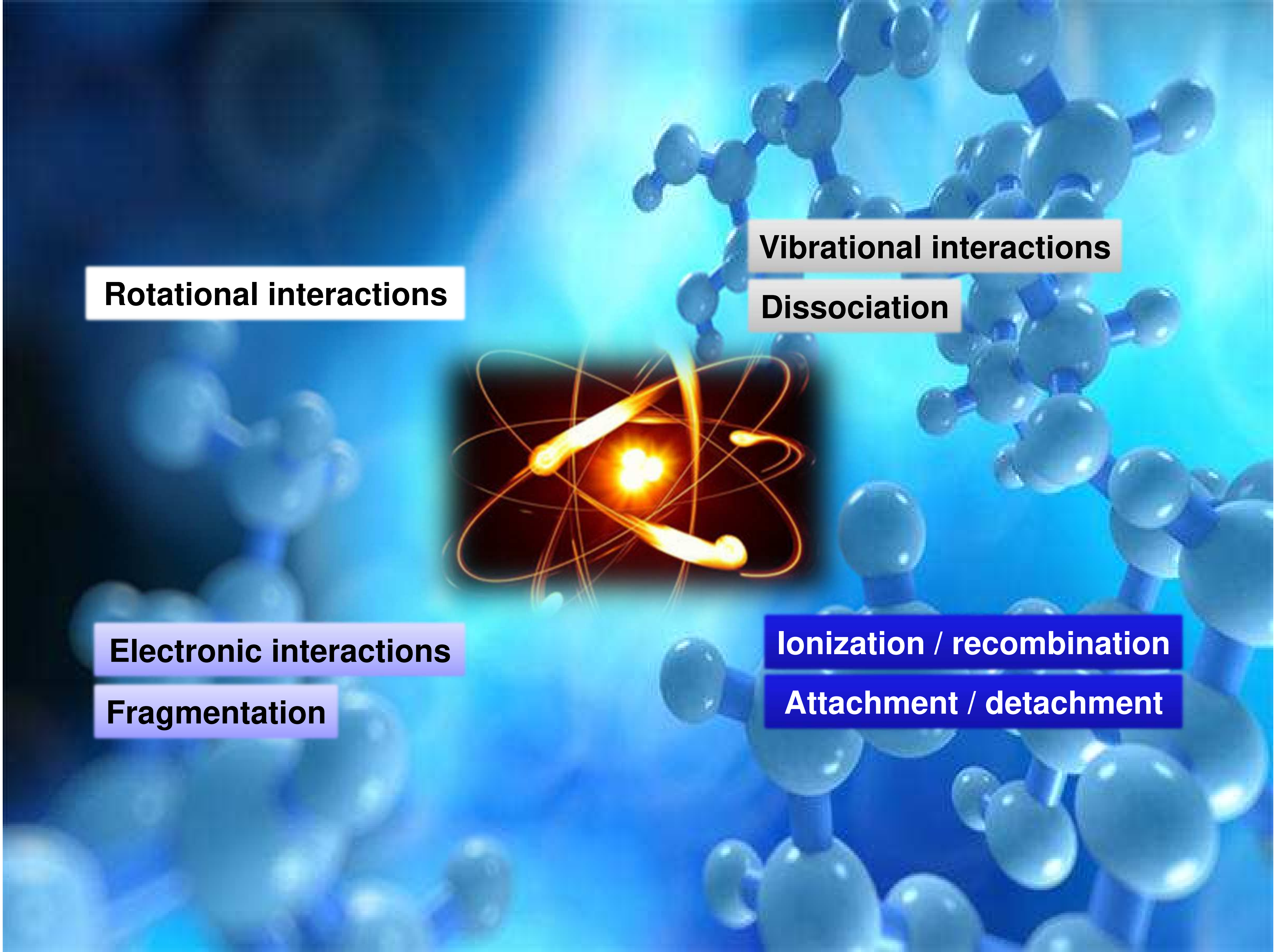
Influence of the electron description on the modelling of plasma-based applications scenarios

L.L. Alves

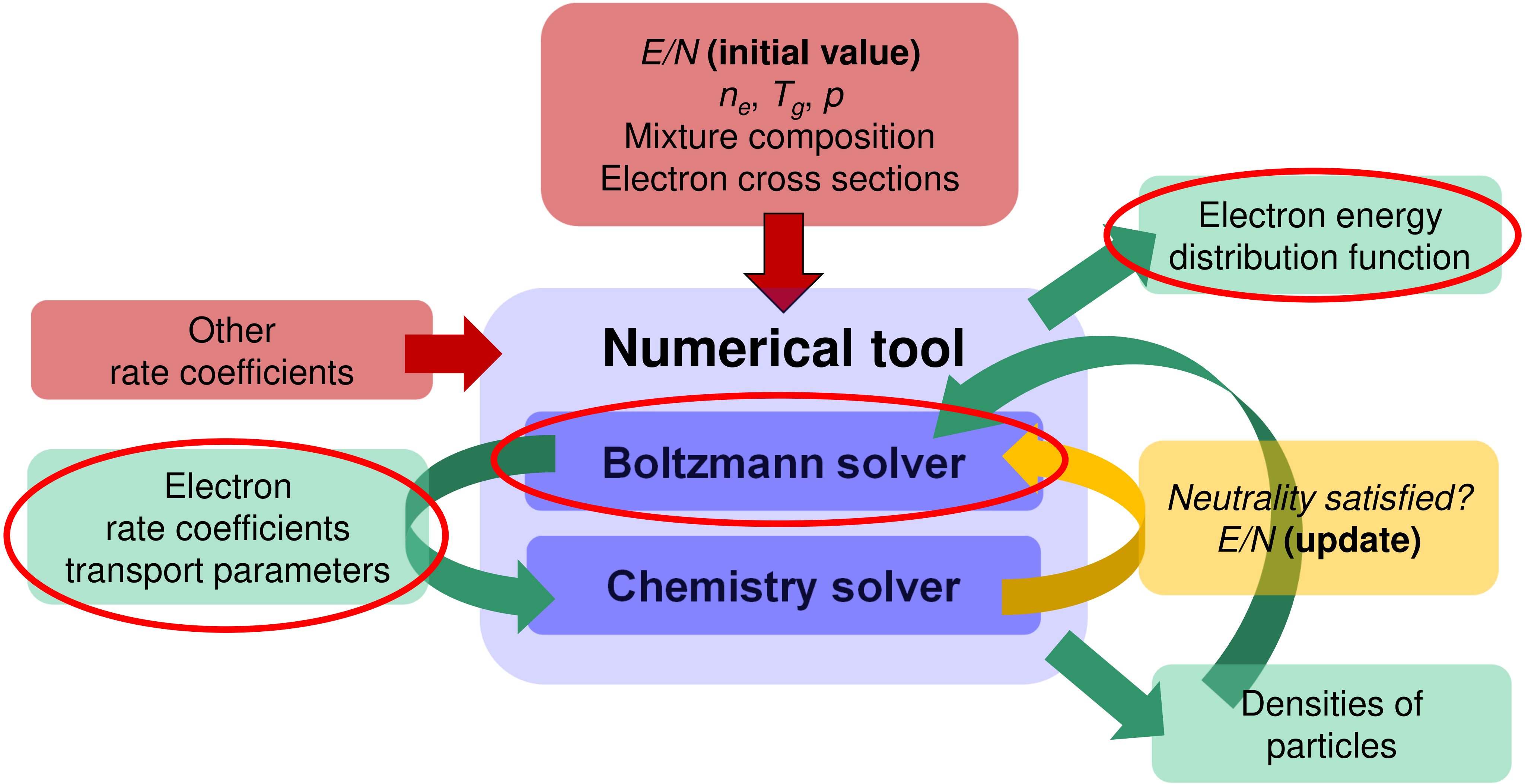
llalves@tecnico.ulisboa.pt

Instituto de Plasmas e Fusão Nuclear
Instituto Superior Técnico, Universidade de Lisboa
Lisboa, Portugal
http://www.ipfn.ist.utl.pt
https://www.ipfn.tecnico.ulisboa.pt/nprime/

Plasma Thin film International Union Meeting
13-17 September 2021


Vibrational interactions
Dissociation
Rotational interactions
Electronic interactions
Fragmentation
Ionization / recombination
Attachment / detachment

Electrons at the heart of modelling in LTPs



Outline

- **Modelling of low-pressure ccrf discharges in N_2-H_2**

  Time-dependent hybrid (fluid+kinetic) code, with beam model for fast electrons

  Results
  - the coupling between fast/slow electrons
  - the normalized ion flux
  - ammonia production

- **Electron kinetics in dry-air pulsed plasmas**

  Formulations adopted in solving the EBE
  - time-dependent solution
  - quasi-stationary approach

  Results in dry air (80%N2 : 20%O2)
  - step-fields ($\tau_{on} \rightarrow \infty$) with different τ_{rise} ~ 0 - 1 μs
  - typical discharge pulses at limited τ_{on} and τ_{rise} ~ ns, μs

- **Final remarks**

Modelling of low-pressure ccrf discharges in N_2-H_2

M Jiménez-Redondo *et al* 2020 *Plasma Sources Sci. Technol.* **29** 085023

Studies of low-pressure N_2-H_2 plasmas

Synthesis of ammonia

(surpassing the efficiency of the thermochemical Haber–Bosch process)

focus on the role of plasma-surface interactions

Fusion research

use of N_2 to attenuate the local heat loads on tungsten divertors

- drawbacks
  - implantation of nitrogen and nitriding of plasma-facing materials
  - sputtering by energetic nitrogen ions, and formation of tritiated ammonia

Technological applications

- deposition of thin films
- etching of organic low permittivity films
- surface treatment by nitriding of metals or semiconductors
- carbon nanotube functionalization
- catalyst pretreatment for carbon nanotube growth

Titan: artist's conception, airspacemag (2020)

Planetology

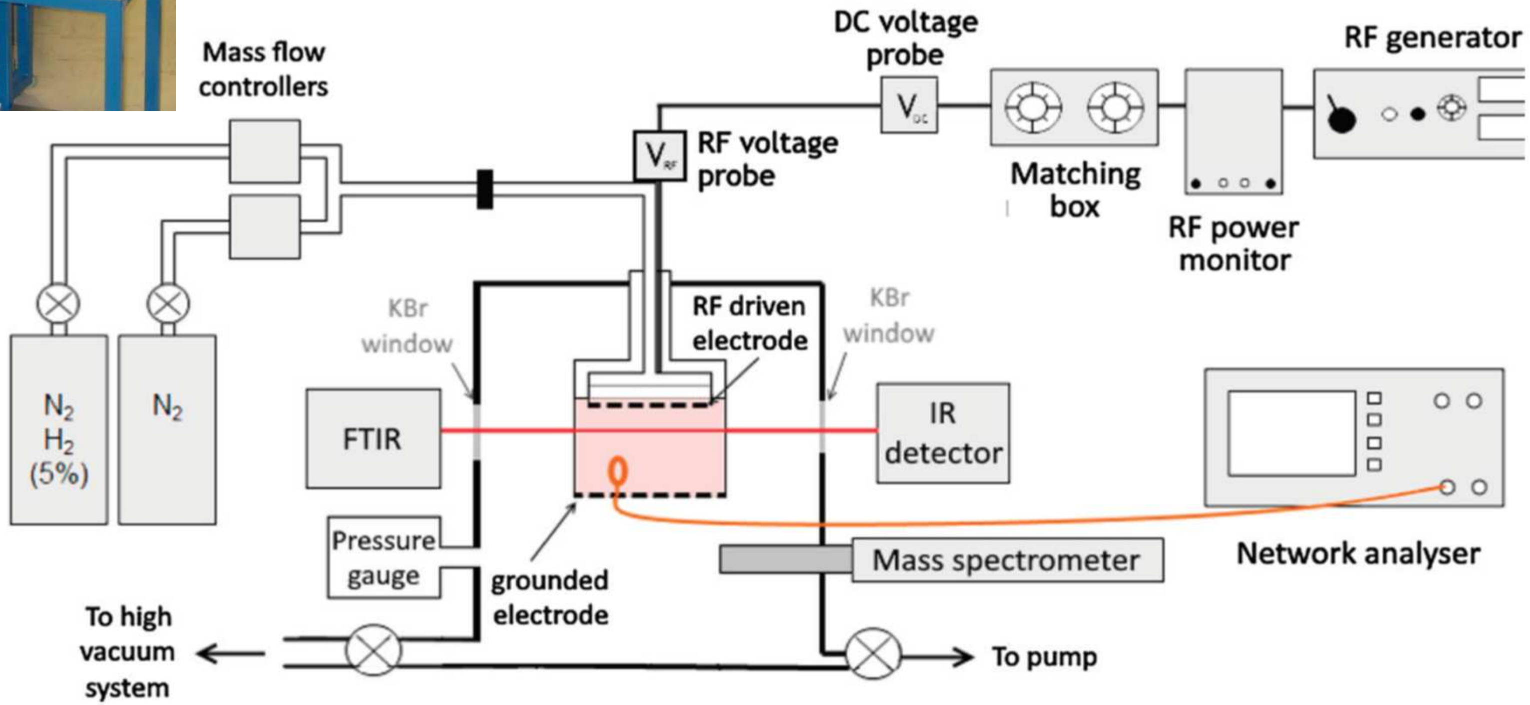
laboratory simulation of the chemistry of Titan's atmosphere

N_2/CH_4 ccrf discharges leading to the production of Tholins-analogues (solid aerosols)

CCRF discharges in N_2-H_2 plasmas

PAMPRE @ LATMOS
Guyancourt, France

Working conditions
Chamber: SS + aluminium alloy ; 30x40 cm^2
$N_2 - H_2$ mixtures (up to 5% H_2)
P ~ 5 – 30 W (@ generator)
f = 13.56 MHz
p ~ 0.3 – 1 mbar
Flow rates ~ 10 - 70 sccm



The time-dependent hybrid model

2D fluid module for charged particle dynamics
(+ Poisson's eq.)

