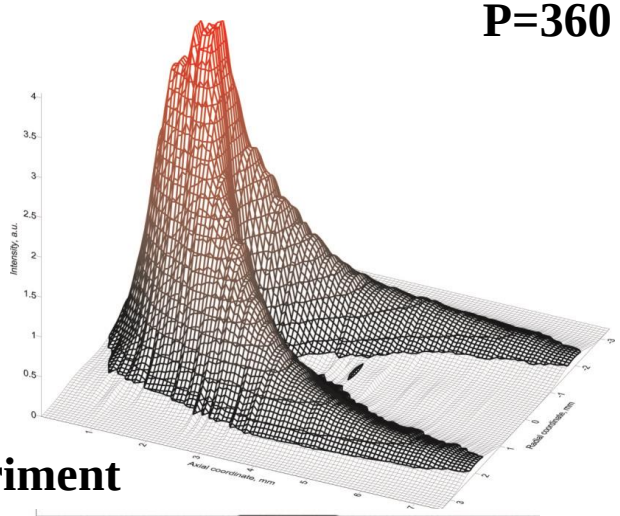


camera gate of 300 ps.
P=460 Torr, U=38 kV,
gap length is 30 mm.

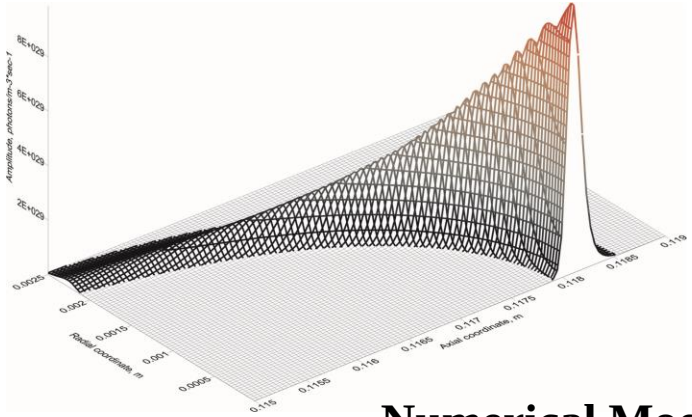
Time delay is:
1) 5 ns,
2) 10 ns,
3) 15 ns.

Restored Emission Distribution Field in the Streamer Head Cross-section

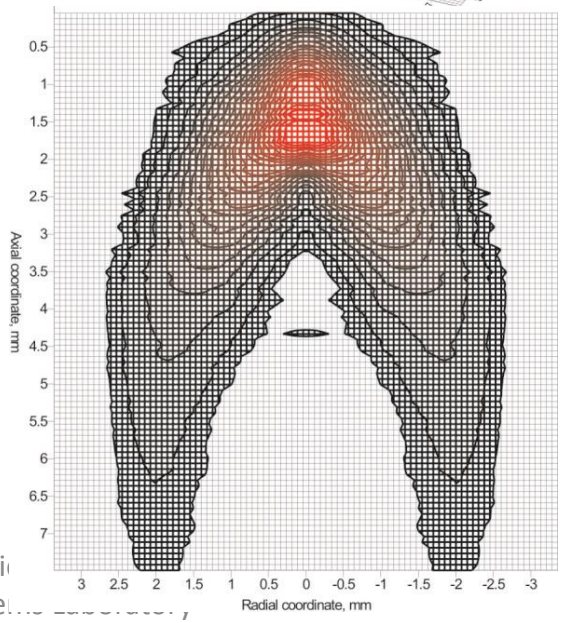
P=360 torr, U=38 kV, d=30mm

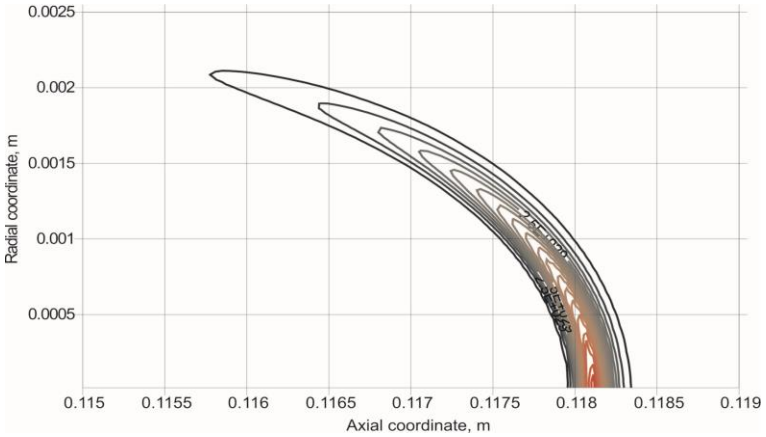


Experiment

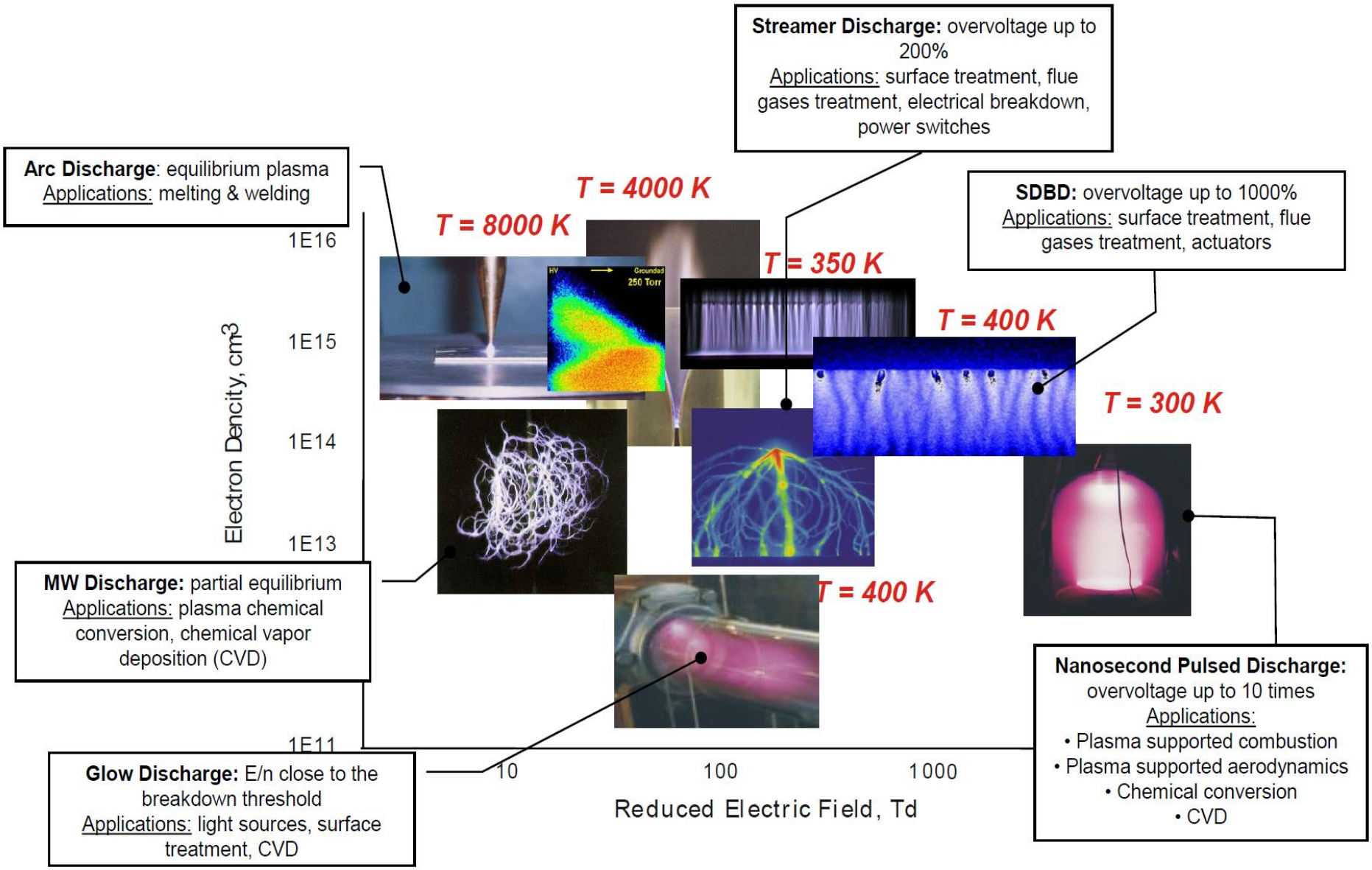


Numerical Model

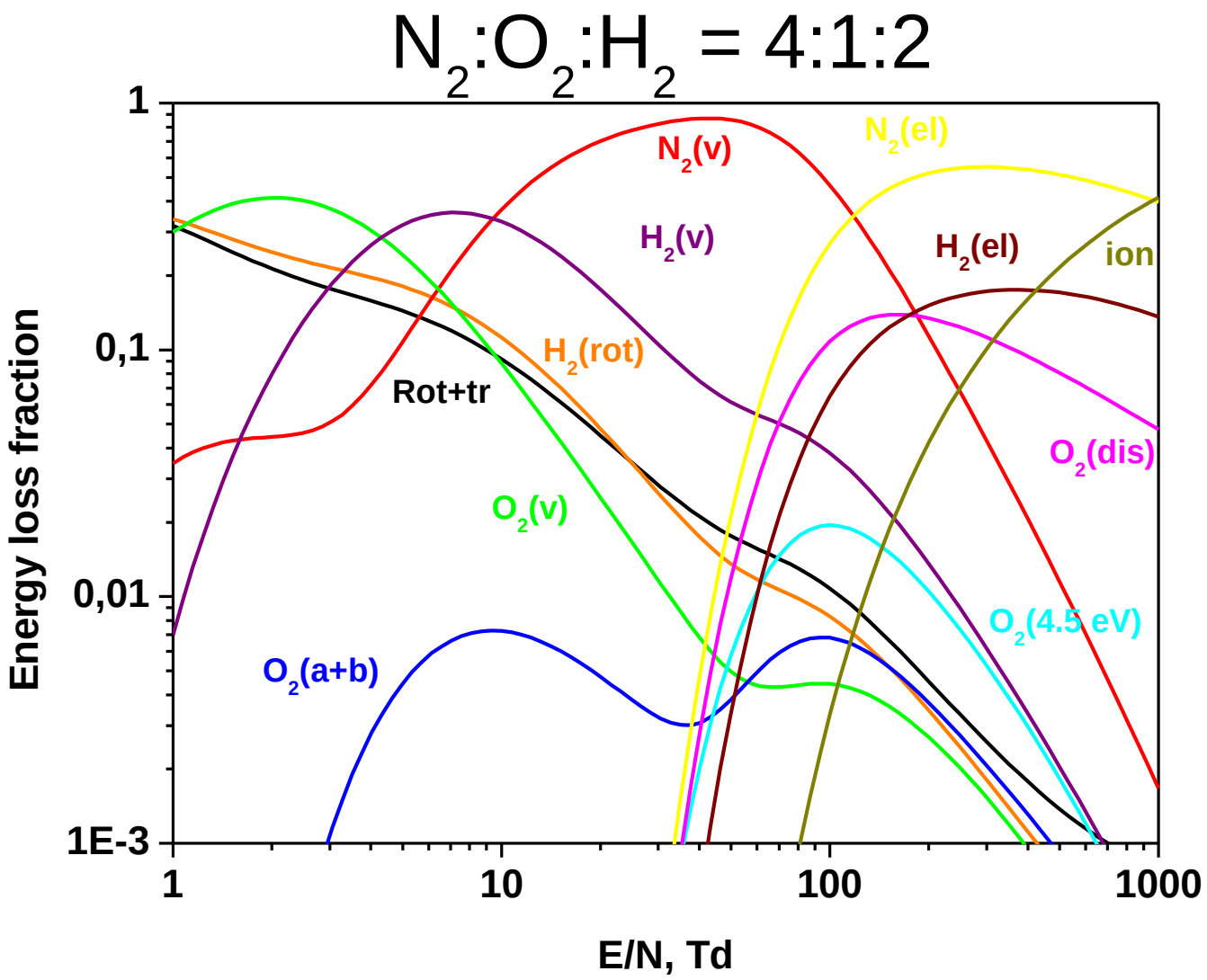




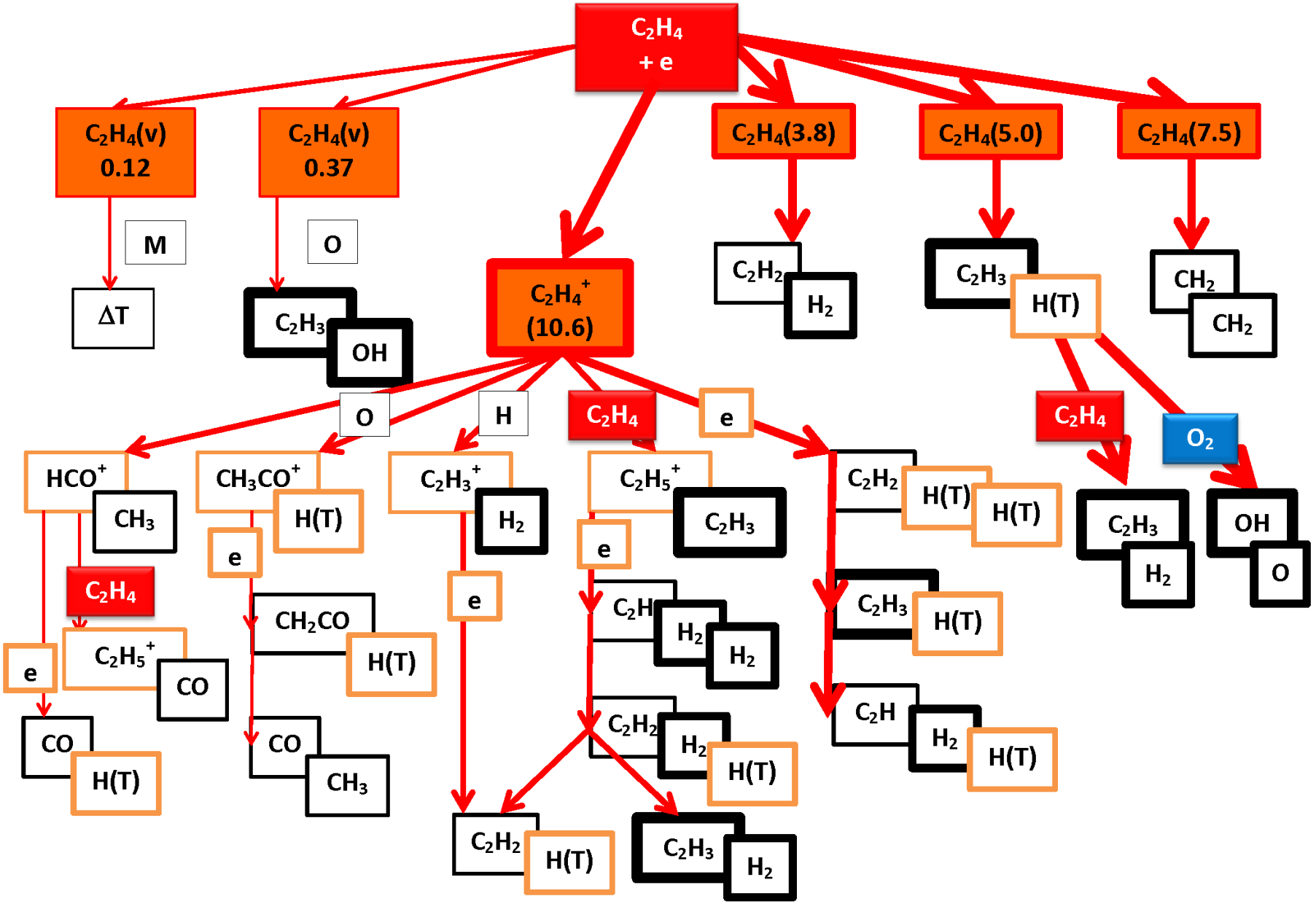
Types of Gas Discharges and Their Applications