0D kinetic module for volume & surface excited species
(Collisional Radiative Model + electron Boltzmann equation)

Beam model for fast electrons
generated by secondary emission at the walls

Charged particles
e, N^+, N_2^+, N_3^+, N_4^+, H^+, H_2^+, H_3^+, N_2H^+, NH^+, NH_2^+, NH_3^+, NH_4^+, H^-, NH_2^-

Volume species
$N_2(X,v=0\text{-}14)$, $N_2(X,v=0\text{-}45)$, N_2^*, N^*, NH_3, NH_2, NH, H

Surface species
N(s), H(s), NH(s), $NH_2(s)$, F

The single-beam model for fast electrons

M Surendra et al Phys. Rev. A **41**, 1112 (1990)
M Goujon et al Thin Solid Films **475**, 118 (2005)

- fast electrons (with initial energy 1eV) created at the walls by impingent positive ions

$$n_f u_{\perp_f} = -\gamma\, j_+$$

- secondary electron yield adjusted to fit the experimental trend n_e = f(W_{eff})

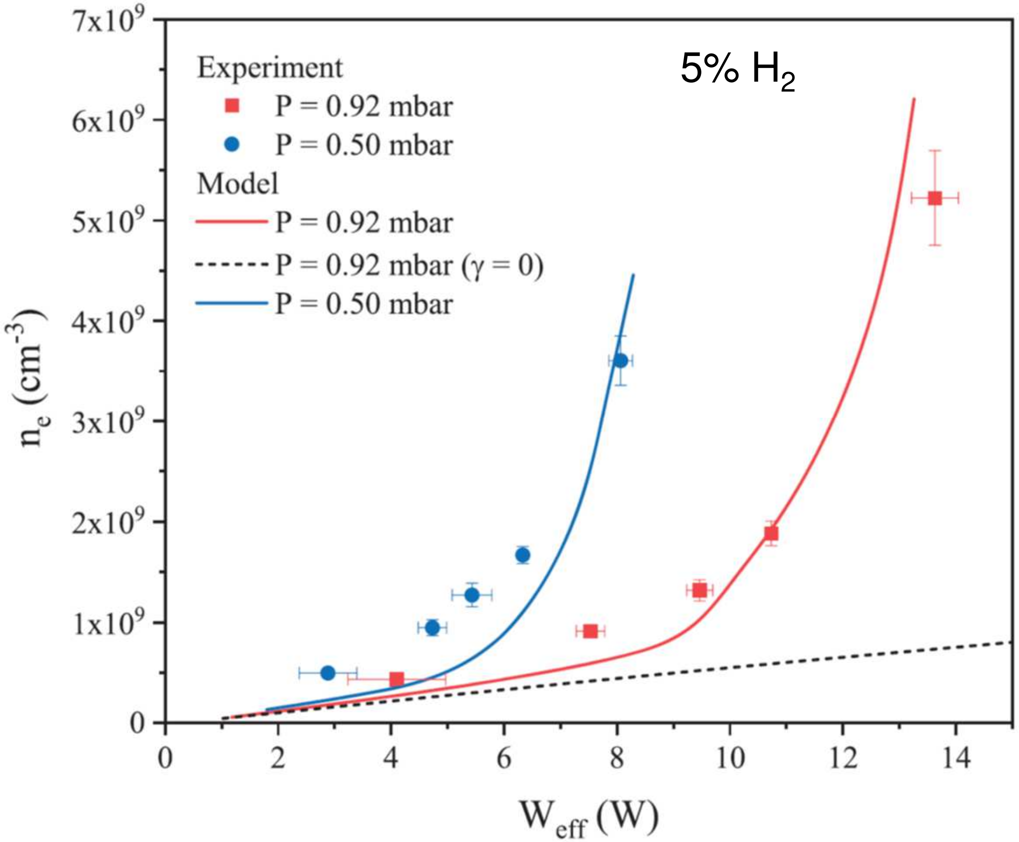
$$\gamma = \begin{cases} 0.09 & @\ 0.5 \text{ mbar} \\ 0.06 & @\ 0.92 \text{ mbar} \end{cases}$$ (less energetic ions reaching the wall)

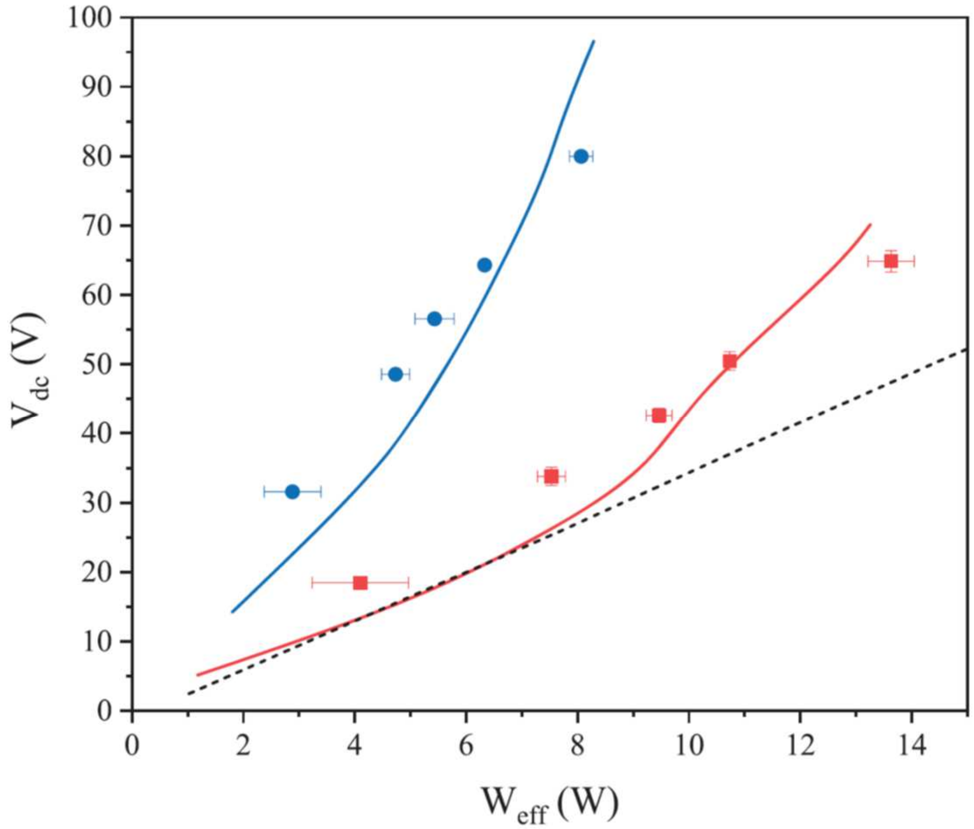
- particle and energy balance equations for the fast electrons are solved within an enhanced grid that resolves the space-charge sheath

$$\frac{\partial n_f}{\partial t} = -\nabla_\perp \left(n_f u_{\perp_f} \right) + S_f$$

$$\frac{\partial (n_f \varepsilon_f)}{\partial t} = -\nabla_\perp \left(\left(n_f u_{\perp_f} \right) \varepsilon_f \right) + n_f u_{\perp_f} E_\perp - S_f^\varepsilon$$

Adjusting the secondary electron yield





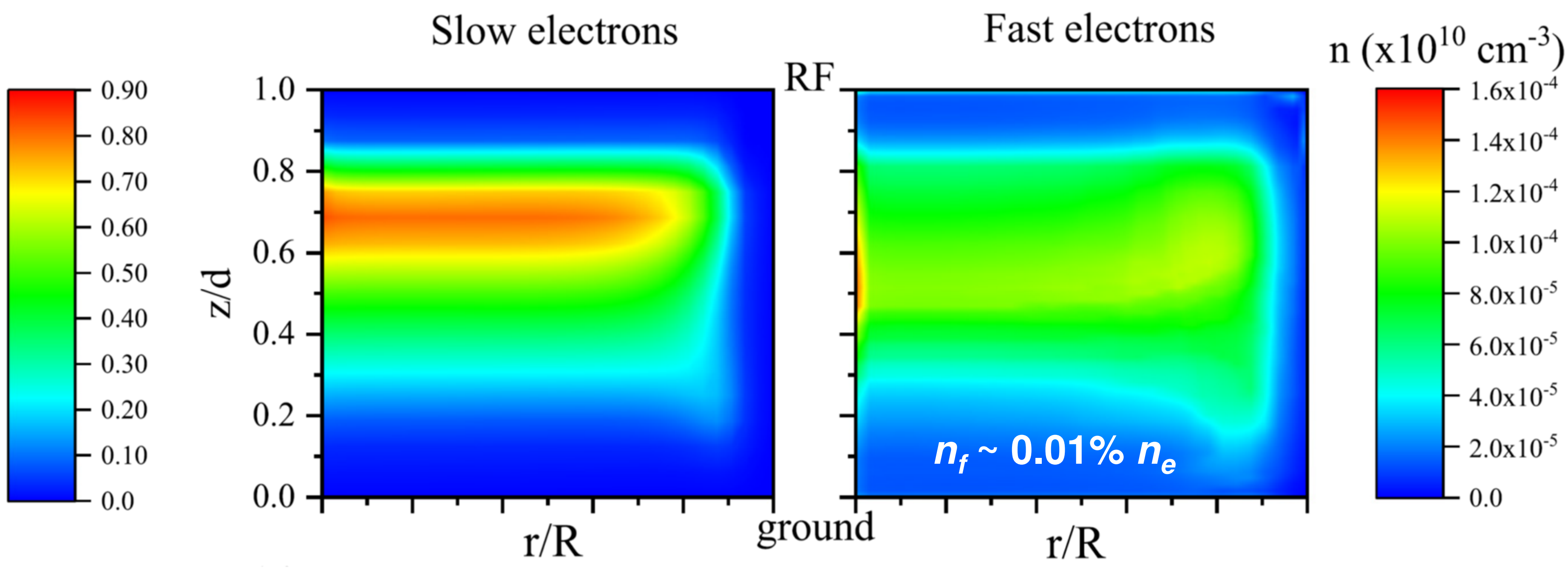
The electron density increases linearly at low power, exhibiting an exponential growth at higher power

The behavior of the self-bias potential is mostly linear, deviating from that trend when the secondary electron emission becomes significant

The coupling between fast and slow electrons

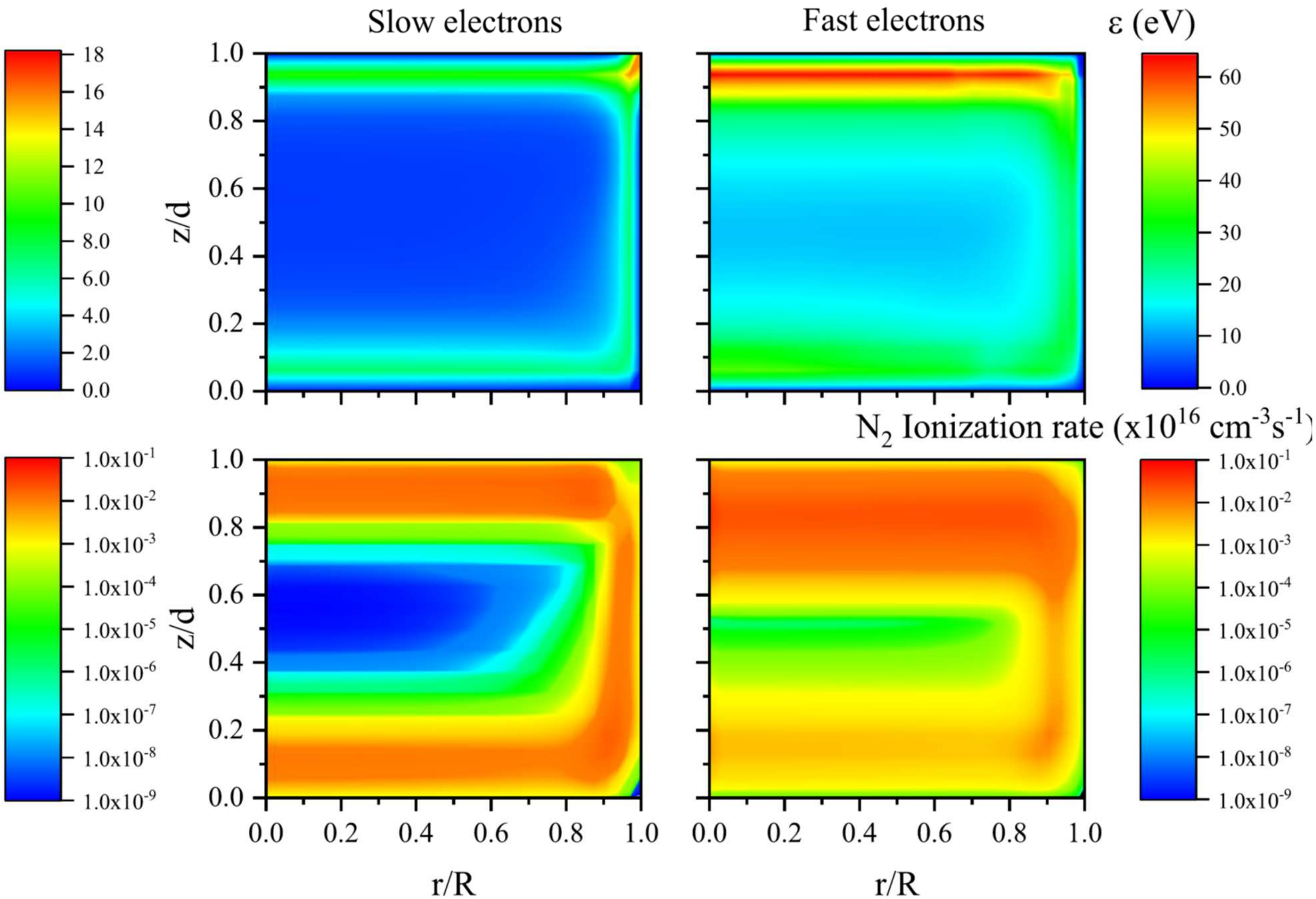
- **Within the sheath**, fast electrons
  - are accelerated by the electric field
  - with $\varepsilon_f > V_{ion}$ produce new beam electrons (flux increase; energy decrease)

- **Within the negative glow**, the beam is dilute into the plasma
  - ionization produces slow electrons
  - the beam energy is progressively lost to inelastic collisions



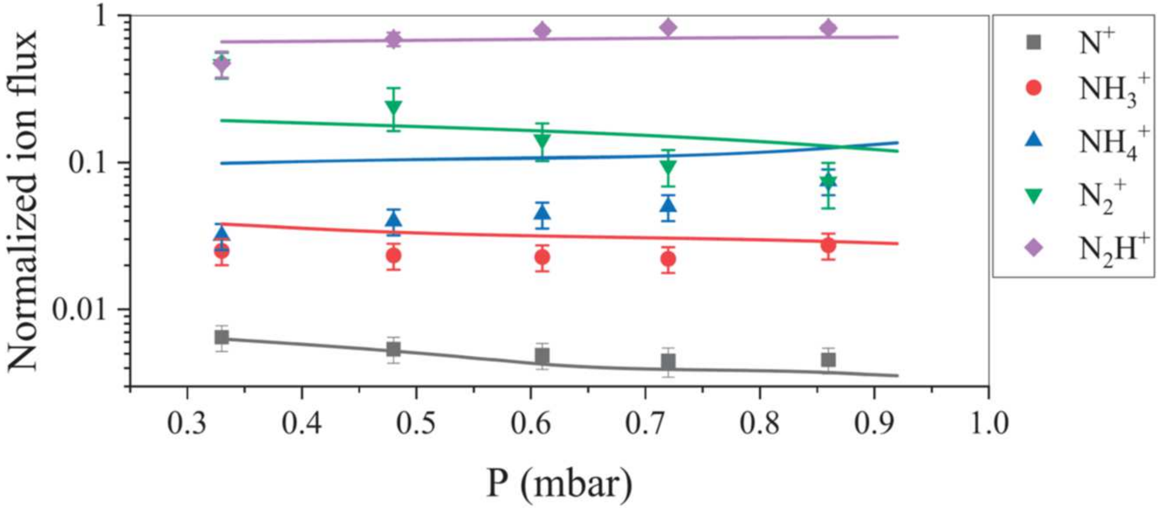
Results for the three beams of fast electrons

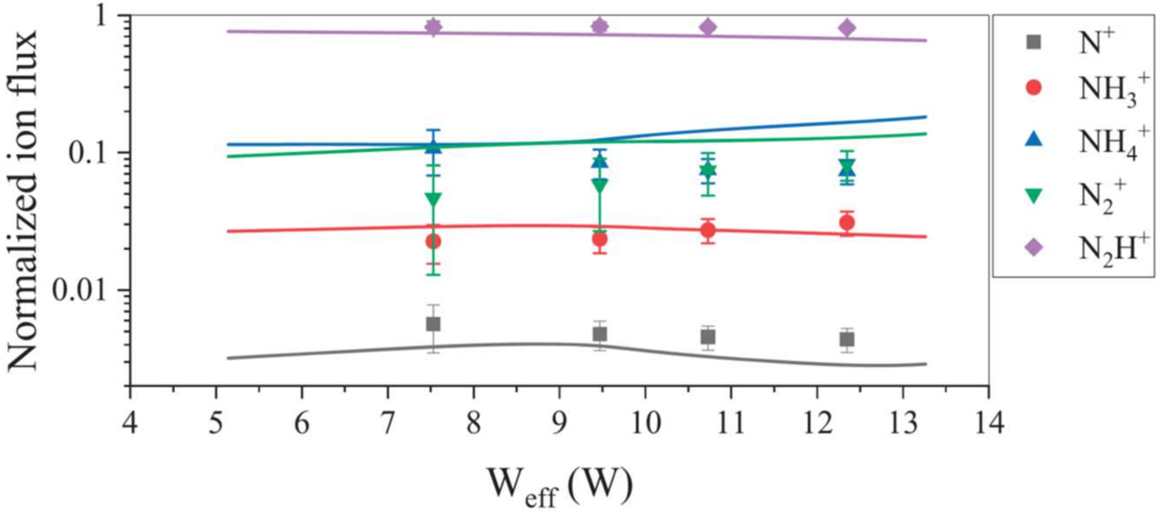
5% H_2, at 0.92 mbar and 11.5 W



Results for the normalized ion flux - I

5% H_2, at 0.92 mbar and 10 W

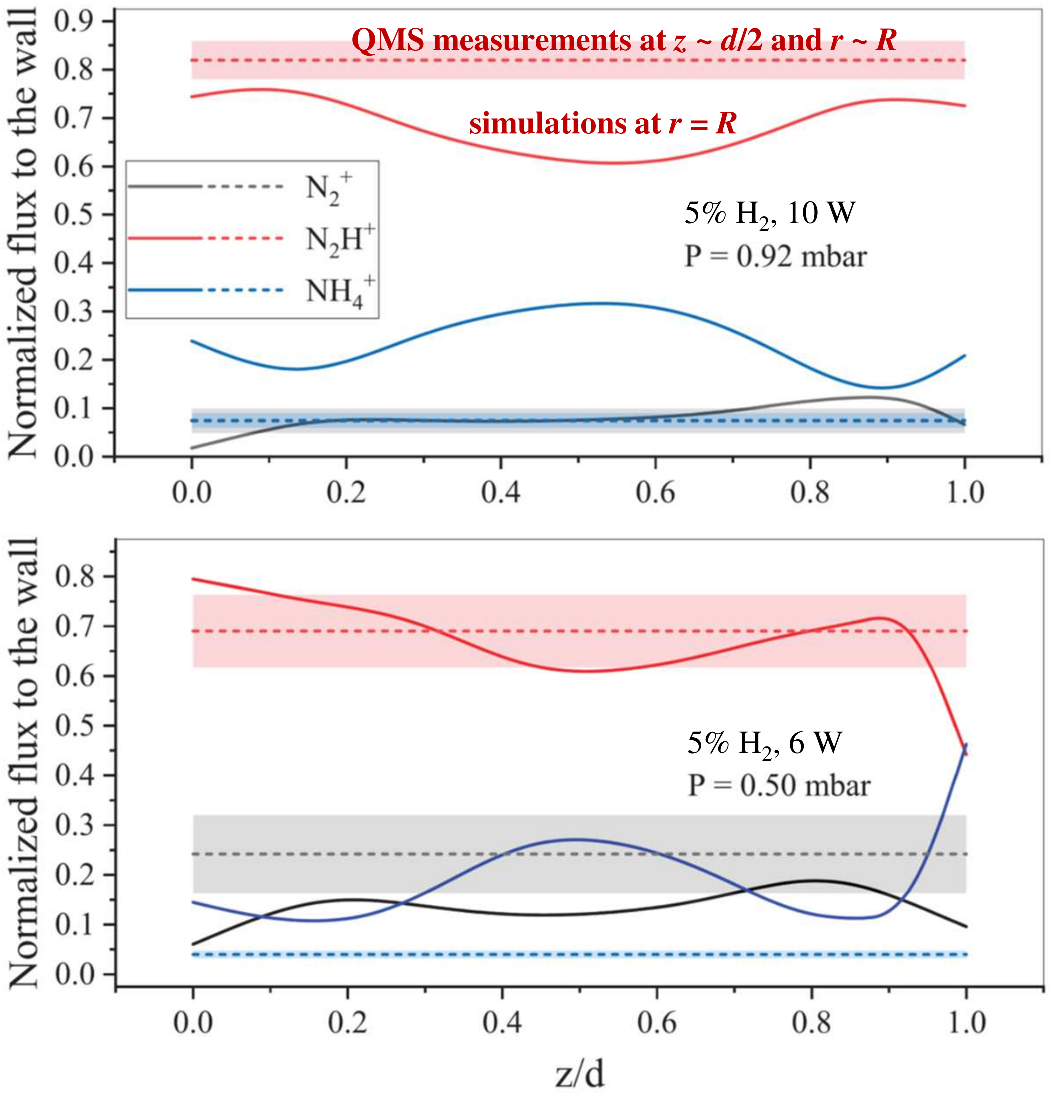




The model reproduces adequately the global trends of the ion flux measurements

The most abundant ion is N_2H^+

Results for the normalized ion flux - II



Model predictions underestimate the ionization rate in the bulk (high power)