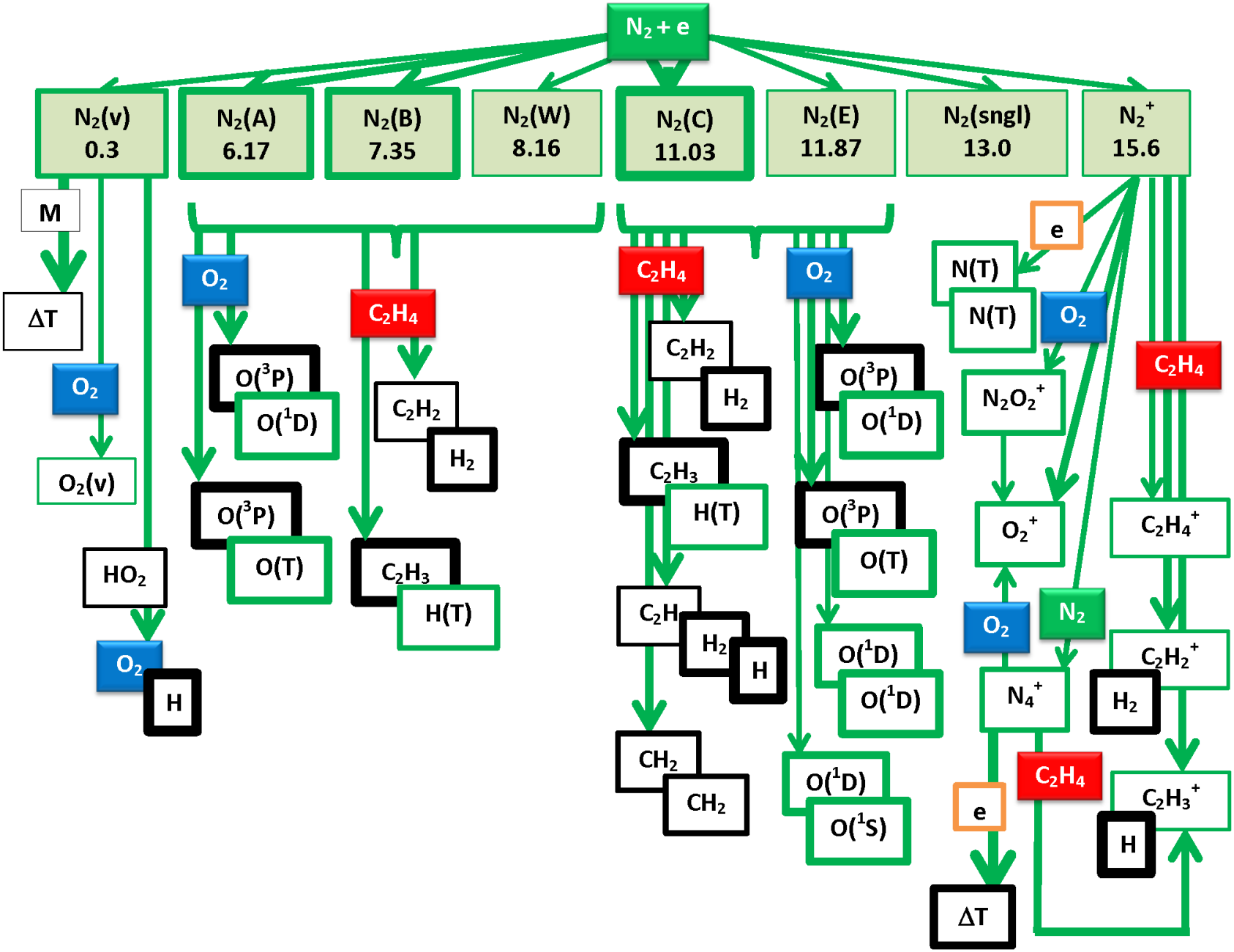
Electron Energy Distribution in Discharge Plasmas