The ions are mostly produced from the reaction chain

$$e + N_2 \rightarrow N_2^+ + 2e$$

$$N_2^+ + H_2 \rightarrow N_2H^+ + H$$

$$N_2H^+ + NH_3 \rightarrow NH_4^+ + N_2$$

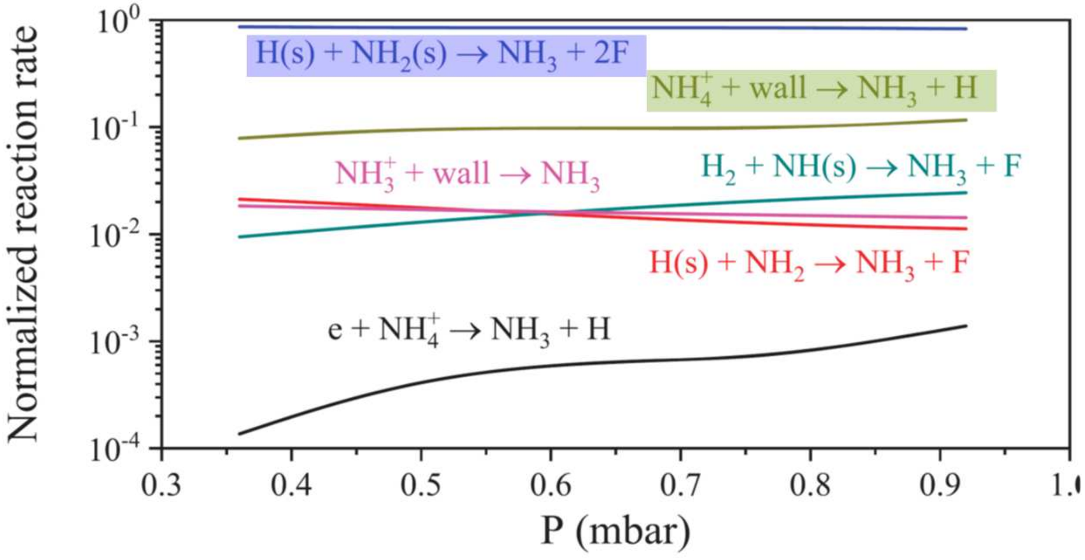
Because the ion-molecule reactions are very efficient the relative abundance of the ions is controlled by the efficiency of the e-ionization reaction

⇒ simple model for fast electrons

⇒ unprecise NH_3 production

Results for ammonia production - I

5% H_2, at 0.92 mbar and 10 W



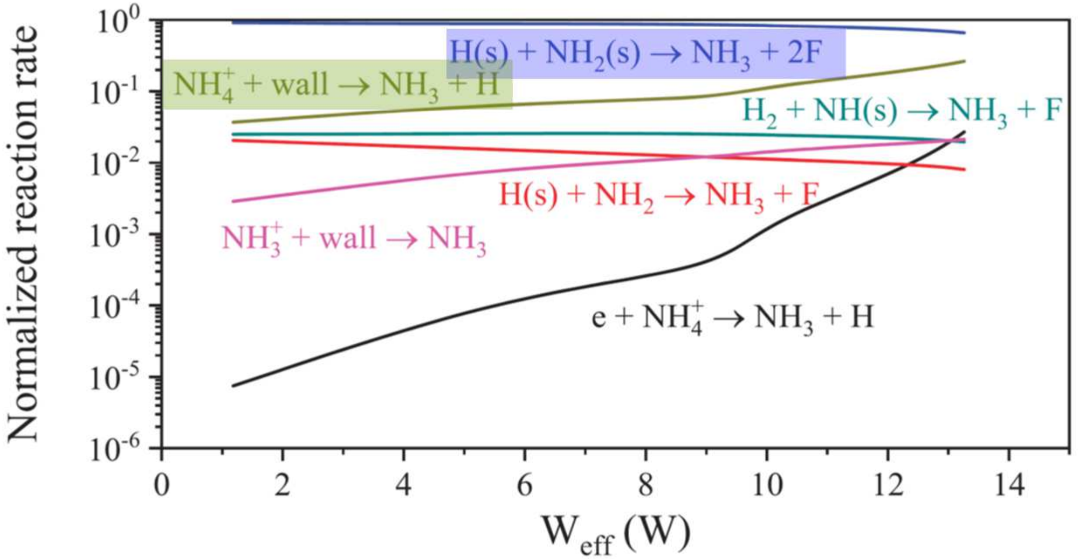
SS + **aluminium alloy** reactor

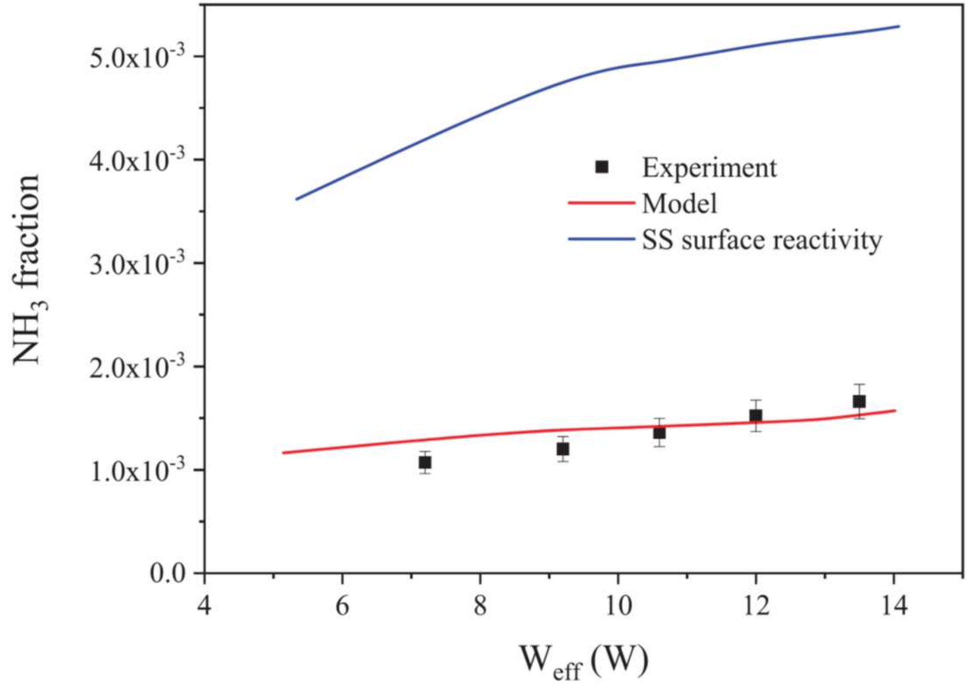
⇒ low reactivity surfaces

N + H(s) → NH(s) [P_{ER} ~ 10^{-3}]

H(s) + NH(s) → NH_2(s) + F

H(s) + NH_2(s) → NH_3 + 2F [E_{LH} ~ 0.7]

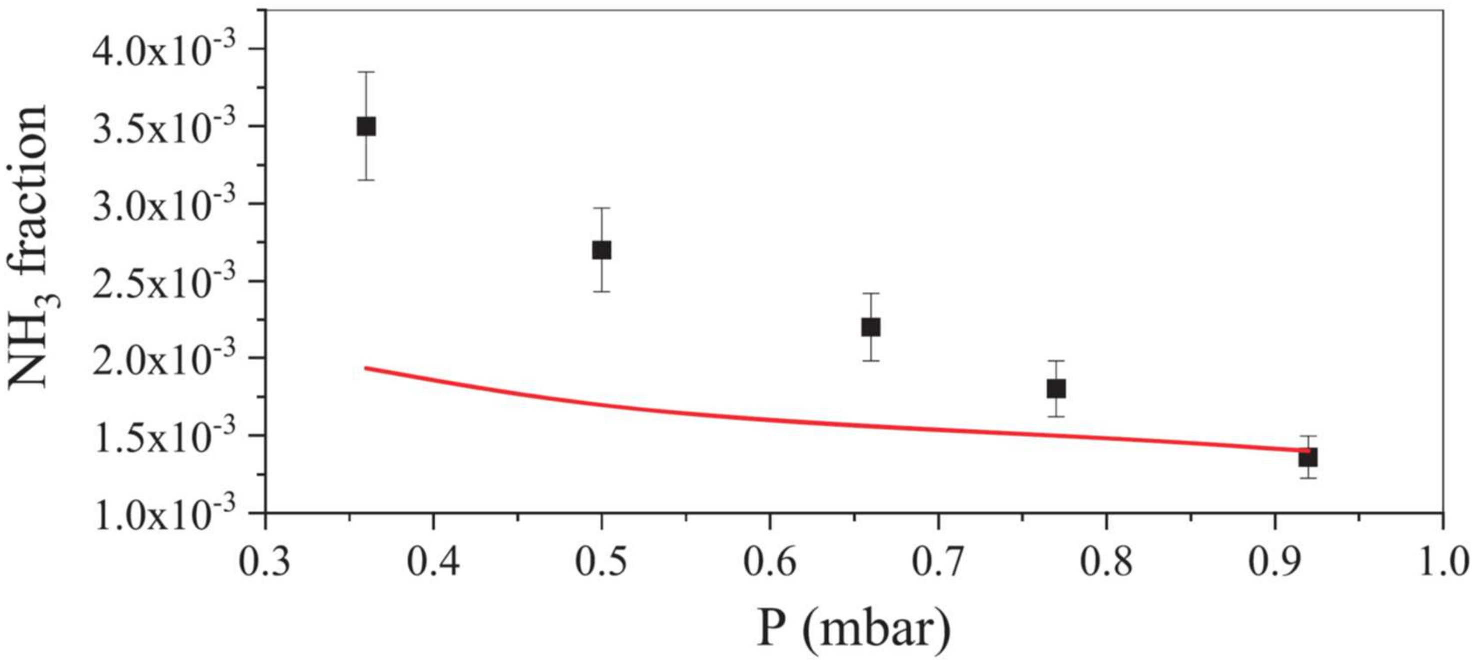




overall low abundance of NH_3

Results for ammonia production - II

5% H_2, at 10 W



Limited description / lack of additional mechanisms
- pressure-dependent surface reactivity
- vibrationally enhanced dissociative adsorption of N_2
- spatially-resolved chemistry coupled to the fast electrons

Electron kinetics in dry-air pulsed plasmas

A Tejero-del-Caz *et al* 2021 *Plasma Sources Sci. Technol.* **30** 065008

Studies of time-dependent electron kinetics

Motivation

- **Increasing interest in non-equilibrium LTPs created by pulsed discharges**, for different technological applications
  [plasma-assisted ignition and combustion; plasma chemical-conversion involving dry reforming, plasma pyrolysis and management of CO_2]
- **The voltage applied to gases** at intermediate-to-high pressures, during the nanosecond to microsecond time-scale typical of breakdown, **greatly affects the plasma parameters and composition**

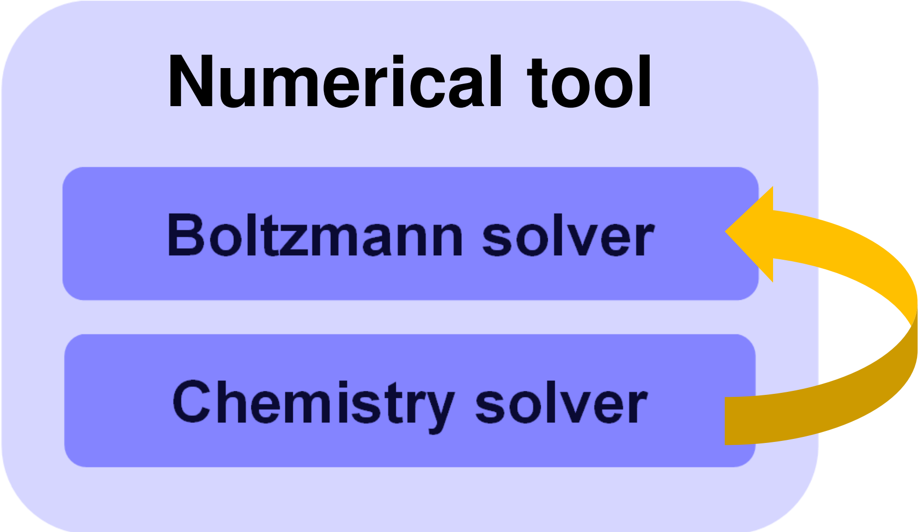
Efforts to study the time-dependent electron kinetics

- **homogeneous plasmas excited by time-varying sinusoidal electric-fields**
  [Fourier-development of 2-term electron Boltzmann equation (EBE)]
- **discharges and afterglows** [solving the time-dependent EBE]
  + coupling with heavy-particles balance equations (including VDF) or discharge models
- **electron diffusion in time-dependent *ExB* fields** [Monte Carlo simulations]
- **time or the space-time analyses of electron relaxation**
  [2-term / multi-term EBE and Monte Carlo simulations]

Seminal works of Wilhelm, Capitelli and co-workers
Recent works of Colonna et al [Colonna et al (2020); Pietanza et al (2020)]

Studies of time-dependent electron kinetics

BUT…



time description coupling assuming approximations

- using effective source terms for the electron-impact creation of excited species
  [Carbone et al (2016)]
- considering a quasi-stationary description for electrons by solving a time-independent form of the EBE for chosen values of *E/N*
  [Simek and Bonaventura (2018), Wang et al (2018), Heijkers et al (2019)]

Limitations in publicly available tools for solving the EBE ?