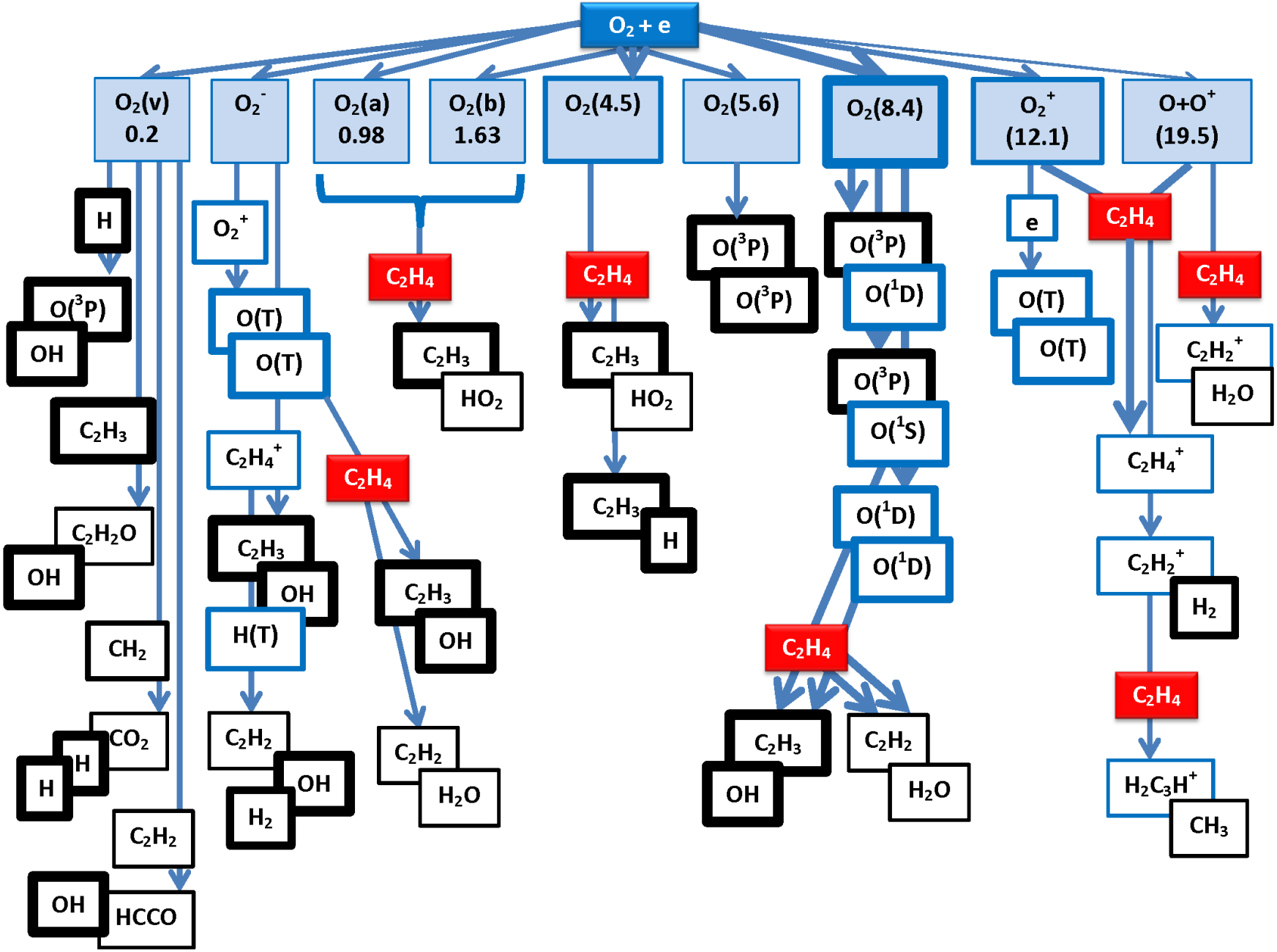
PAC Pathways: C_2H_4-air



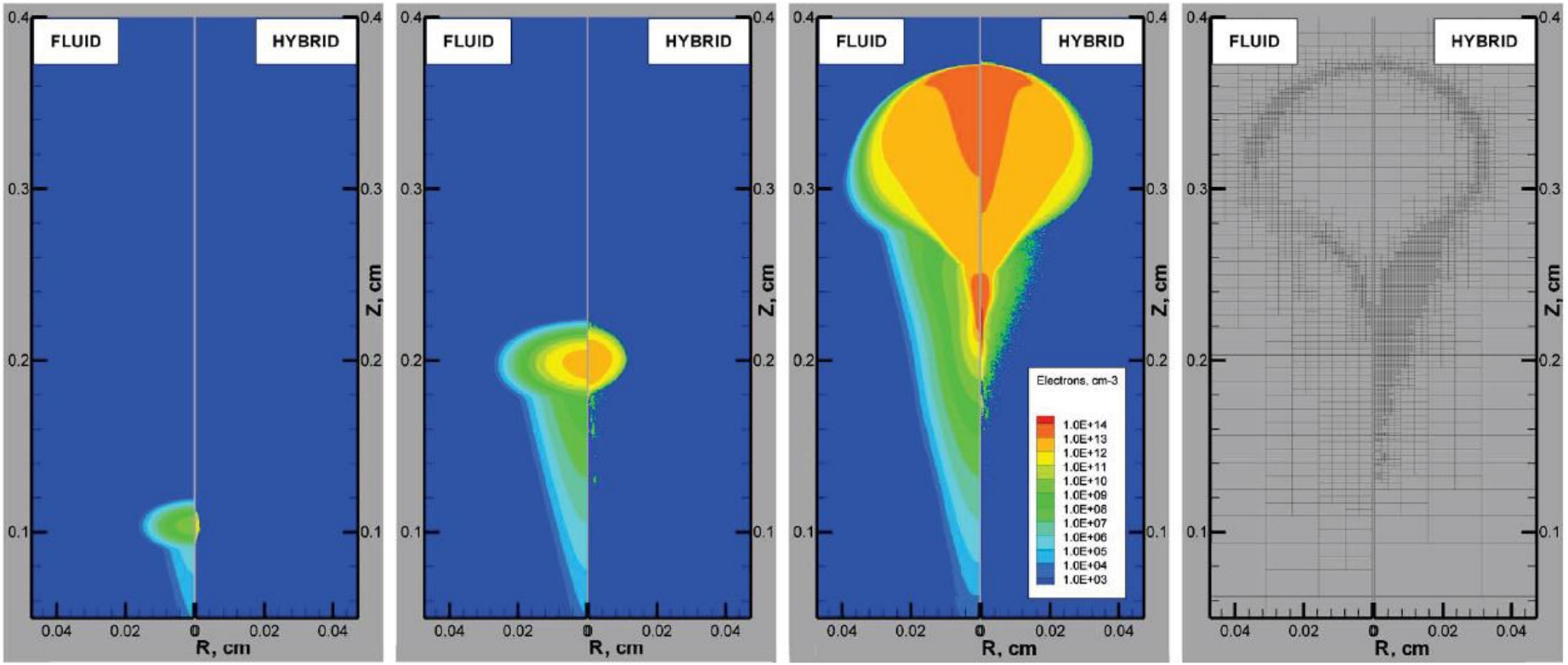
PAC Pathways: C_2H_4-air



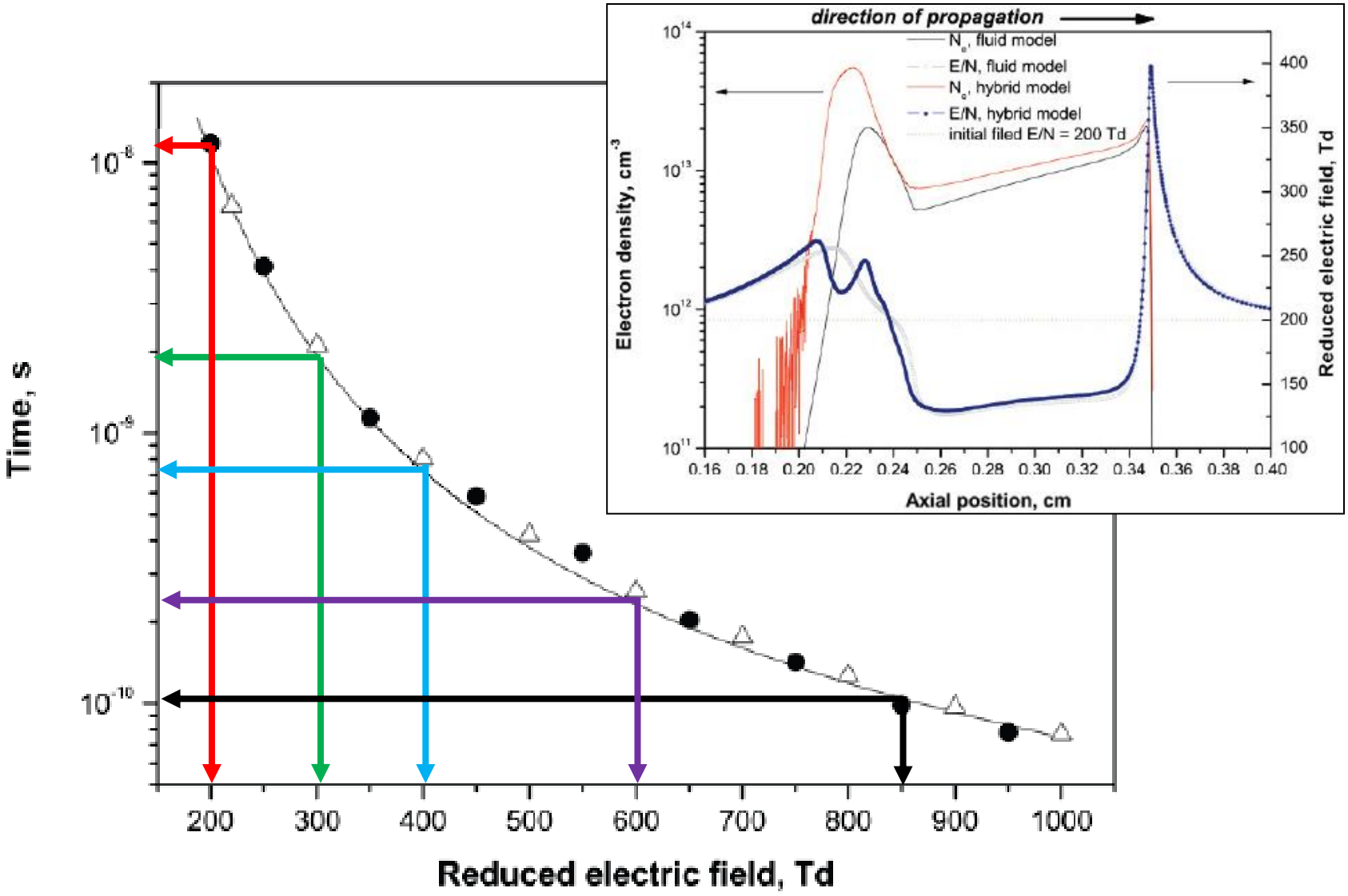
PAC Pathways: C_2H_4-air



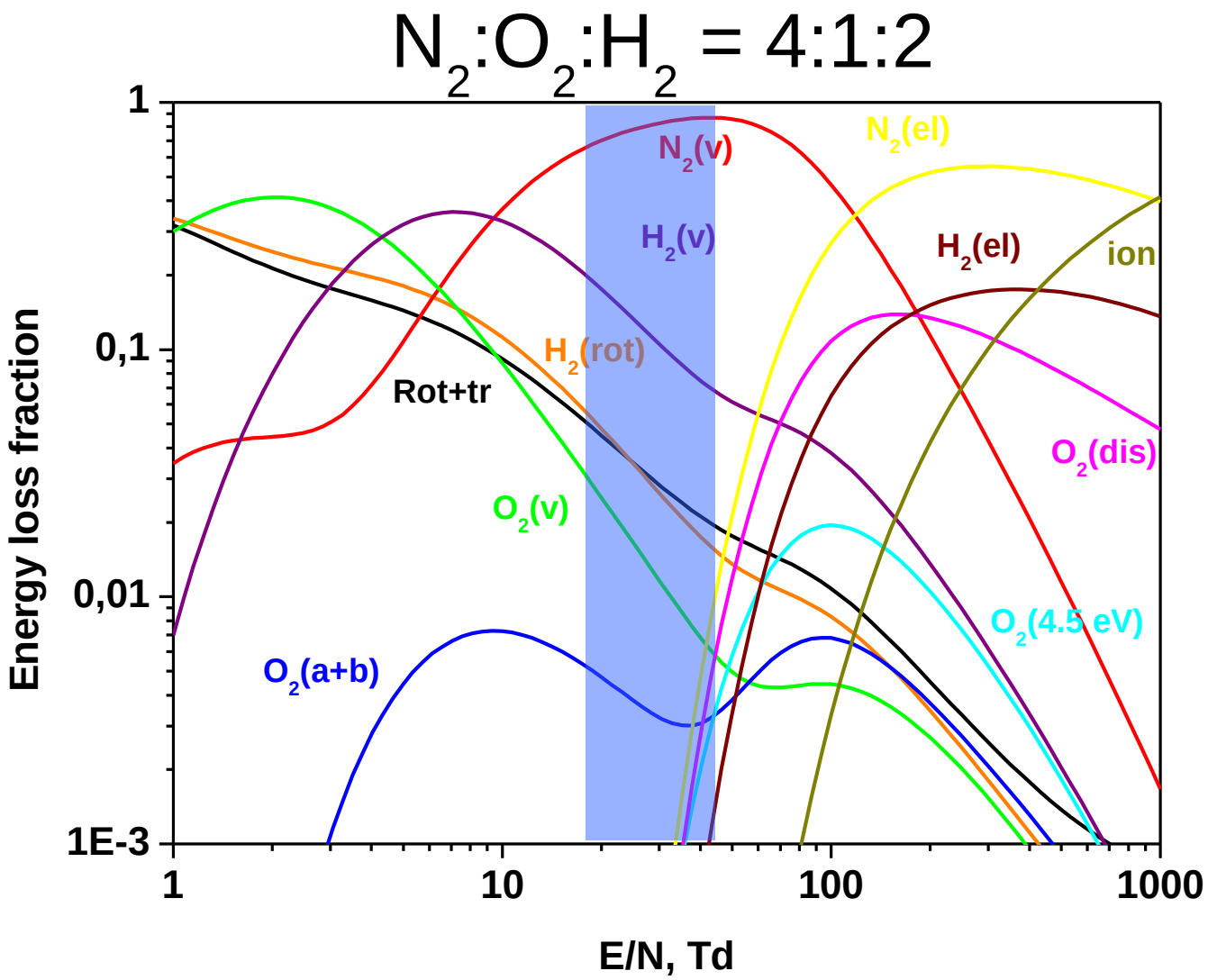
Avalanche to Streamer Transition in Uniform Electric Field
(air, 1 bar, 300 K, 1 cm, various voltages)



Avalanche to Streamer Transition in Uniform Electric Field (air, 1 bar, 300 K, 1 cm, various E/n)

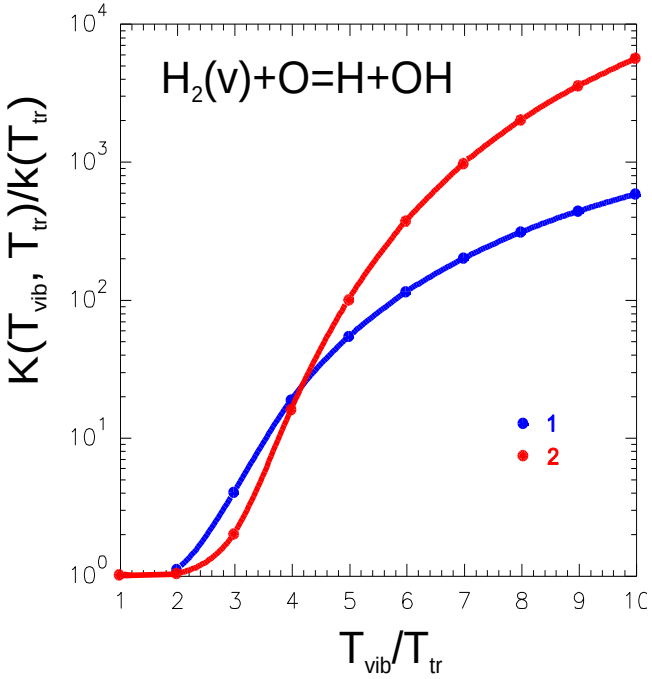


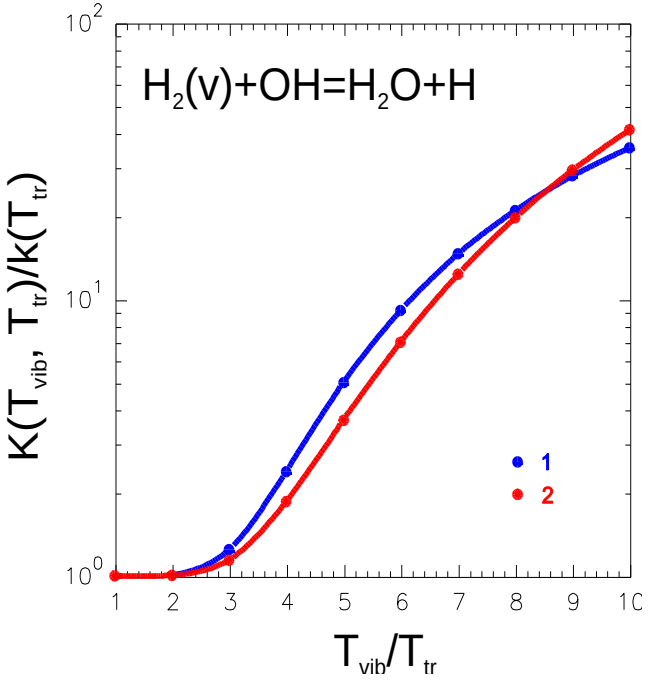
Electron Energy Distribution in Discharge Plasmas



Chemical Reactions with Excited Reagents

AB(v)+C = A +BC(w)
Rate constant from modified α-model (Starikovskii, Lashin 1996)



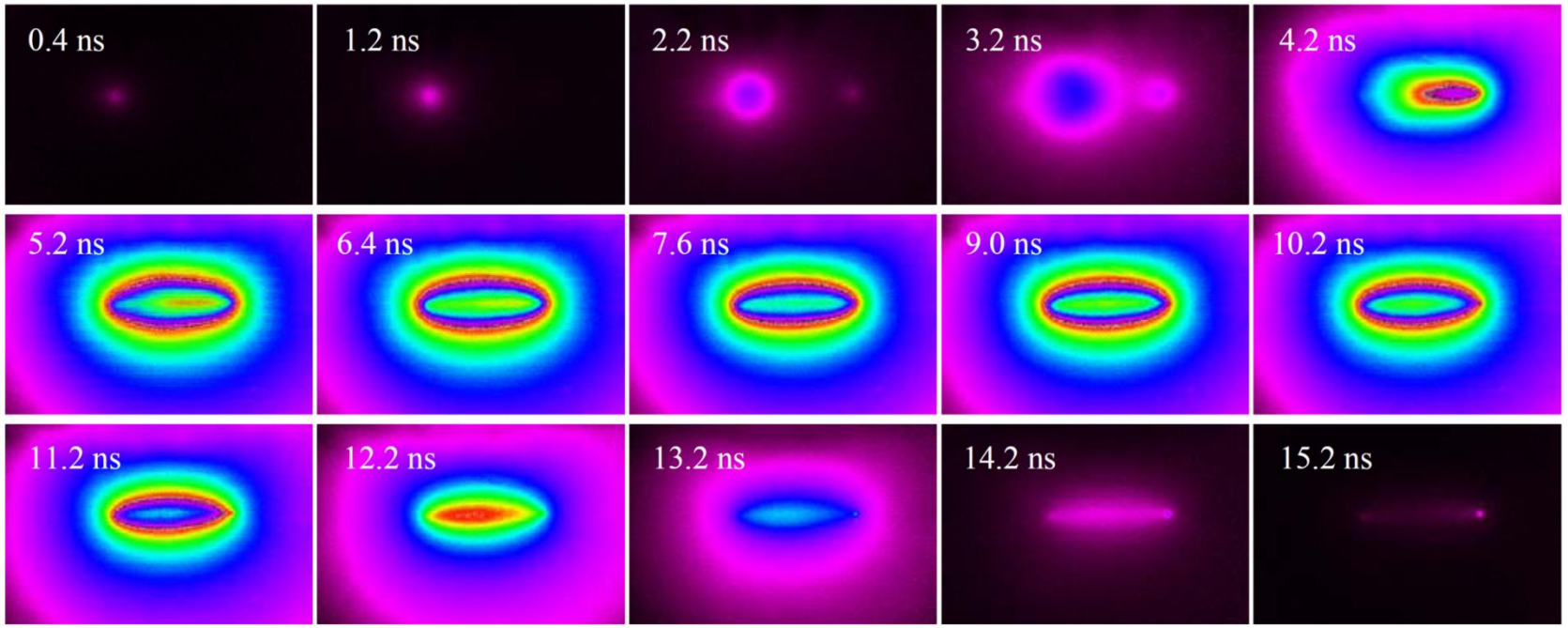


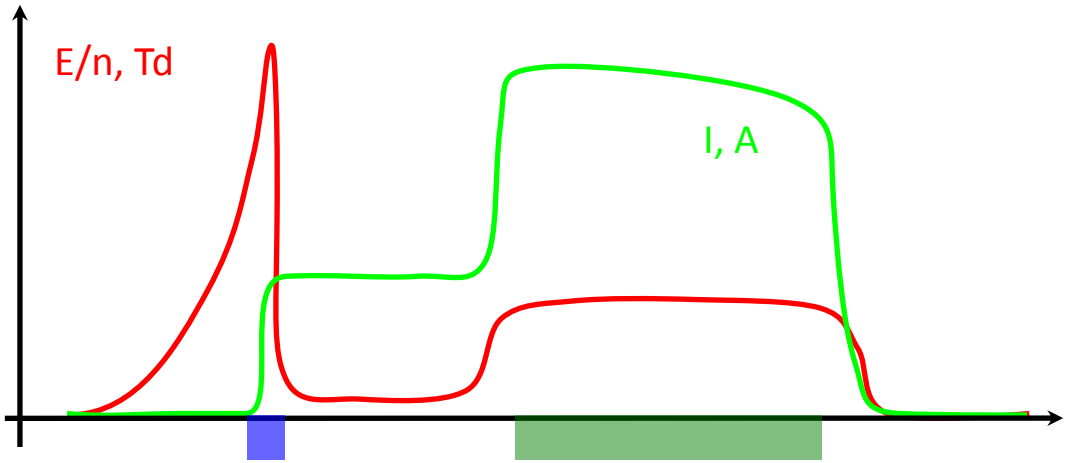
$H_2(v=1) + O = OH(w=1) + H$ (R1)

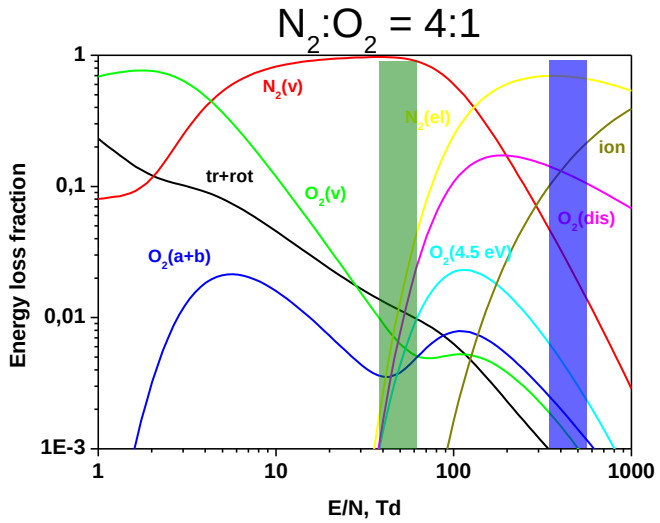
$H_2(v=0) + O = OH(w=0) + H$ (R2)

$(k_{R1}/k_{R2})_{exp}$ = 2600 (O'Neal, Benson 1973); $(k_{R1}/k_{R2})_{theor}$ = 2750