- ELENDIF, BOLOS, METHES, Magboltz (DC electric fields)
- BOLSIG+, EEDF, LoKI v1.0.0 (DC and HF electric fields)
- MultiBoltz (multi-harmonic model for intense microwave and THz fields)

The LisbOn KInetics Boltzmann solver (LoKI-B v2.0.0)

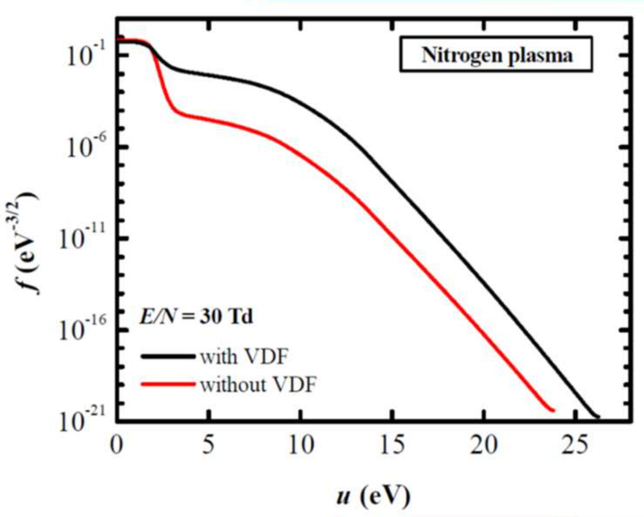
(developed under MATLAB®)

OPEN SOURCE

LoKI-B

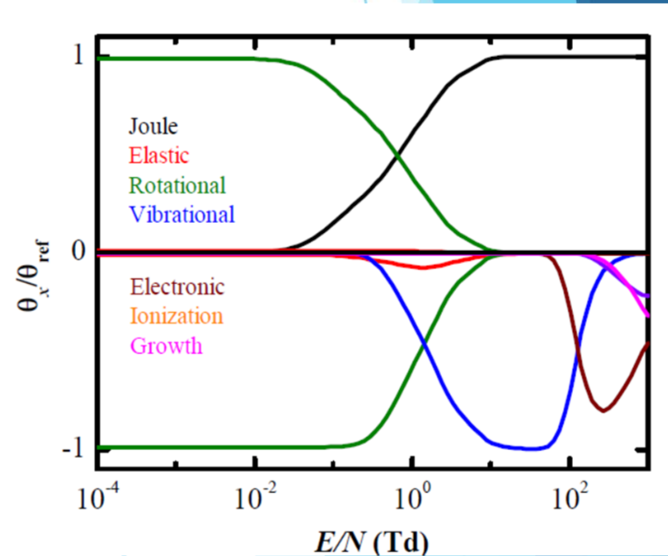
https://github.com/IST-Lisbon/LoKI

- solves the time and space independent form, or the **time-dependent form**, of the two-term electron Boltzmann equation
- includes e-e collisions, CAR operator, and growth models for the electron density.



The LisbOn Kinetics Boltzmann solver

was developed as a response to the need of having an electron Boltzmann solver easily addressing the **simulation of the electron kinetics** in **any complex gas mixture** (of atomic / molecular species), describing first and second-kind electron collisions with **any target state** (electronic, vibrational and rotational), characterized by **any user-prescribed population**.



A. Tejero-del-Caz *et al* Plasma Sources Sci. Technol. 30 (2021) 065008

loki@tecnico.ulisboa.pt

Formulation adopted - I

Time-dependent electron Boltzmann equation

- two-term approximation
- homogeneous (space-independent) description

$$F(u,\theta,t) \simeq n_e(t)\left[f(u,t) + f^1(u,t)\cos\theta\right]$$

- variation of the electron density due to non-conservative binary events (ionization and attachment)

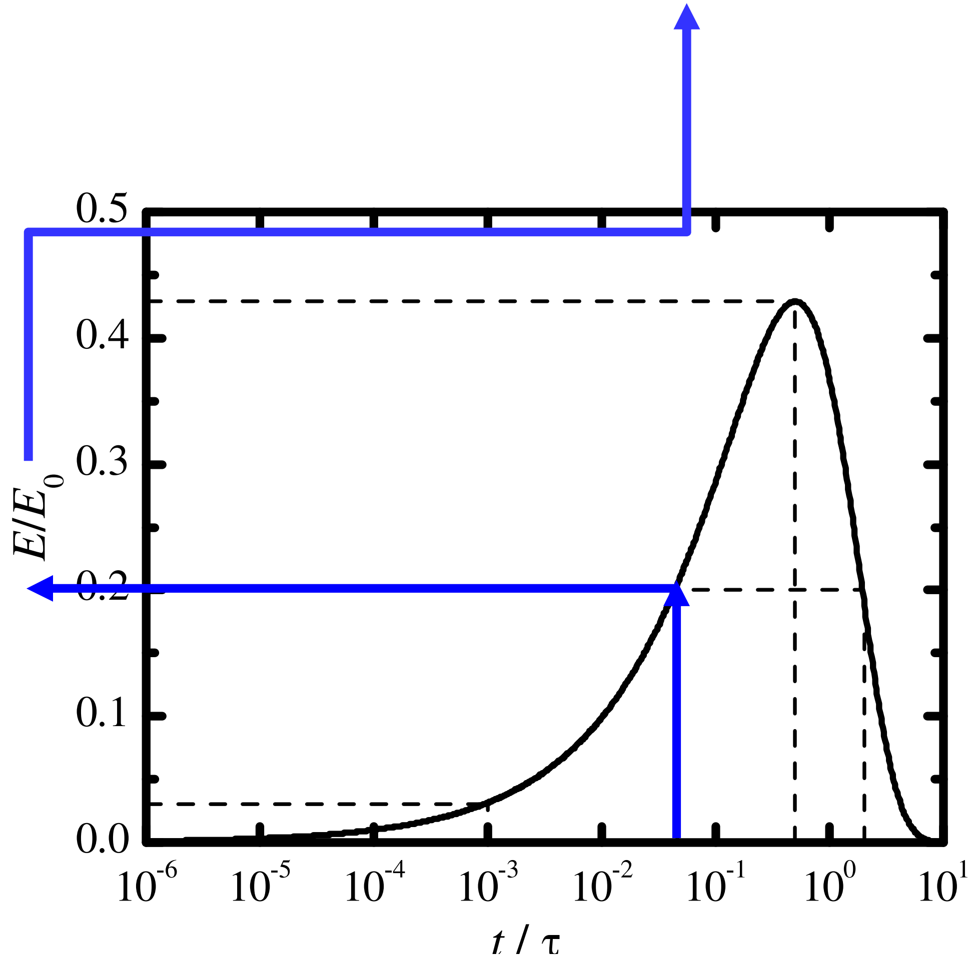
$$\begin{aligned} \frac{dn_e(t)}{dt} &= \langle\nu_{\text{eff}}\rangle(t)\, n_e(t) \\ \langle\nu_{\text{eff}}\rangle(t) &\equiv \langle\nu_{\text{ion}}\rangle(t) - \langle\nu_{\text{att}}\rangle(t) \end{aligned}$$

$$\frac{1}{N}\sqrt{\frac{m_e}{2e}}\sqrt{u}\frac{\partial f(u,t)}{\partial t} + \sqrt{\frac{m_e}{2eu}}\frac{\langle\nu_{\text{eff}}\rangle(t)}{N}uf(u,t) + \frac{1}{N}\sqrt{\frac{m_e}{2e}}\frac{\partial G(u,t)}{\partial u} = S(u,t)$$

Formulation adopted - II

Quasi-stationary electron Boltzmann equation

$$\frac{1}{N}\sqrt{\frac{m_e}{2e}}\sqrt{u}\frac{\partial f(u,t)}{\partial t} + \sqrt{\frac{m_e}{2eu}}\frac{\langle\nu_{\text{eff}}\rangle(t)}{N}uf(u,t) + \frac{1}{N}\sqrt{\frac{m_e}{2e}}\frac{\partial G(u,t)}{\partial u} = S(u,t)$$



Results in dry air

Working conditions

Dry air (80%N_2 : 20%O_2) @ $p = 10^5$ Pa and 133 Pa ; T_g = 300 K

Initial condition : Maxwellian EEDF at 300 K

Assuming

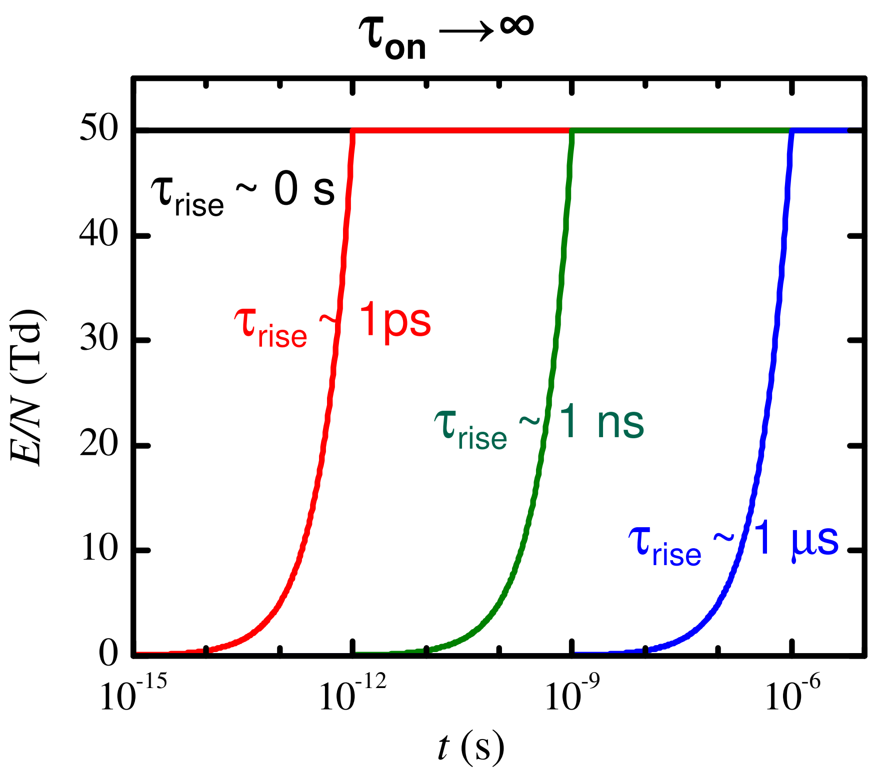
- **stationary neutral gaseous background**
  no coupling with chemistry model
- Boltzmann distributions at 300 K for the VDFs of N_2(X,v=0-10) and O_2(X,v=0-4)
- the continuous approximation to describe rotational excitations / deexcitations

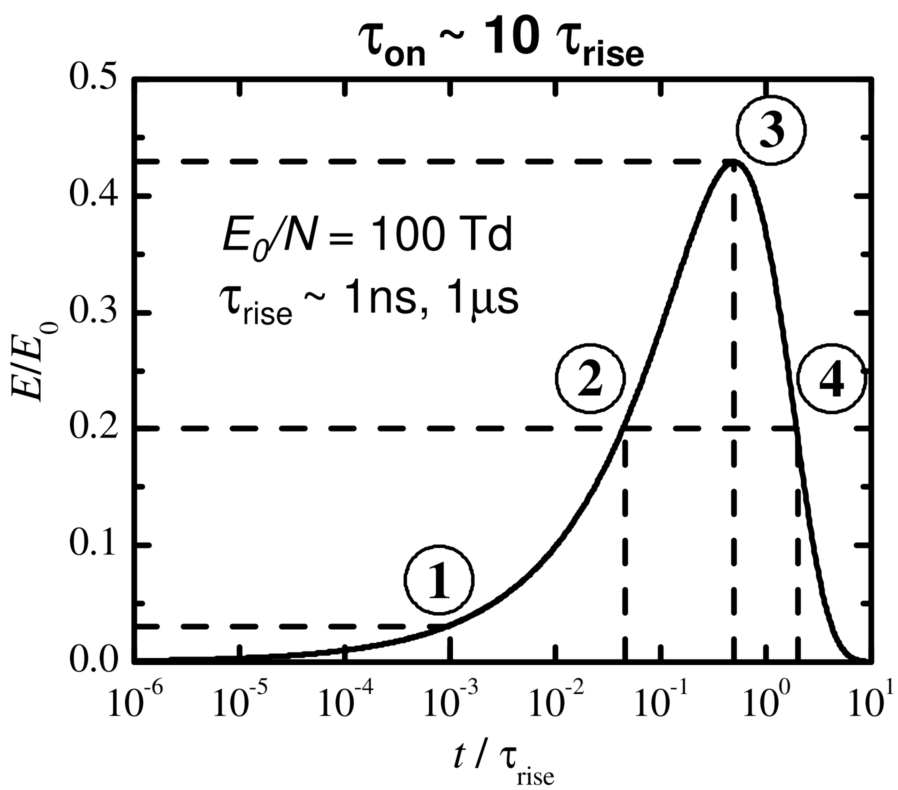
Electron-scattering cross sections published at the IST-Lisbon database with LXCat

Results in dry air

Working conditions (cont)

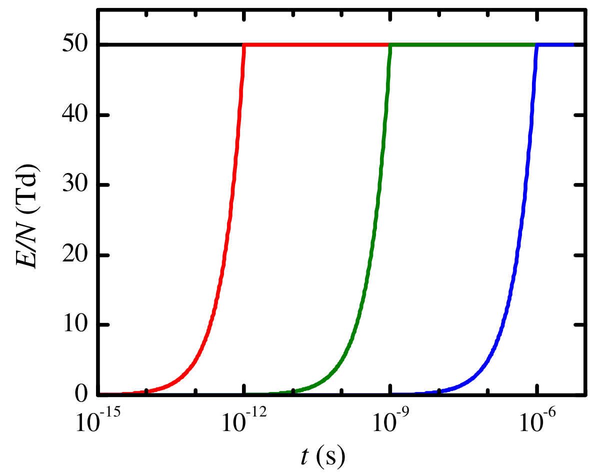
Excitation by applying electric field pulses



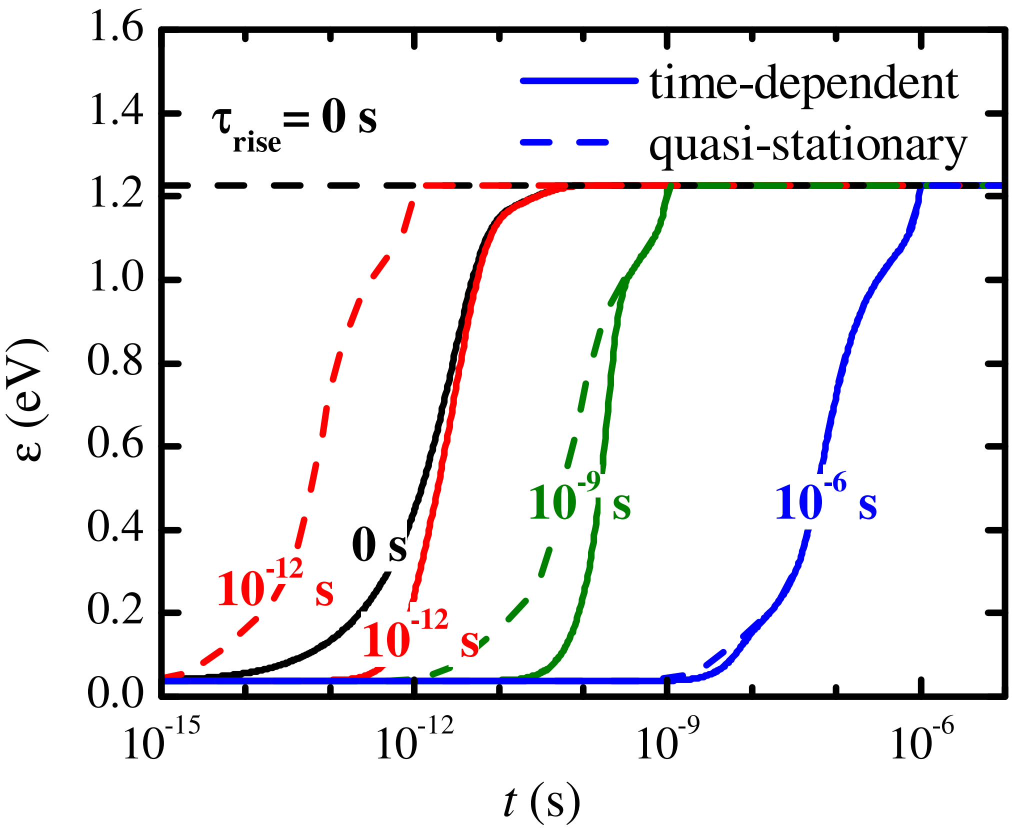


Results in dry air – step fields

The electron mean energy



$p = 10^5$ Pa



The natural response time of the electrons at atmospheric pressure is of the order of ~10ps

The quasi-stationary approach holds for rise-times much larger than the characteristic evolution time of the EEDF

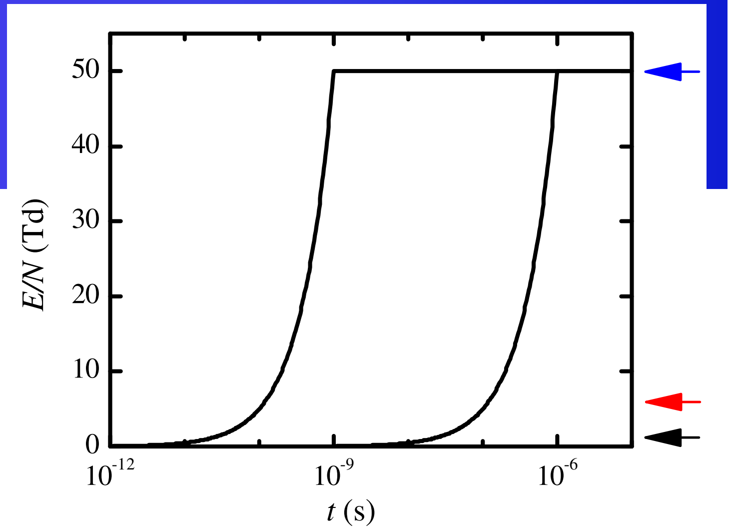
$$\tau_{\text{rise}} \gg \tau \simeq \frac{1}{\sum_k \frac{m_e}{M_k} \nu_{k,c}^{\text{el}}} \simeq \frac{5 \times 10^{17}}{N(\text{m}^{-3})}$$

At 1atm and room temperature

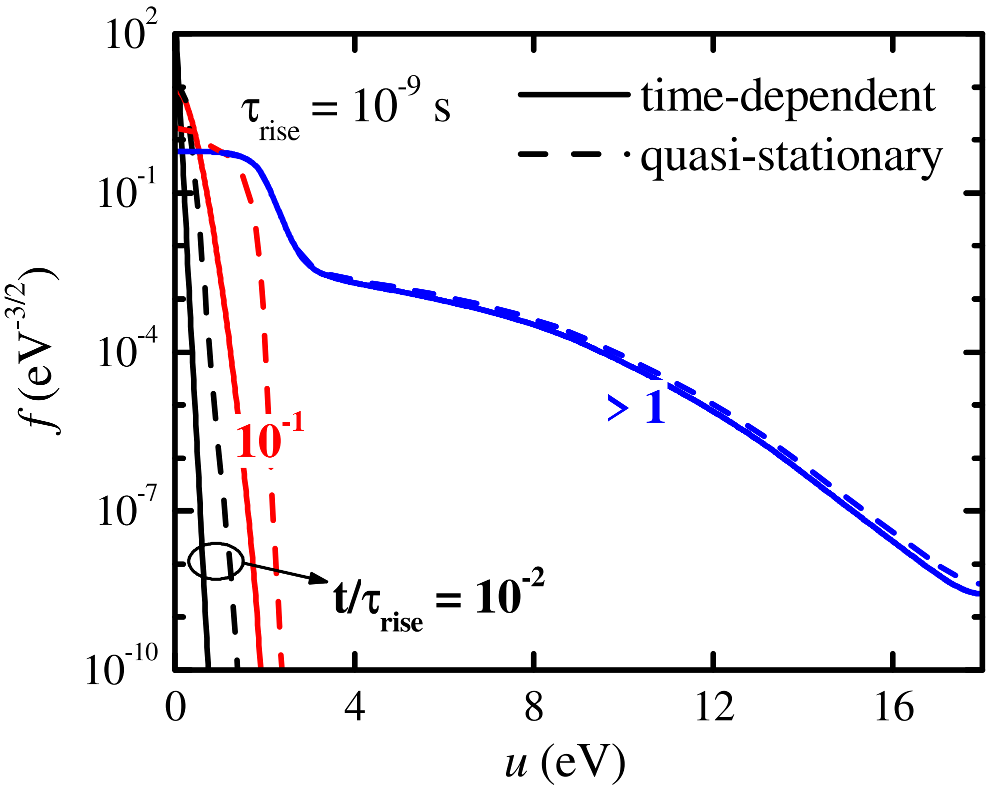
$$\tau_{\text{rise}} \gg 2 \times 10^{-8} \text{s}$$