Pin-to-Pin Discharge Development







Influence of Vibrational Excitation on Low-Temperature Kinetics

$N_2 + e = N_2(C^3) + e$

$N_2(C^3) + O_2 = N_2 + O + O$

$O_2 + e = O + O + e$

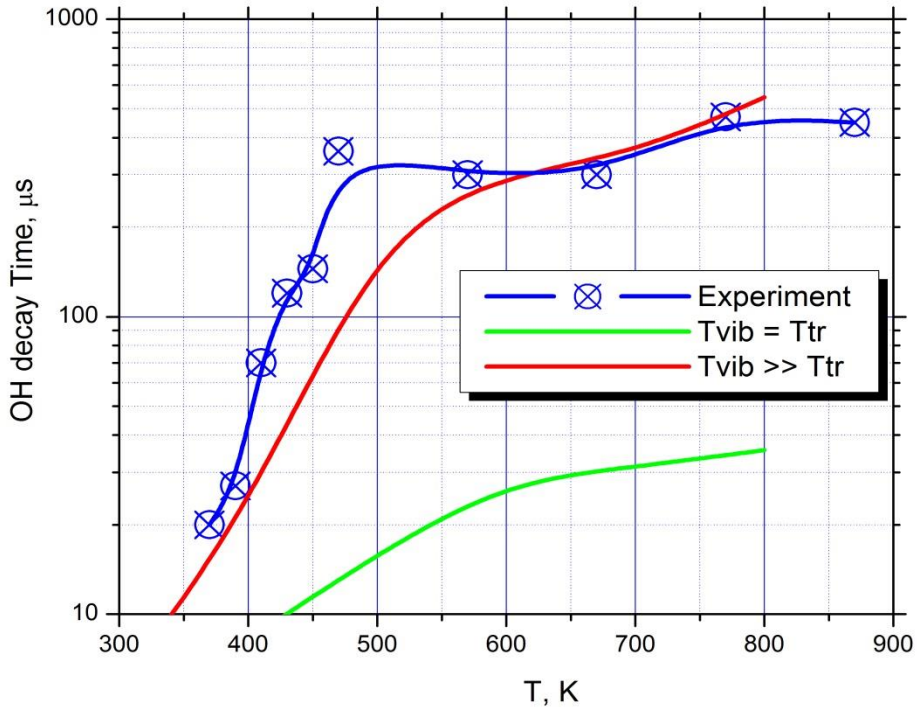
$N_2 + e = N_2(v) + e$

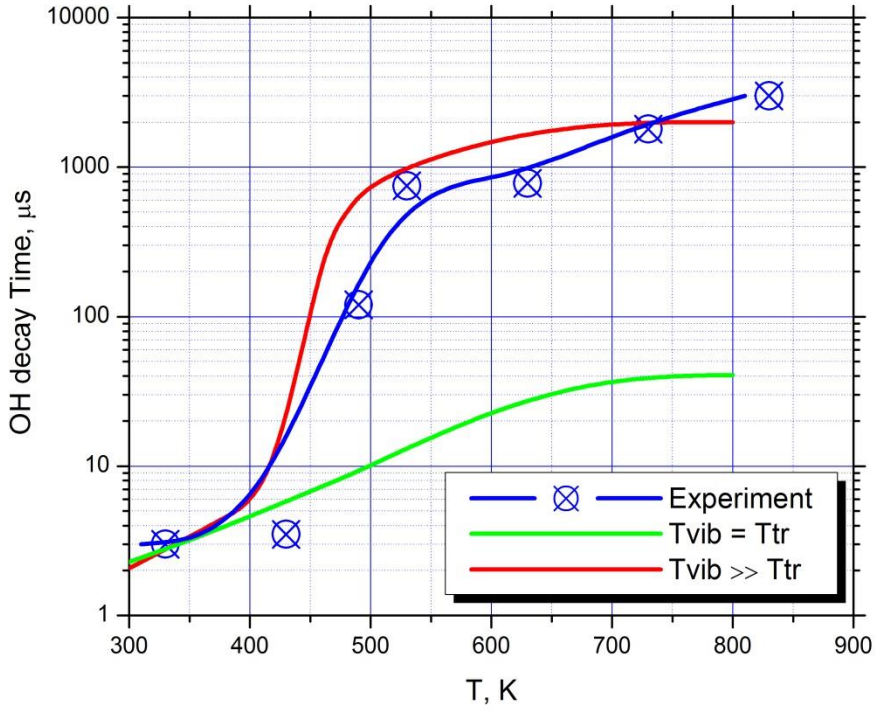
$N_2(v) + HO_2 = N_2 + HO_2(v)$

$HO_2(v) = O_2 + H$

SYNERGETIC EFFECT OF HIGH AND LOW ELECTRIC FIELDS

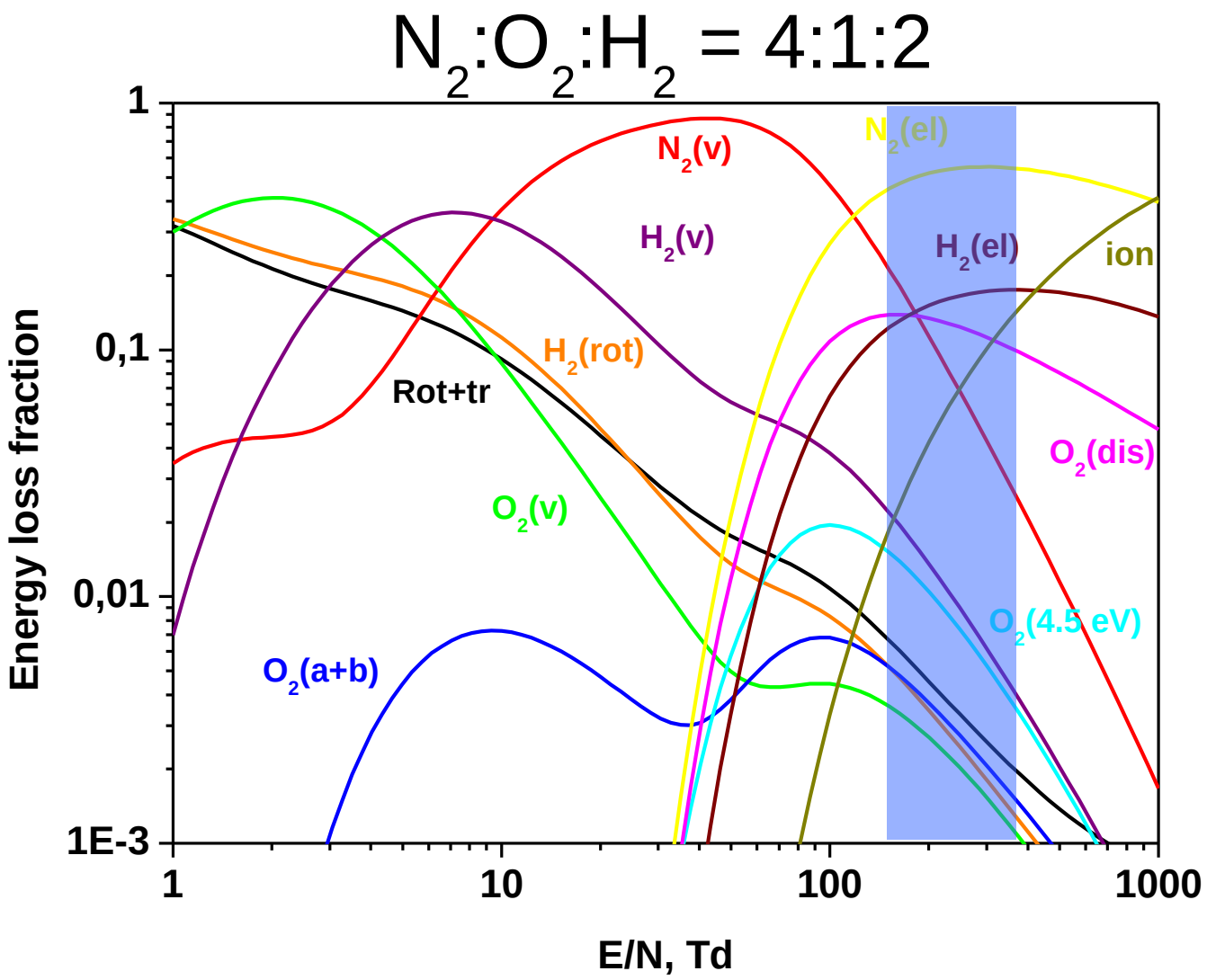
Influence of Vibrational Excitation on Low-Temperature Kinetics: HO_2 Decomposition



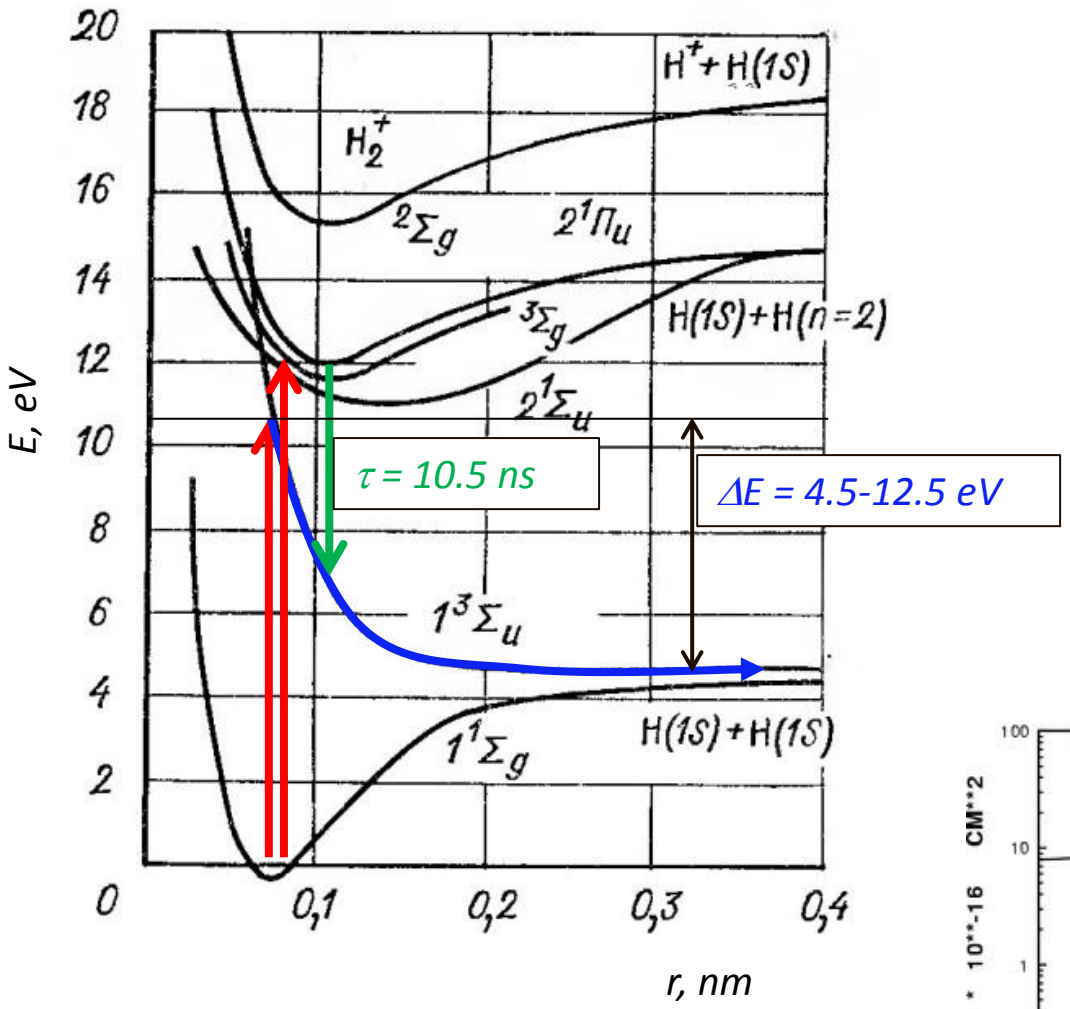


Measured and calculated OH decay time. P = 1 atm.
a) 3%H_2 + air; b) 0.3%C_4H_{10} + air.

Electron Energy Distribution in Discharge Plasmas



Excitation of Molecular Hydrogen

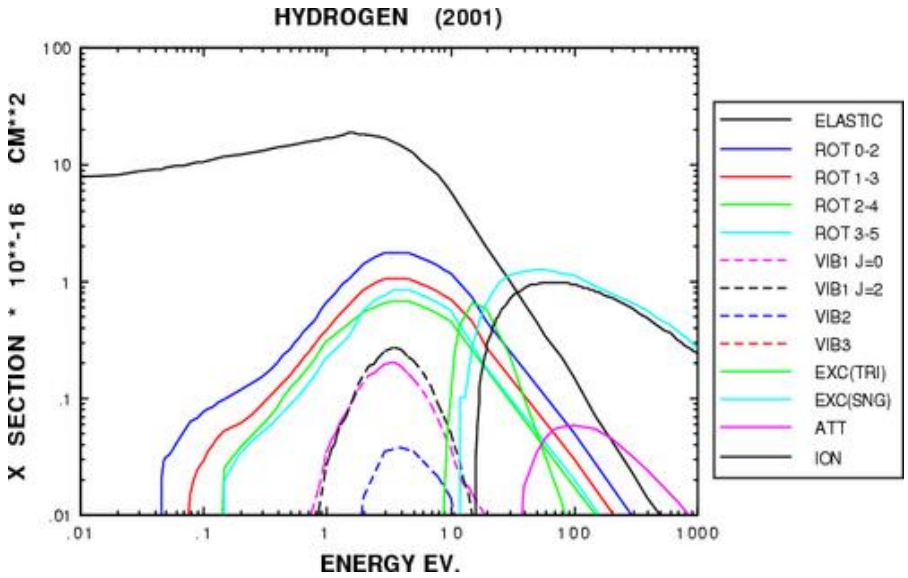


$H_2(b^3\Sigma_u)$, 8.9 eV
σ_{max} = 0.33 A^2 (17 eV)

$H_2(a^3\Sigma_g)$, 11.8 eV
σ_{max} = 0.12 A^2 (15 eV)

$H_2(B^1\Sigma_u)$, 11.3 eV
σ_{max} = 0.48 A^2 (40 eV)

$H_2(C^1\Pi_u)$, 12.4 eV
σ_{max} = 0.40 A^2 (40 eV)



Major Channels of Hot Atoms Production

$N_2 + e = N_2(C^3\Pi_u) + e$; $k = f(E/n)$

$N_2(C^3\Pi_u) + H_2 = N_2 + 2H(^1S) + 6.55\ eV$; $k = 3.2 \times 10^{-10}\ cm^3/s$

$N_2(C^3\Pi_u) + O_2 = N_2 + 2O(^3P,^1D) + 3.9\ eV$; $k = 2.7 \times 10^{-10}\ cm^3/s$

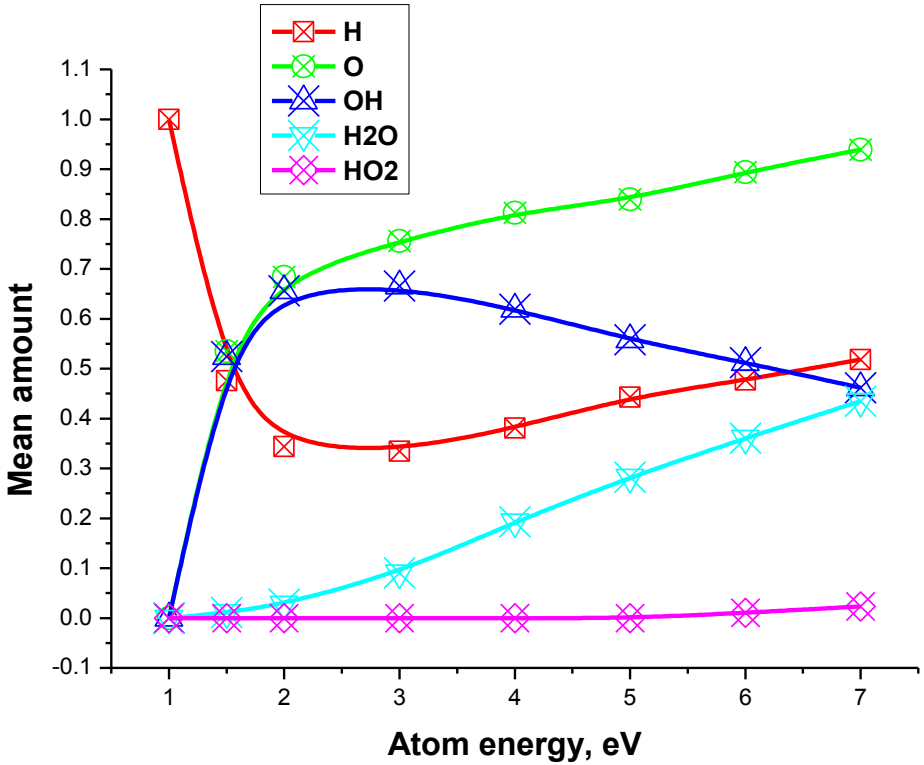
$O_2 + e = e + 2O(^3P,^1D) + 1.3\ eV$; $k = f(E/n)$

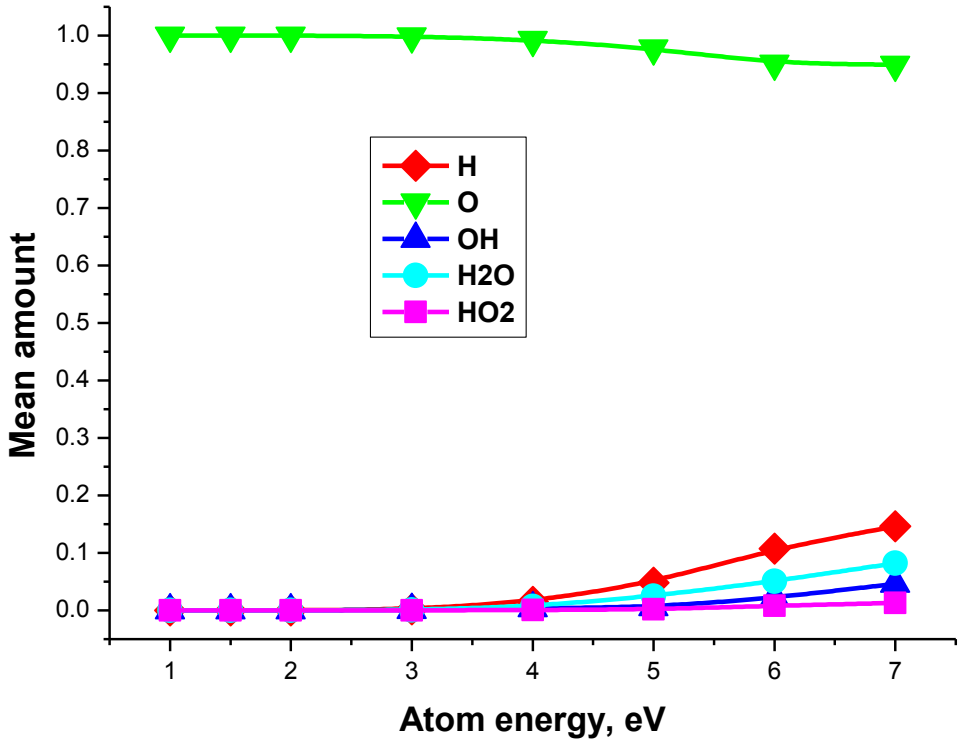
$H_2 + e = e + 2H(^1S) + 4.4\ eV$; $k = f(E/n)$

$H_2^+ + e = 2H(^1S) + 11.2\ eV$; $k = f(E/n)$

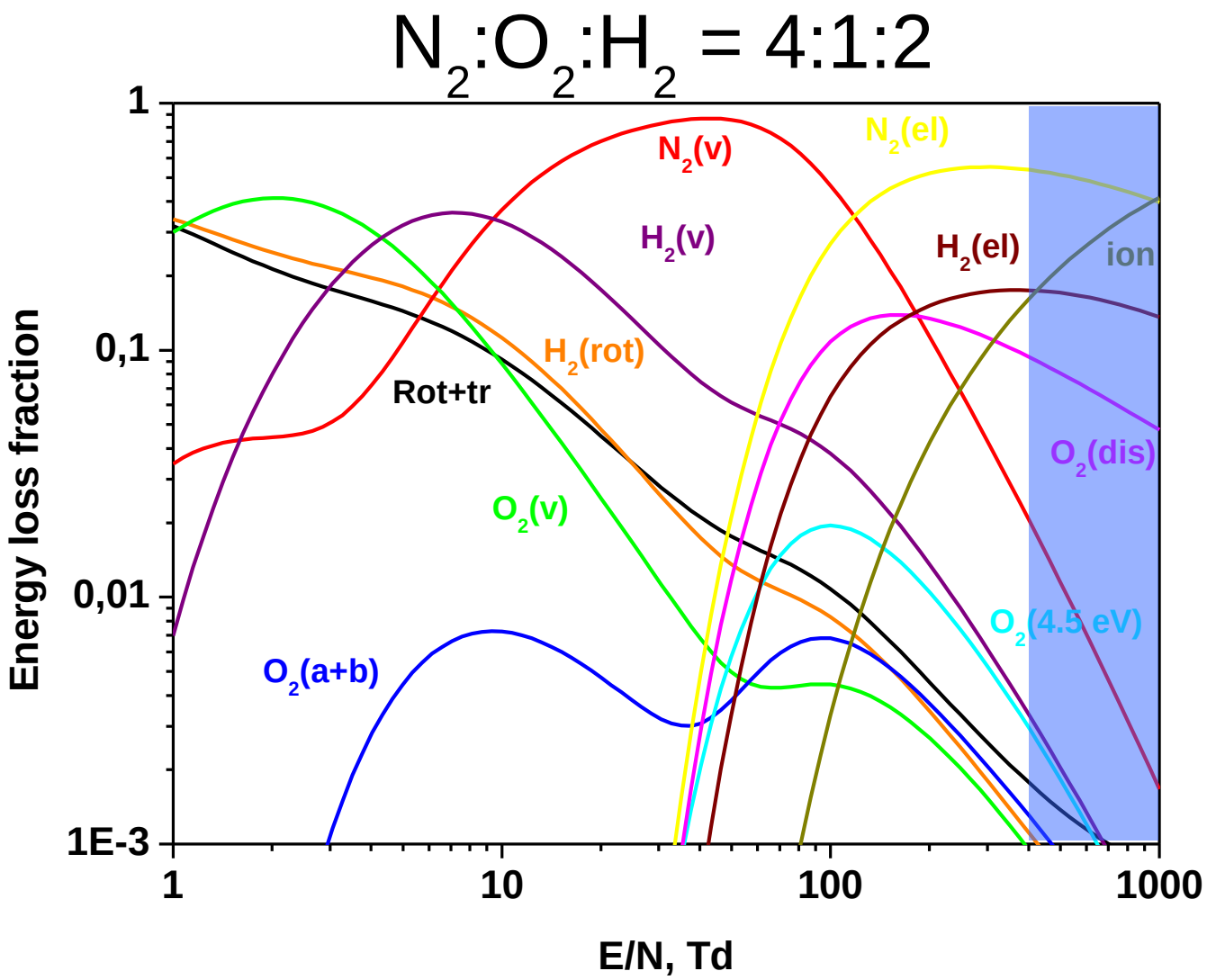
$O_2^+ + e = 2O(^3P,^1D) + 7.5\ eV$; $k = f(E/n)$

The mean amount of particles produced during energy degradation of one “hot” H (a) or O (b) atom in the stoichiometric H_2:O_2 mixture at 300 K as a function of their initial energy

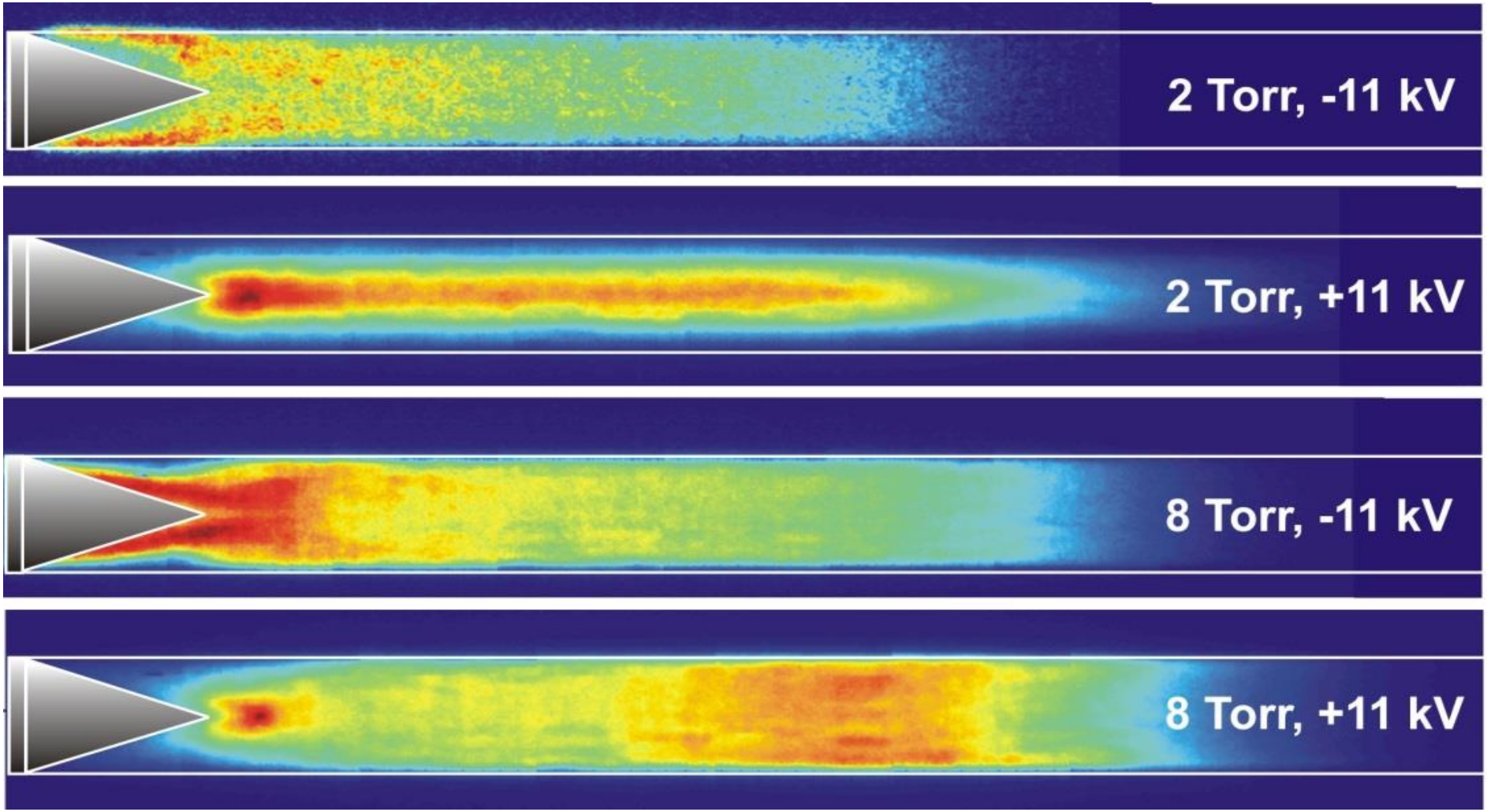




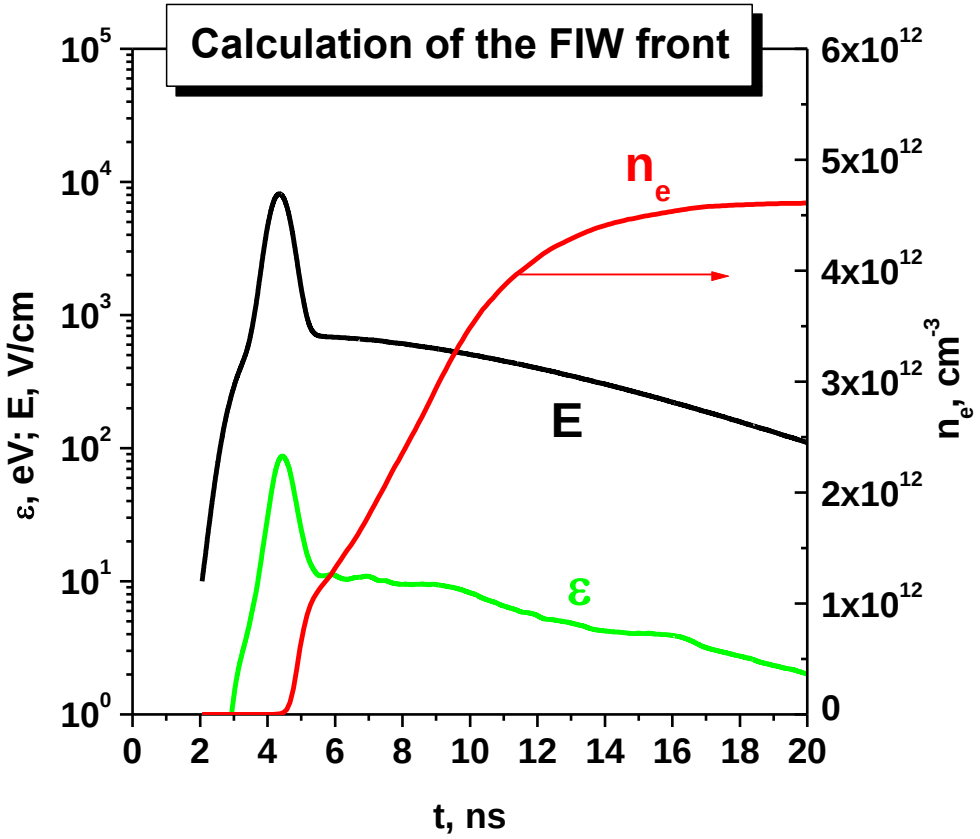
Electron Energy Distribution in Discharge Plasmas