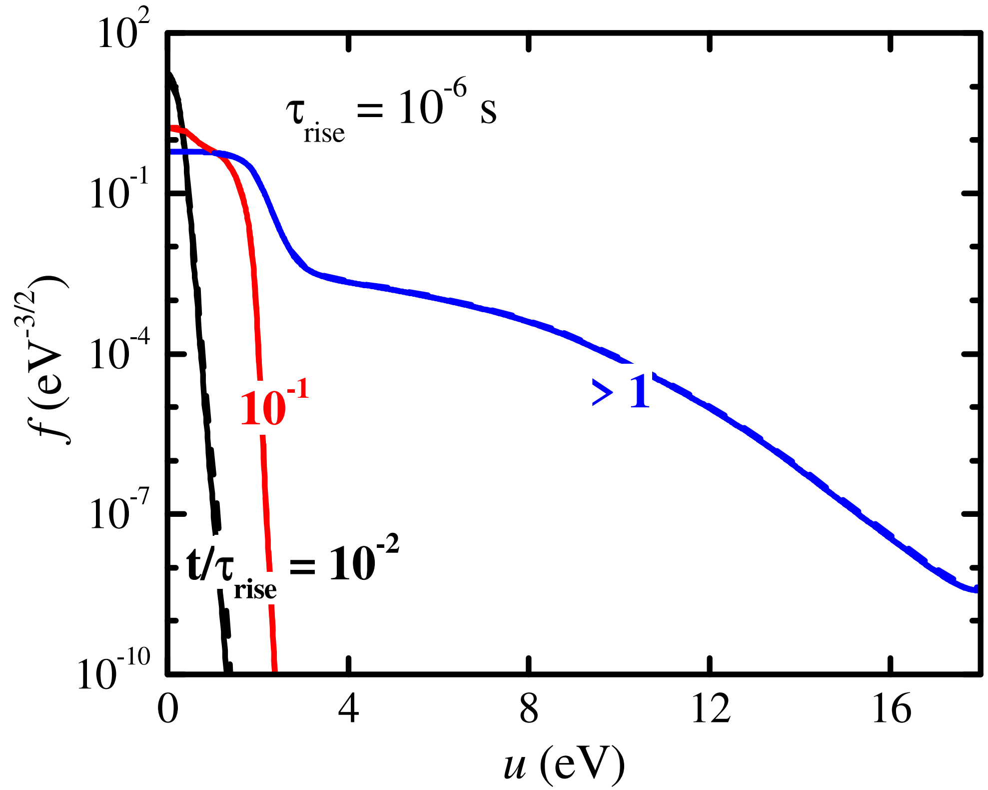
Results in dry air – step fields

The electron energy distribution function



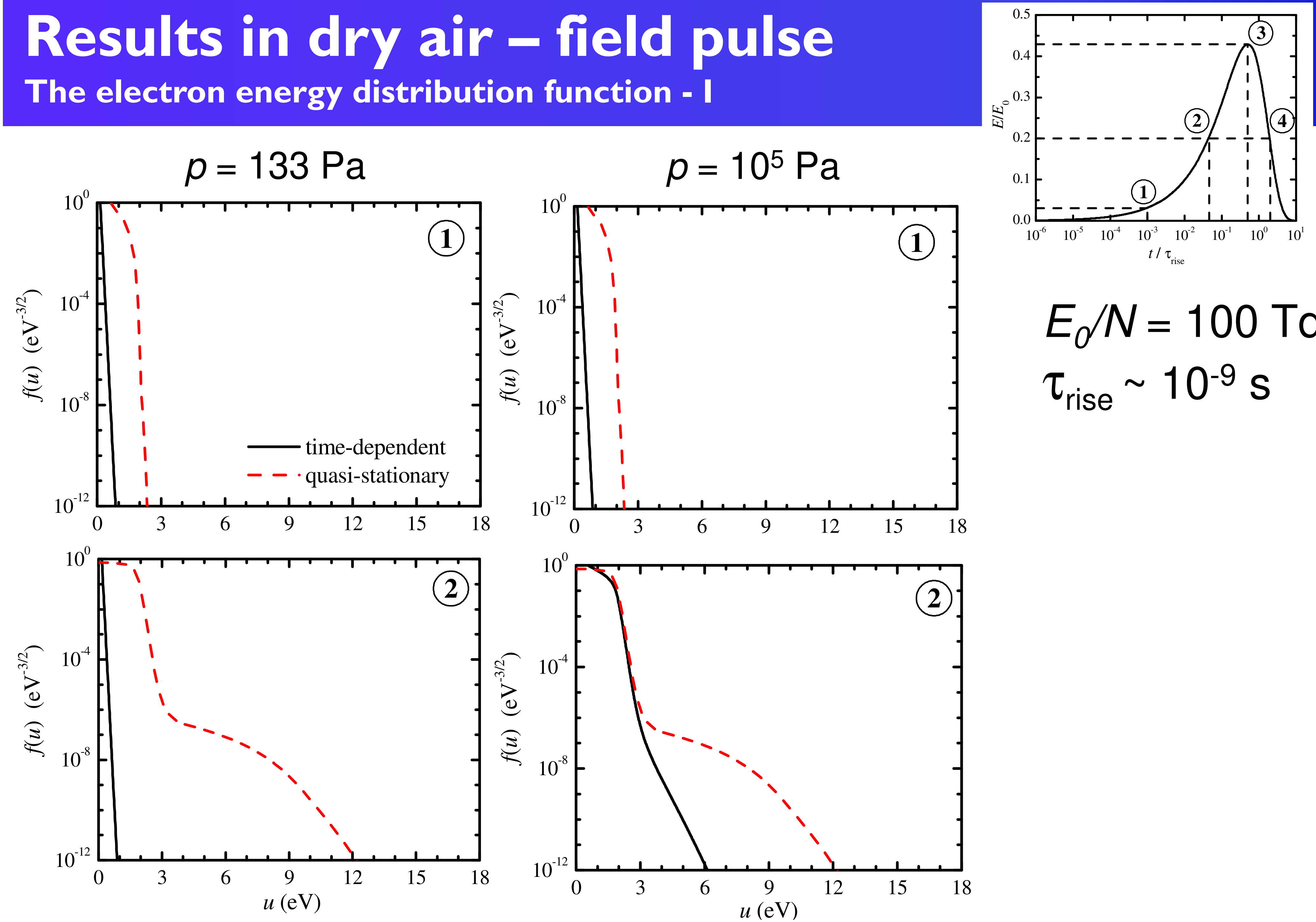
$p = 10^5$ Pa





Results in dry air – field pulse

The electron energy distribution function - I



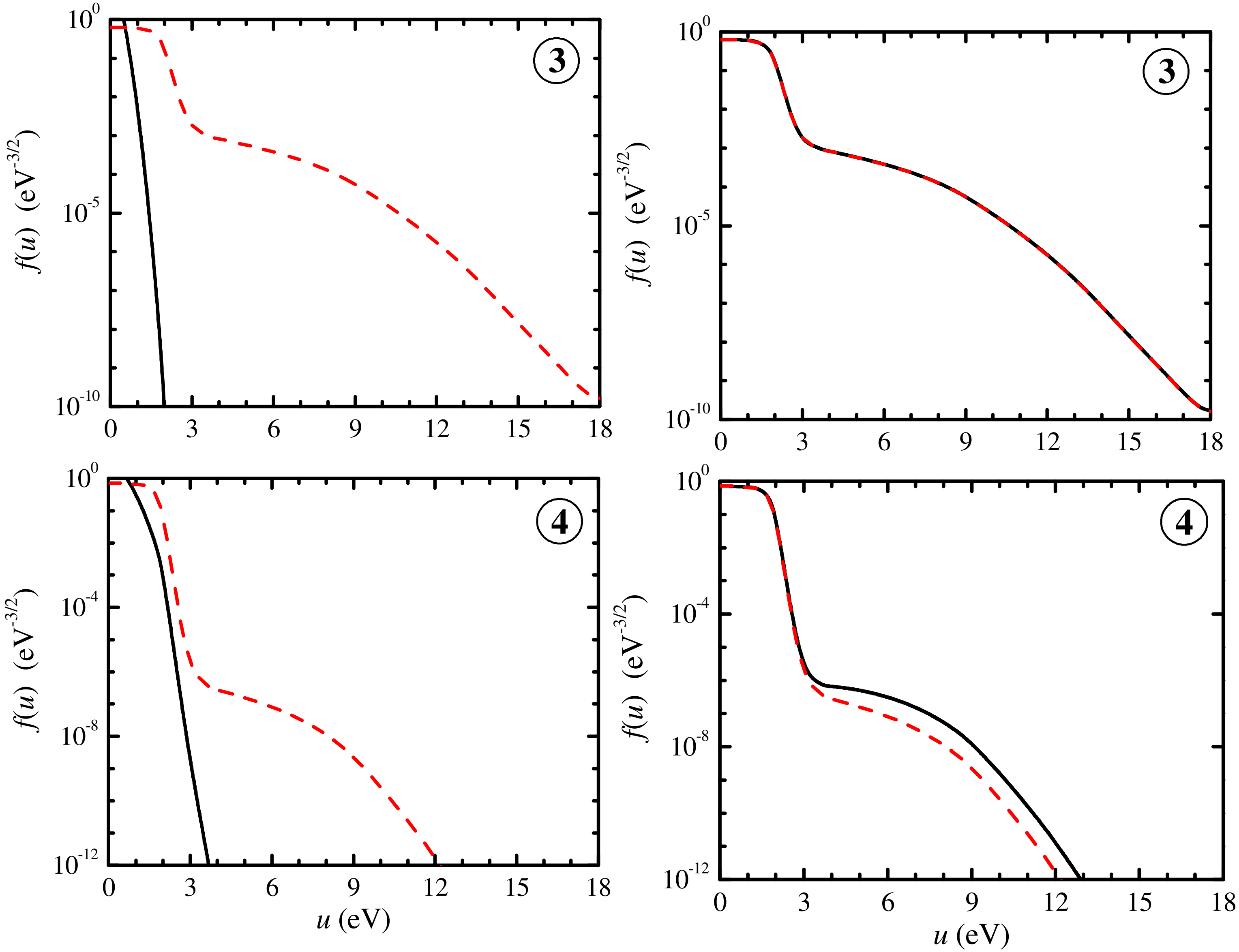
E_0/N = 100 Td

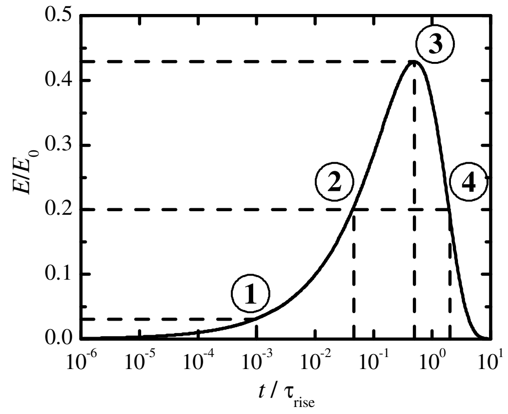
$\tau_{rise} \sim 10^{-9}$ s

Results in dry air – field pulse
The electron energy distribution function - II

p = 133 Pa

p = 10^5 Pa



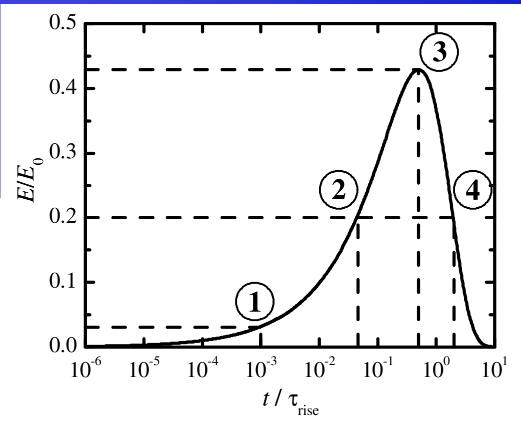


E_0/N = 100 Td

τ_{rise} ~ 10^{-9} s

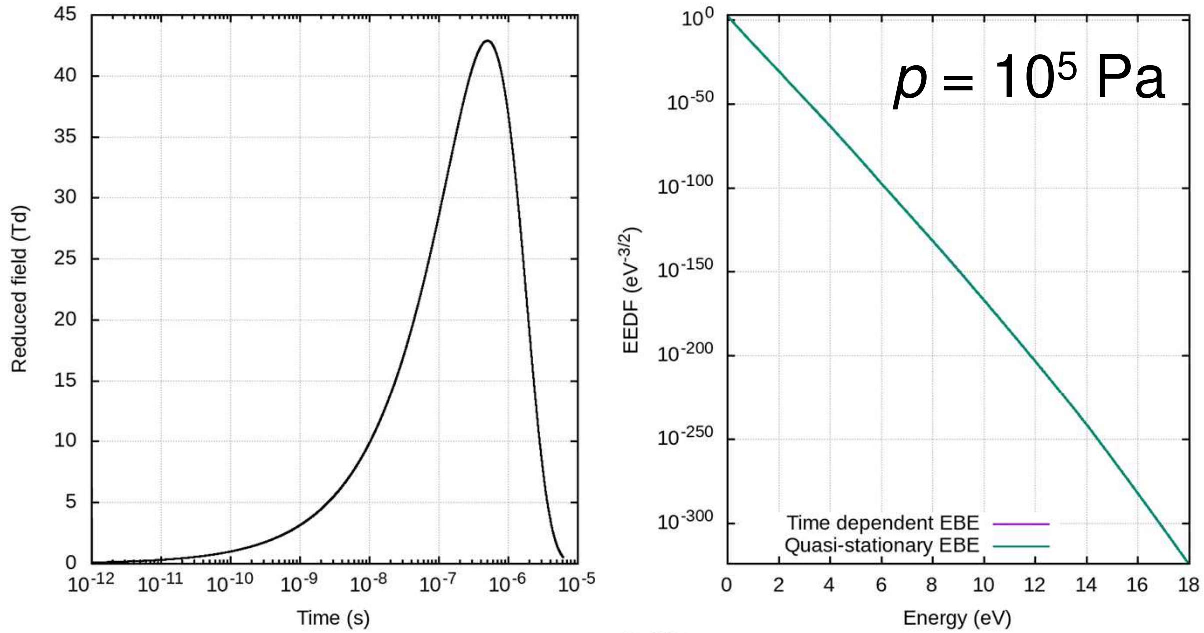
Results in dry air – field pulse

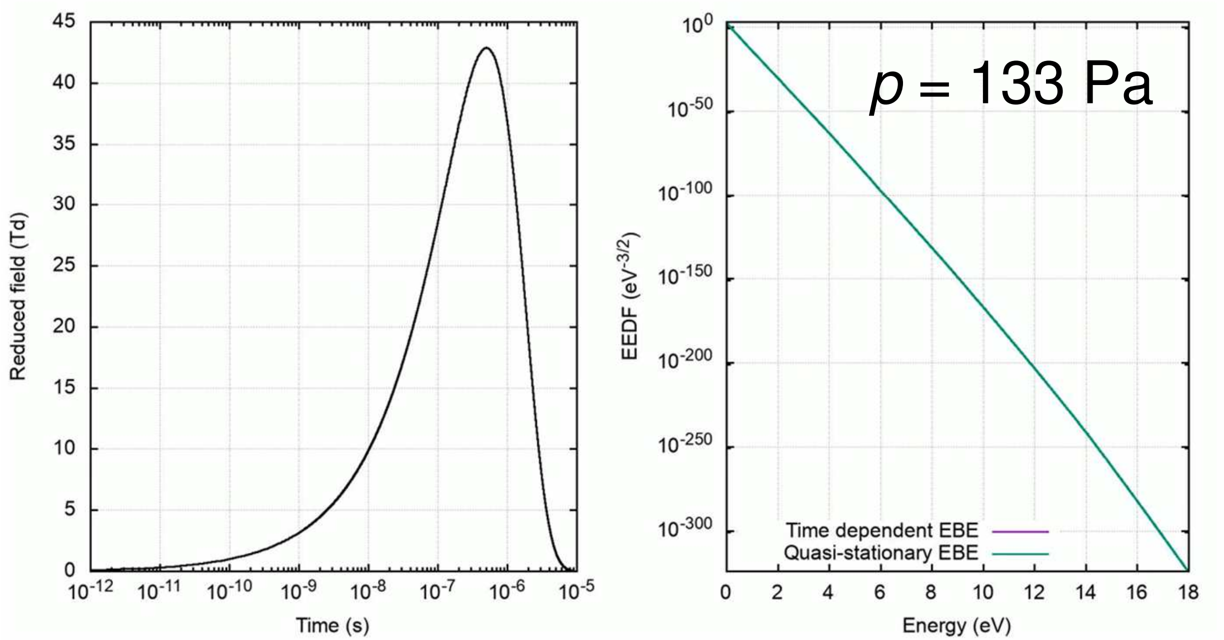
The electron energy distribution function - III



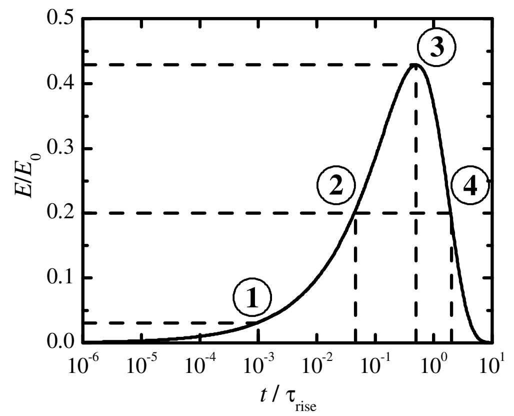
E_0/N = 100 Td

$\tau_{rise} \sim 10^{-6}$ s





Results in dry air – field pulse
Criterion for quasi-stationary simulations



The quasi-stationary approach holds for

$$\tau_{\text{rise}} \gg \tau \simeq \frac{1}{\sum_k \frac{m_e}{M_k} \nu_{k,c}^{\text{el}}} \simeq \frac{5 \times 10^{17}}{N(\text{m}^{-3})} \implies \tau_{\text{rise}} N \simeq \text{const}$$

		p = 10^5 Pa and τ = $2\text{x}10^{-8}$ s	p = 133 Pa and τ = $2\text{x}10^{-5}$ s
τ_{rise}	10^{-9} s	Fail	Fail
τ_{fall}	10^{-8} s	Fail	Fail
τ_{rise}	10^{-6} s	**OK**	Fail
τ_{fall}	10^{-5} s	**OK**	Fail

At low pressure, there is no “instantaneous” collisional transfer of the E-field energy into the gas, hence the slow temporal increase of the electron mean (kinetic) energy

Final remarks

Relevance of the electron kinetics in the predictive modelling of LTPs
Two examples

- **Modelling of low-pressure ccrf discharges in N_2-H_2**
  - a proper treatment of electron secondary emission is key to obtain realistic predictions for the plasma / discharge parameters
  - when adopting fluid simulations, a beam model for fast electrons improves the description of the electron particle and energy distribution
  - the model reproduces adequately the global trends of the ion flux measurements
  - model predictions for NH_3