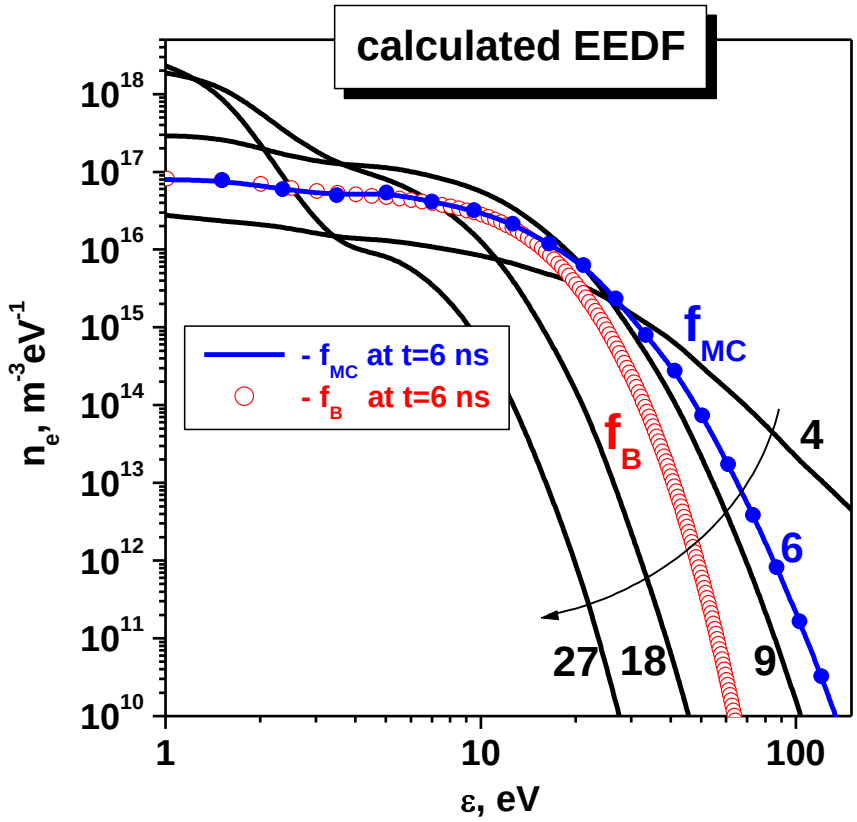


Development of Fast Ionization Wave in Air



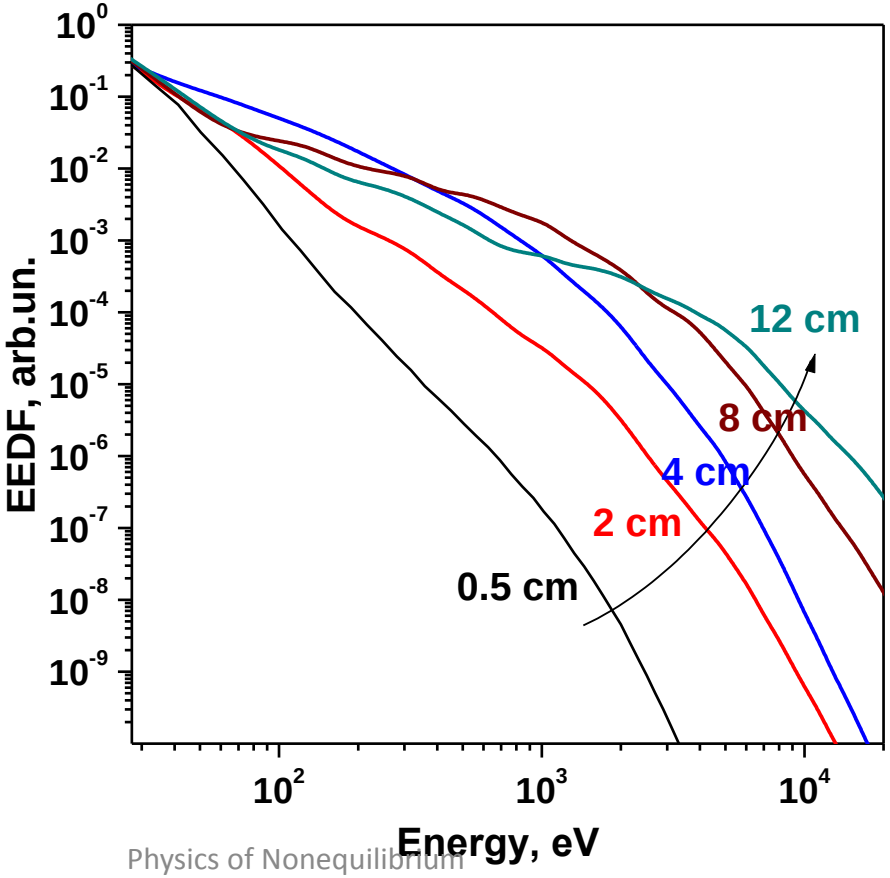
Analysis of EEDF.
Results of 0-D calculations



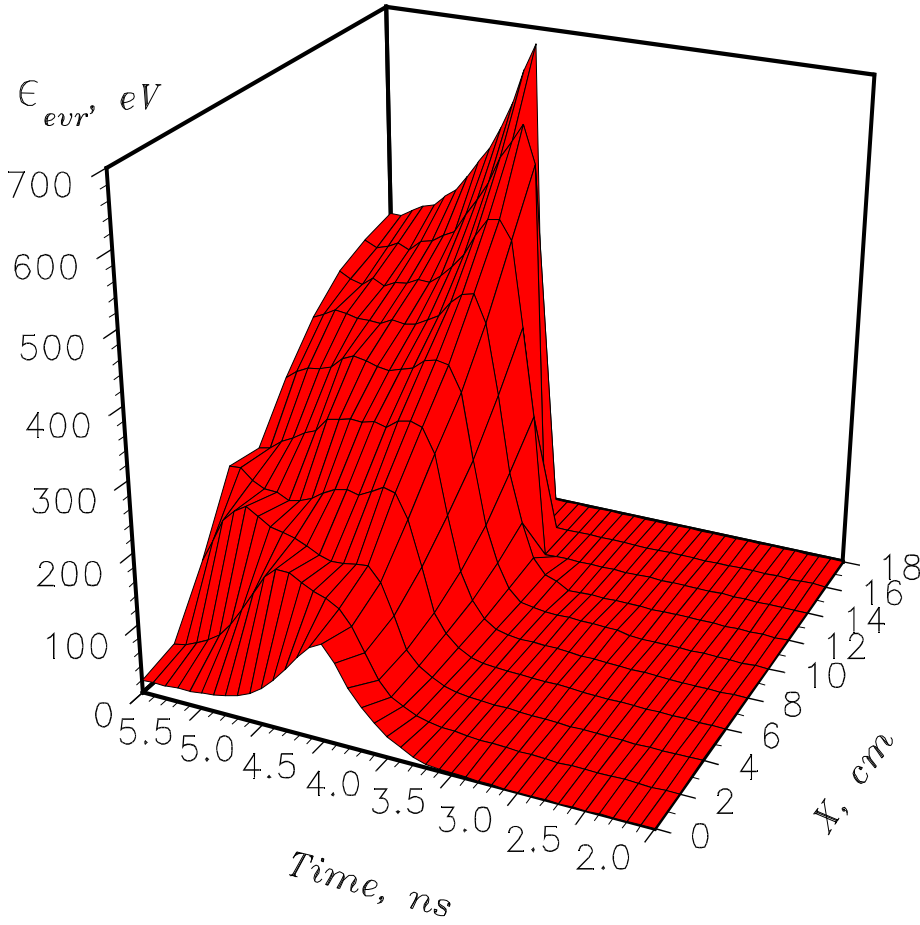


Analysis of EEDF.
Results of 1-D calculations

EEDF modification

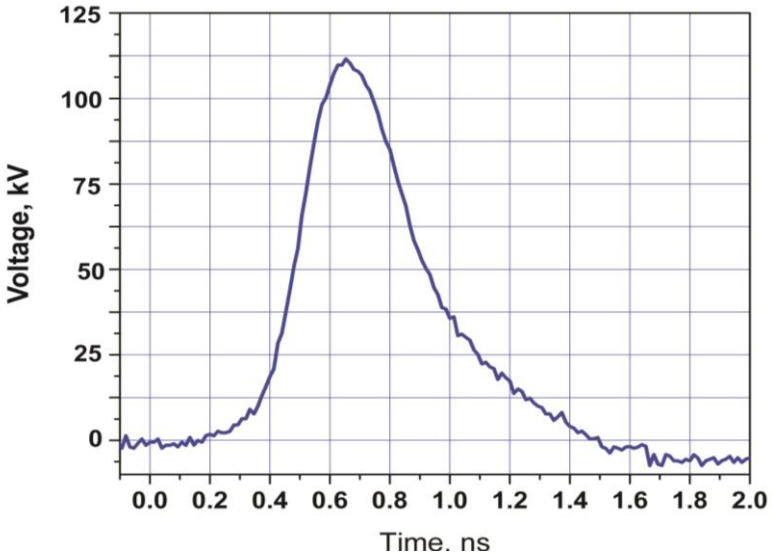


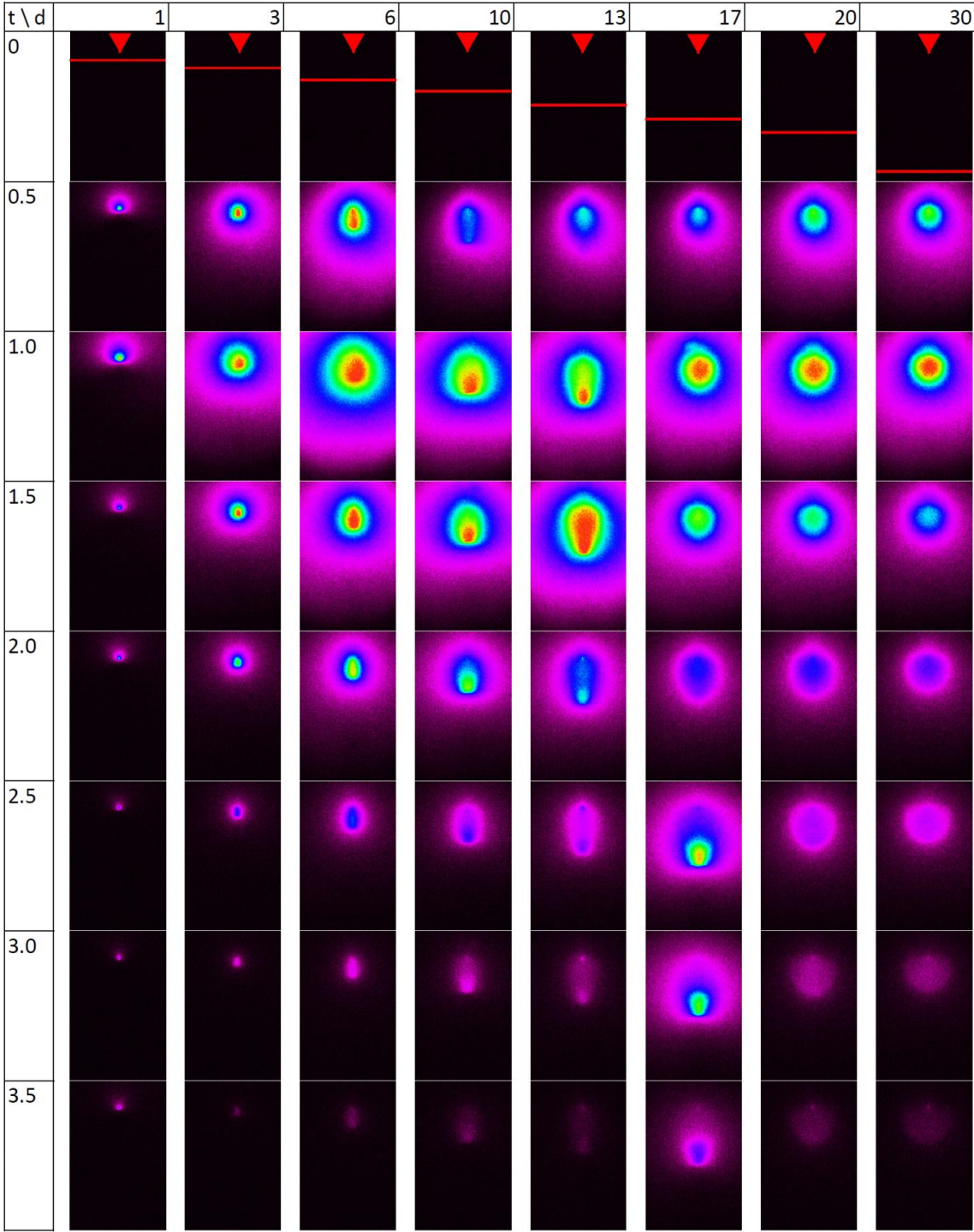
Mean energy



Pulsed Discharge at High Overvoltage

Dynamics of plasma emission in the gap. U_{peak} = 224 kV, Air. t is the time from the process start, *d* is the distance between high-voltage anode (point) and grounded cathode (plate). *d* was varied from 1 to 30 mm.



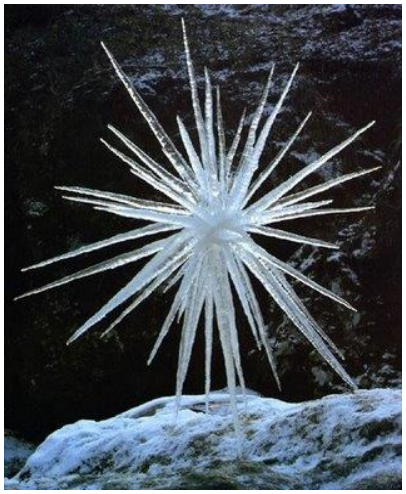


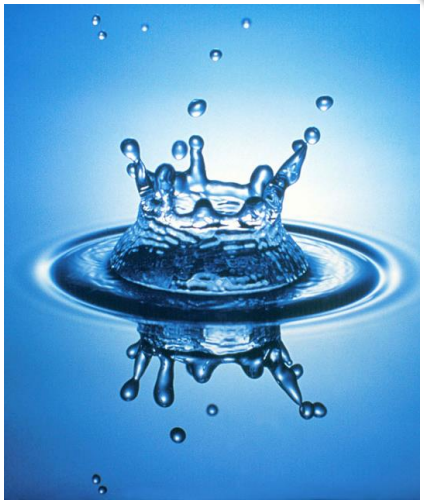
4 States of Matter: solid/liquid/gas/plasma

- Underwater pulsed discharges:
  - Efficient in various water treatment applications
  - Simple configuration (however scaling to large throughput required)
- Typically plasma is only considered to exist through the ionization of gases and production of plasmas in liquids has generated bubbles through heating or cavitation

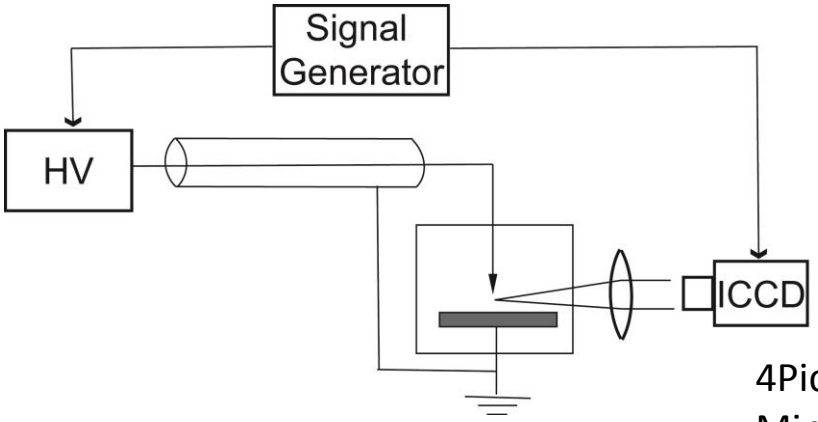
Paul CECCATO. Filamentary plasma discharge inside water. PhD report. Ecole Polytechnique. Paris. 2009

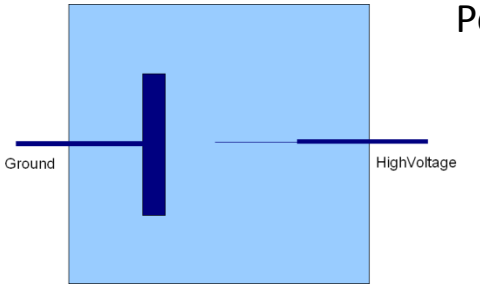
Is it possible to ionize the liquid without bubble formation?





Picosecond Discharges in Liquids

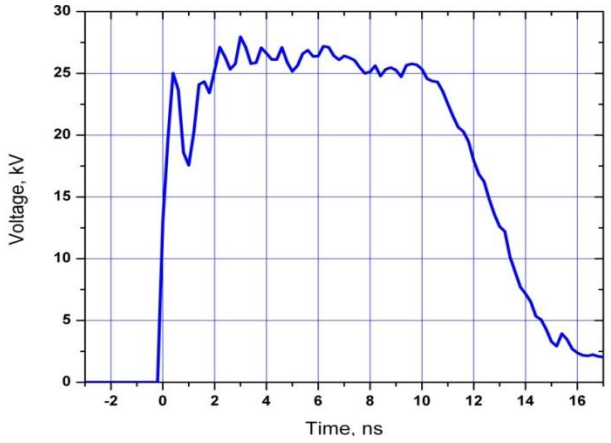




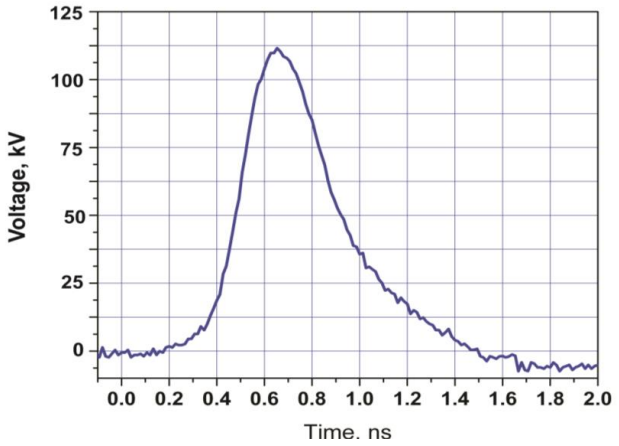
Point-Plane Electrode
Electrode Diameter:
100 µm
Inter-electrode
Distance: 3 mm

4Picos ICCD Camera:
Minimum gate: 200 ps,
Spectral Response: $\Delta\lambda$ = 220 – 750 nm

To avoid bubble formation,
Very short pulses were used:

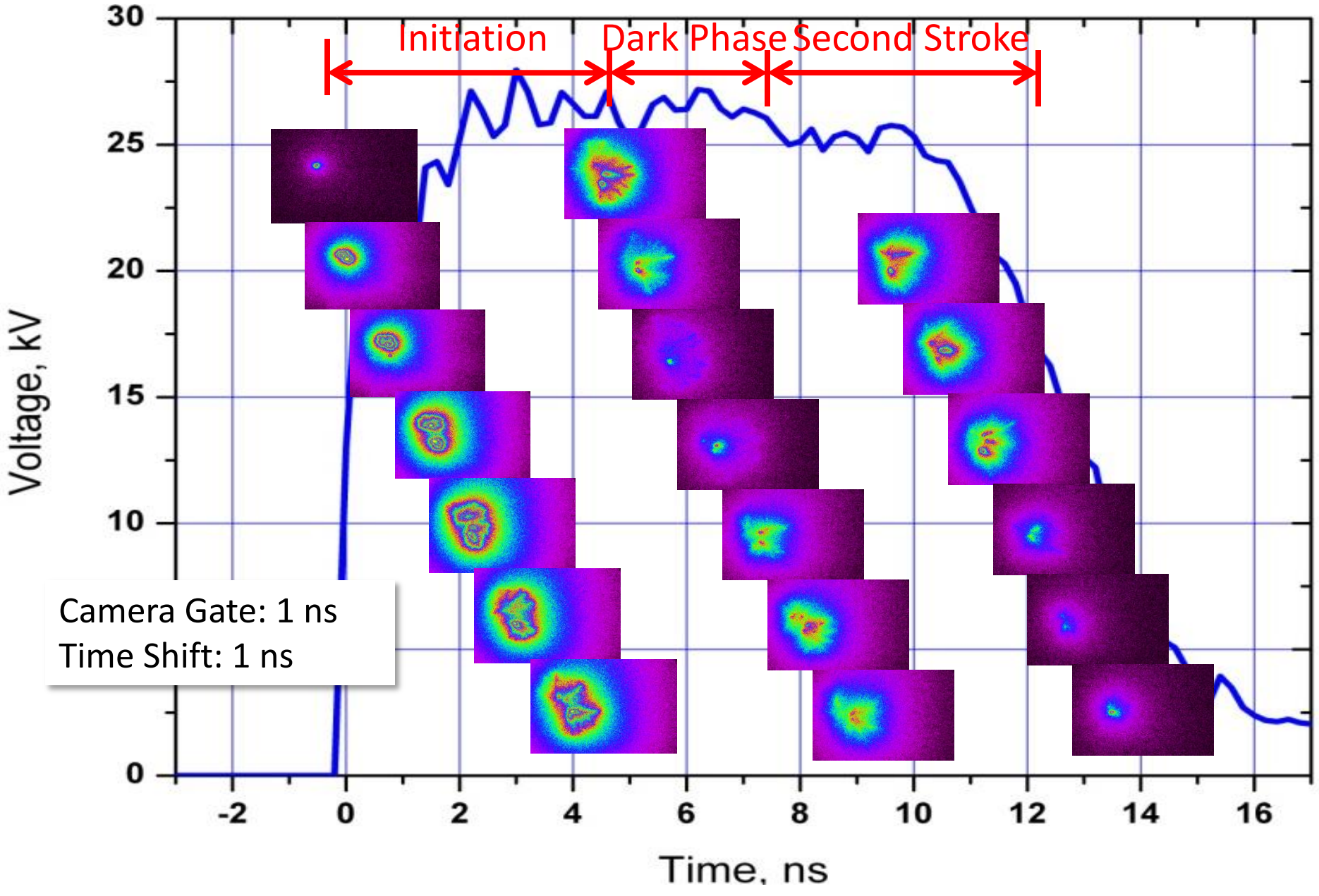


Peak Voltage 27 kV
Rise Time: 0.2 ns
Duration: 12 ns



Peak Voltage 224 kV
Rise Time: 0.15 ns
Duration: 0.5 ns

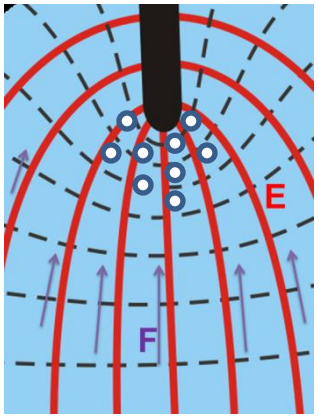
Dynamics of Nanosecond Discharge



Bubble-free Breakdown Mechanism at Nanosecond High-voltage Pulses.

Shneider, Pekker, Fridman, IEEE Transactions on Dielectrics and Electrical Insulation (2013)

- It is known that at certain values of the stress tension (negative pressure) – cavitation occurs
- Such negative pressure arises **faster than in ps-time scale** in the vicinity of a needle electrode under ponderomotive electrostrictive action of highly non-uniform electric field
- A large amount of micro-pores forms in the vicinity of needle electrode where liquid becomes a highly dispersive media



Volumetric force (Helmholtz, 1881)

$$\vec{F} = e\delta n\vec{E} - \frac{\varepsilon_0}{2}E^2\nabla\varepsilon + \frac{\varepsilon_0}{2}\nabla\left(E^2\frac{\partial\varepsilon}{\partial\rho}\rho\right)$$

For nonpolar dielectrics: $\vec{F} = \frac{\varepsilon_0}{2}\nabla\left(E^2\frac{\partial\varepsilon}{\partial\rho}\rho\right) = \frac{\varepsilon_0}{2}\frac{(\varepsilon-1)(\varepsilon+2)}{3}\nabla E^2$

For polar dielectrics: $\vec{F} = \frac{\varepsilon_0}{2}\nabla\left(E^2\frac{\partial\varepsilon}{\partial\rho}\rho\right) \approx 0.5\alpha\varepsilon_0\varepsilon\nabla E^2 \quad (\alpha \approx 1.5)$

If the conditions for cavitation are satisfied, pores can appear in any point where $P < P_c$=-(5-100) MPa.

$$P_{tot} = -\left(0.5\varepsilon_0 E^2\frac{\partial\varepsilon}{\partial\rho}\rho - p\right); \quad |P_E| = 0.5\varepsilon_0 E^2\frac{\partial\varepsilon}{\partial\rho}\rho \approx 0.5\alpha\varepsilon_0\varepsilon E^2 \approx \varepsilon_0\varepsilon\frac{U^2 r_0^2}{R^4} > |P_c|$$

$$R < r_0\left(\varepsilon_0\varepsilon\frac{U^2}{|P_c|r_0^2}\right)^{1/4}$$

The region with cavitation, $R(V,r_0)$ can be measured in experiments!

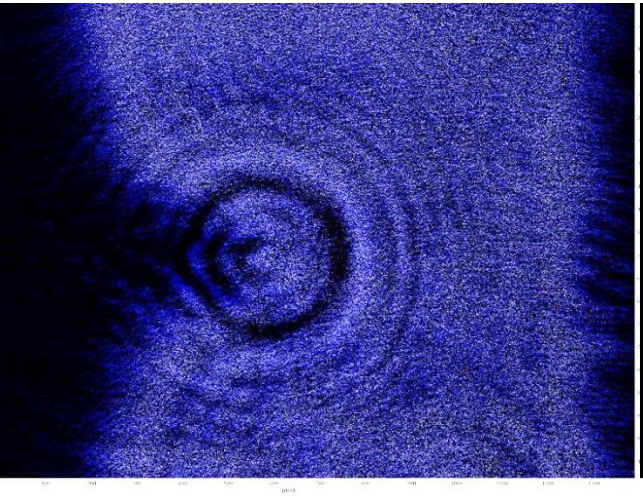
Electric field inside a spherical micropore $E_p = \frac{3\varepsilon}{1+2\varepsilon}E$

Ionization condition (necessary for breakdown): $\Sigma \approx 2E_p r_p \geq I \sim 10\,\text{eV}$

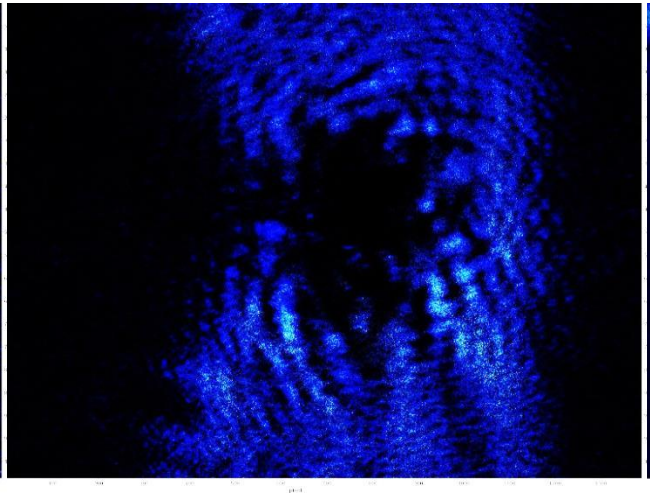
Pulsed Nanosecond Discharge Development in Liquids with Various Dielectric Permittivity

Liquid	Formula	Dielectric permittivity	Critical Electric Field M, MV/cm	Speed of sound (m/s)	Conductivity (Ohm×cm)	Isothermal compressibility (P = 1 atm), MPa
Water	H_2O	81	0.3	1480	10^5–10^6	2200
Ethanol	C_2H_5OH	27	0.5	1180	10^6–10^7	889
n-Hexane	C_6H_{14}	2	0.7	1083	10^{12}	633

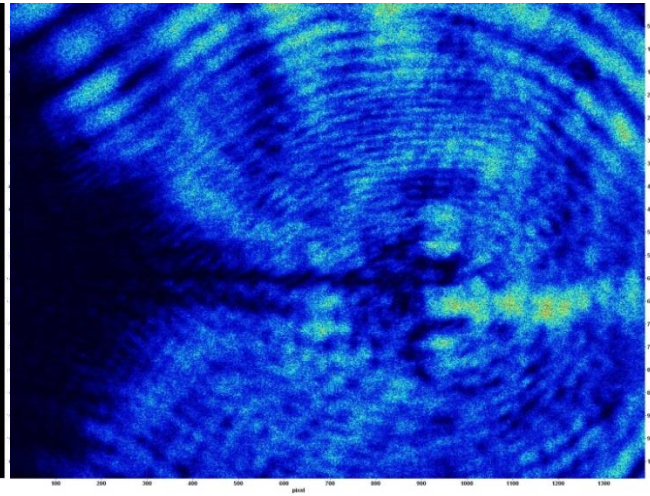
Water, U = 9 kV, 20 ns.



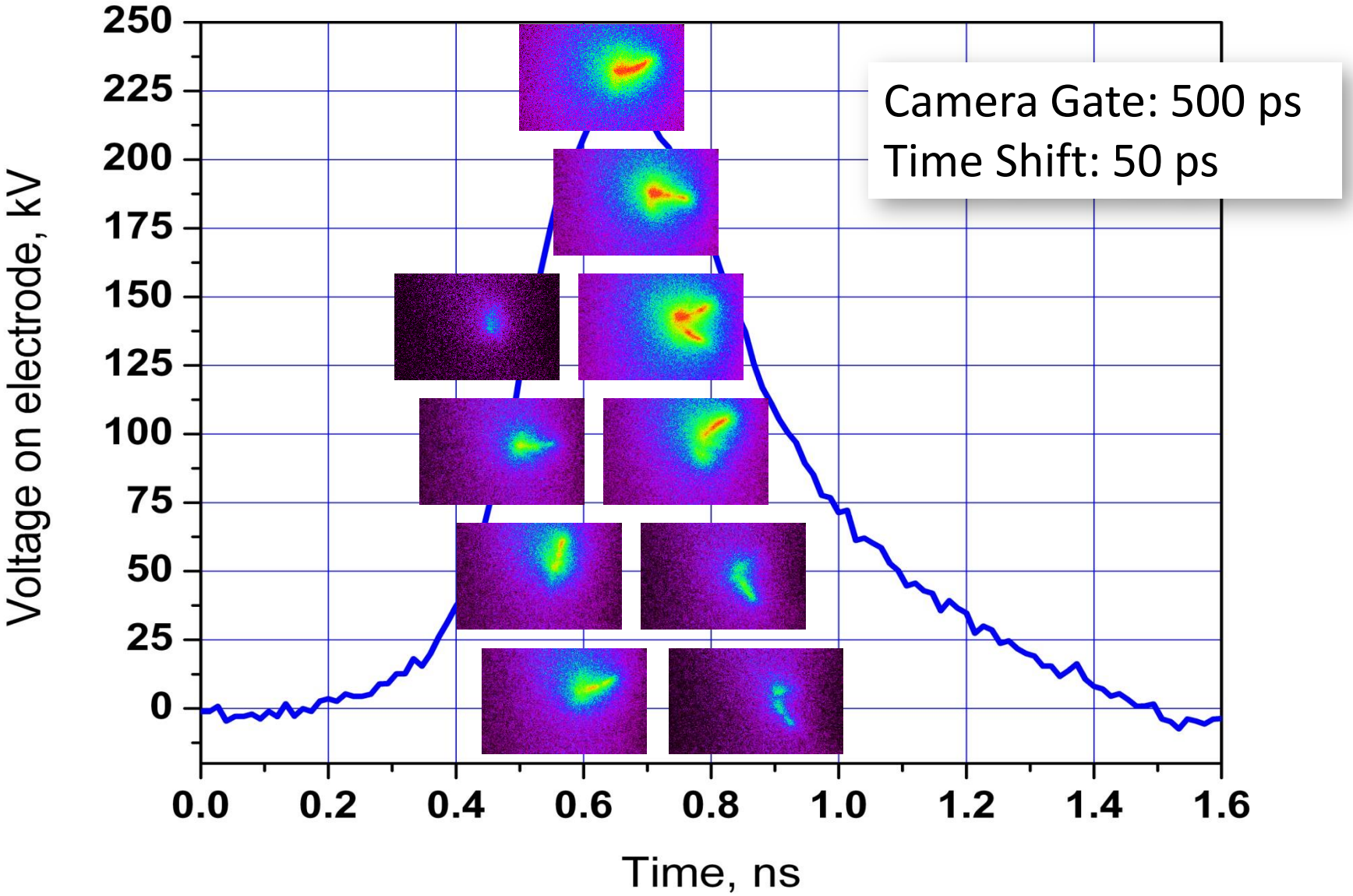
Water, U = 12 kV, 20 ns



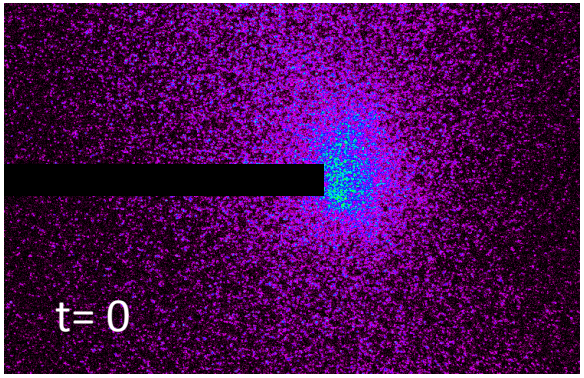
Ethanol, U = 20 kV, 60 ns

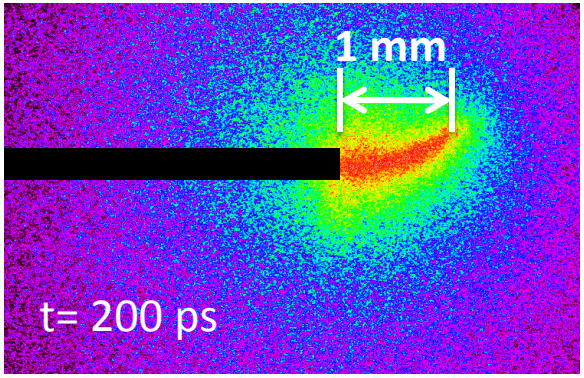


Dynamics of Sub-Nanosecond Discharge



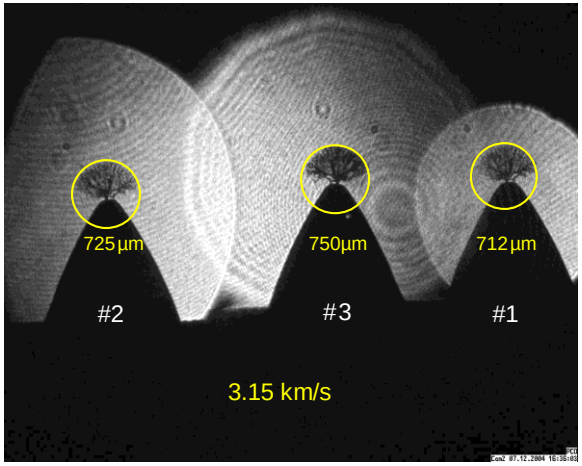
Velocity of Streamer Propagation

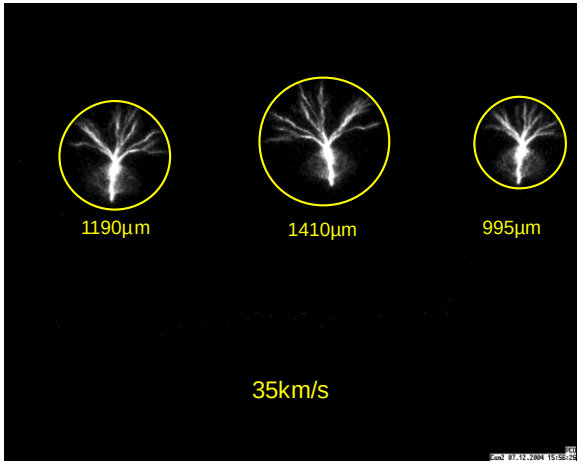




- 150 ps Rise Time, 0.8 MV/ns: Growth Rate $v_z = L/\Delta t \approx 1mm/200ps = 5000$ km/s ~ 15% c
- Expansion Rate $v_r = r/\Delta t \approx 0.05mm/200ps = 250$ km/s

Velocity of Microsecond Streamer Propagation (~ 40 ns rise, 10 µs duration)



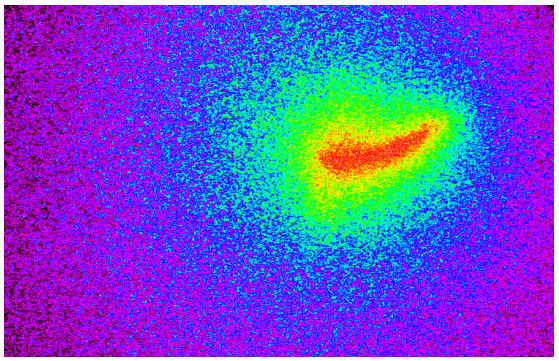


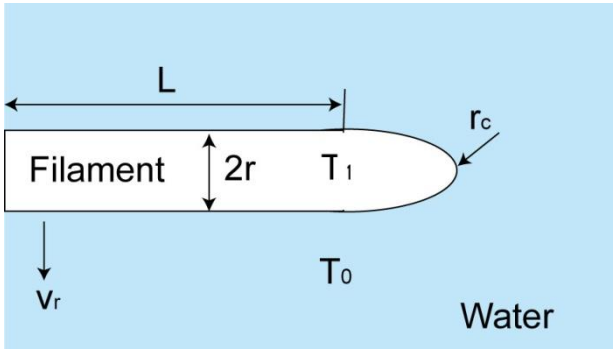
W An, K Baumung, and H Bluhm, Investigation of pulsed corona discharges in water by fast imaging diagnostics, 32nd IEEE International Conference on Plasma Science, Monterey, California 20-23 June 2005

Liquid Plasma - No Bubble Formation!

Bubbles vs E-impact

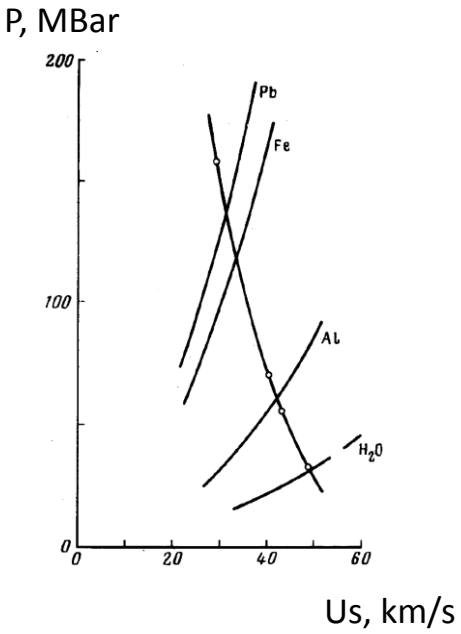
r ~ 10 μm
τ ~ 50-100 ps
U ~ 100 km/s





r ~ 10 μm
E ~ 225 MV/cm
E/n ~ 670 Td

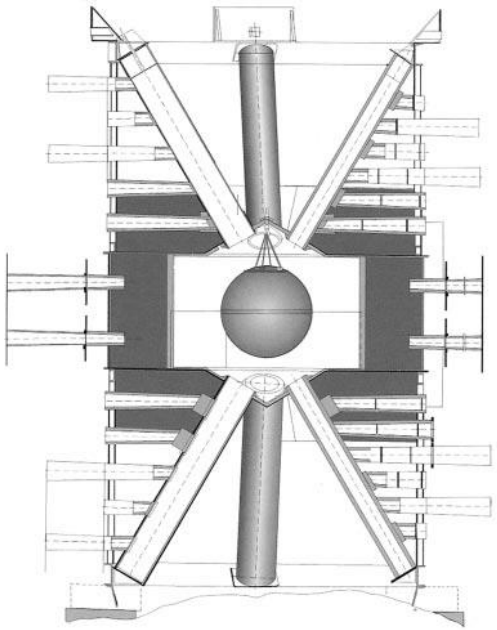
Media	D, km/s	U, km/s	P, GPa	ρ, g/cm³	$\sigma = \rho/\rho_0$
H_2O	43.95	32.54	1430	3.852	3.852



Trynin (1994) UFN
Shock Compressibility of Condensed Matter
in Strong Shock Waves
of Underground Nuclear Explosions

Avrorin et al (2006) UFN
Physical Investigations under Nuclear Tests

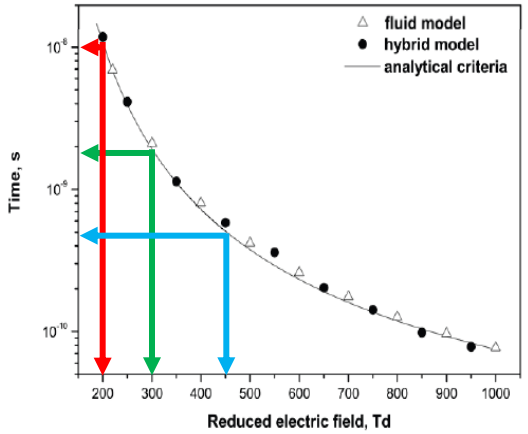
Avrorin et al (1980) JETF Letters
Shock Compressibility at ~ 100 MBar



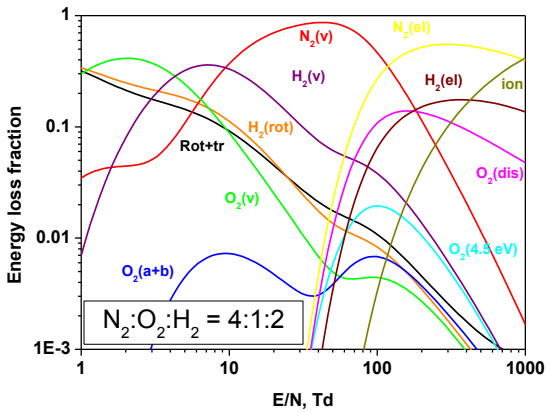
NANO- AND PICOSECOND DISCHARGES AT ULTRAHIGH ELECTRICAL FIELD

- **Ultra-short pulsed discharges allow control over electric field in plasma and the direction of energy deposition and media excitation**
  - **Pulsed gamma and X-rays**
  - **Ultra-short e-beams**

- **Fundamental problems:**
  - **Non-local EEDF and formation of run-away electrons. Differential cross-sections**
  - **Molecular/atomic potential surface modification in external E-field above run-away threshold**



- Critical discharge time at P=1 atm. Air. τ(400Td)~1ns



- Discharge energy distribution in H_2-O_2-N_2 mixture vs E/n

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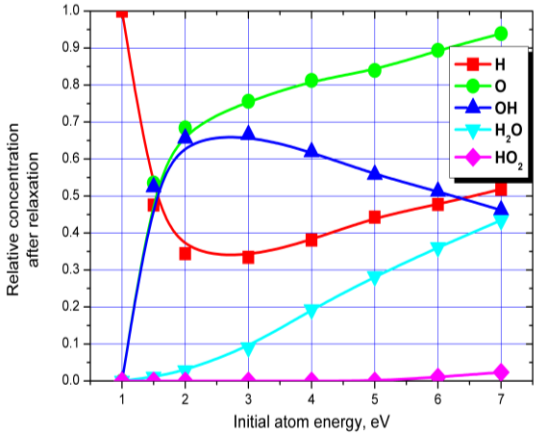
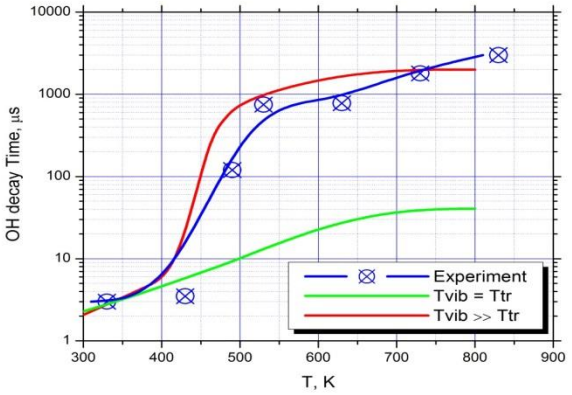
NON-BOLTZMANN CHEMICALLY-ACTIVE SYSTEMS UNDER PULSED EXCITATION

- **Selective molecular excitation/reactions**
  - **Chemical processes under conditions of strong deviation from Maxwell-Boltzmann equilibrium across translational, vibrational and electronic degrees of freedom of the reactive gases.**
- **Fundamental problems:**
  - **Dynamics of energy transfer and chemical reactions at non-Boltzmann conditions**
  - **Non-equilibrium back-coupling in systems with internal energy sources**



Relative concentration of particles produced during energy relaxation of one “hot” H atom in the stoichiometric H_2:O_2 mixture at 300 K as a function of initial atom energy.



Measured and calculated OH decay time. P = 1 atm. 0.3%C_4H_{10} + air

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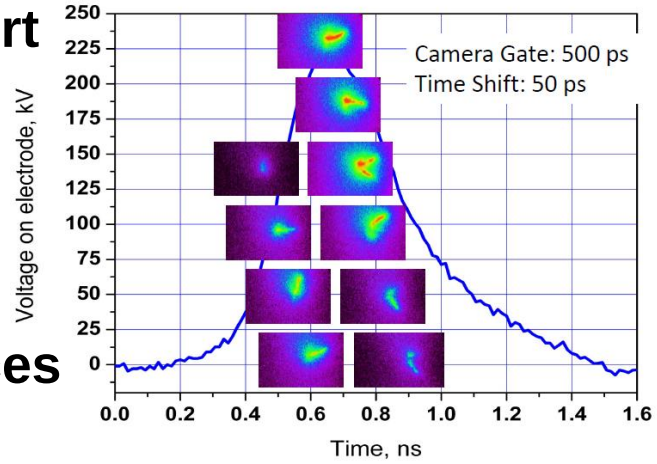
LIQUID AND SOLID-STATE NONEQUILIBRIUM PLASMA GENERATION

- **Liquid or solid media excitation by ultra-short electric discharge without phase change opens the door to new technologies**
  - **Nano-materials synthesis**
  - **Bio-medical technologies**
  - **Direct excitation/picosecond light sources**
- **Fundamental problems:**
  - **Boltzmann equation cannot be used for EEDF calculations**
  - **Electrical fields comparable with intramolecular fields – direct acceleration of free electrons through the atoms**
  - **Electrostriction pressure higher than critical – molecular layers displacement**



- Picosecond water plasma.
- Pulse:
  U = 220 kV
  τ = 150 ps rise time
  U/τ = 1.4 MV/ns rise rate
- Electric field
  E ~ 225 MV/cm
  E/n ~ 670 Td
- Propagation speed
  V = 5000 km/s ~ 15%c

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