    * are in good agreement with measurements, as a function of power

    * could benefit from a better description and/or the inclusion of additional mechanisms as a function of pressure

    [the calculated spatial distribution of ions could also improve]

Final remarks

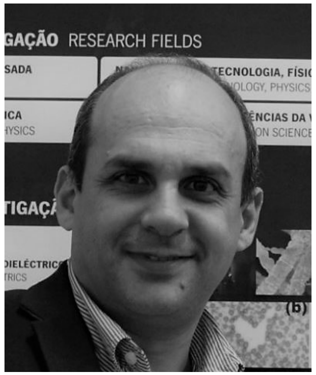
- **Electron kinetics in dry-air pulsed plasmas**
  - excitation by electric-field pulses (τ_{rise} ~ ns to μs) at p = 133 Pa, 10^5 Pa
  - adopting (i) time-dependent formulation; (ii) quasi-stationary approach
  - the quasi-stationary description
    * holds for high-collisionality and long rise-times (τ_{rise} ~ μs at p_{atm})
    * fails for fast risetimes (τ_{rise} ~ ns for all *p's*)
  - similar results are obtained for
    long pulses / low pressures and short pulses / high pressures
    → optimization of the pulse duration, depending on the gas pressure, to maximize electron energy absorption
  - simulations were applied to a stationary neutral gaseous background
    The inclusion of the effects of heavy-particle interactions (e.g., VVs & VTs), in fully-coupled time-dependent Boltzmann-Chemistry calculations, can alter modelling predictions (especially beyond the μs scale and/or in multi-pulse scenarios).

Acknowledgements

People

A Tejero-Del-Caz

M Jimenez-Redondo



L Marques

and

A Chatain
O Guaitella
G Cernogora
N Carrasco
V. Guerra
N Pinhão
C D Pintassilgo

Funding institutions

FCT
Fundação para a Ciência e a Tecnologia
MINISTÉRIO DA CIÊNCIA, TECNOLOGIA E ENSINO SUPERIOR

erc

université PARIS-SACLAY

LATMOS

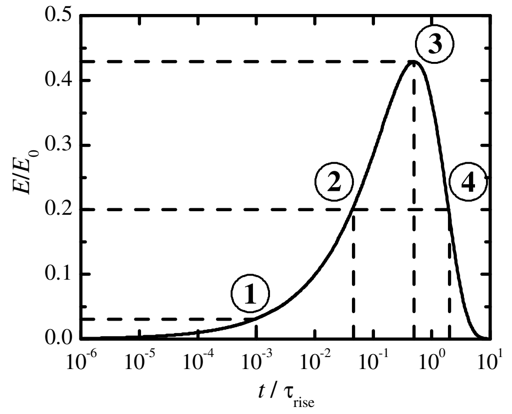
LPP

Questions ?

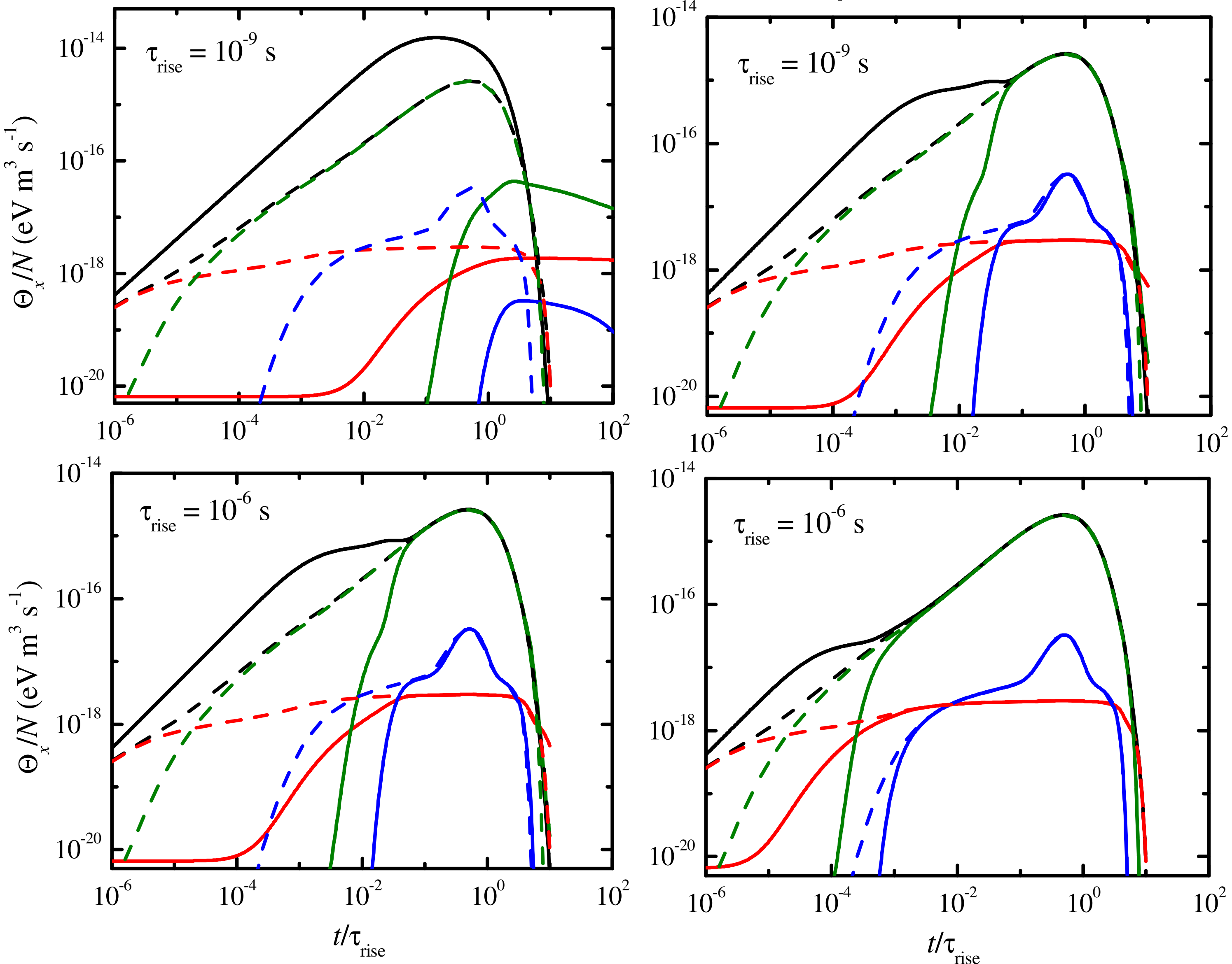
Results in dry air – field pulse

The power balance per electron (at unit gas density)

$$\frac{d\varepsilon(t)}{dt} = \Theta_{\mathrm{growth}} + \Theta_E - \Theta_{\mathrm{rot}} - \Theta_{\mathrm{vib}} - \Theta_{\mathrm{ele}}$$



p = 133 Pa | $p = 10^5$ Pa

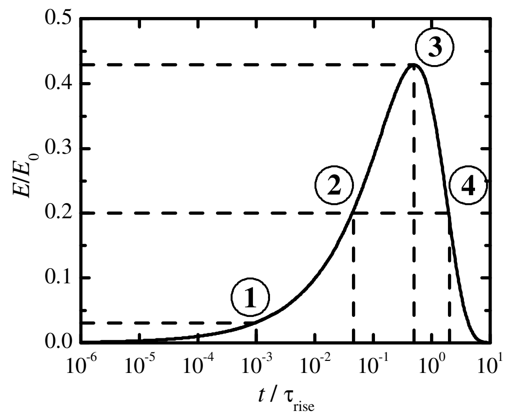


E_0/N = 100 Td

time-dependent
quasi-stationary

Results in dry air – field pulse

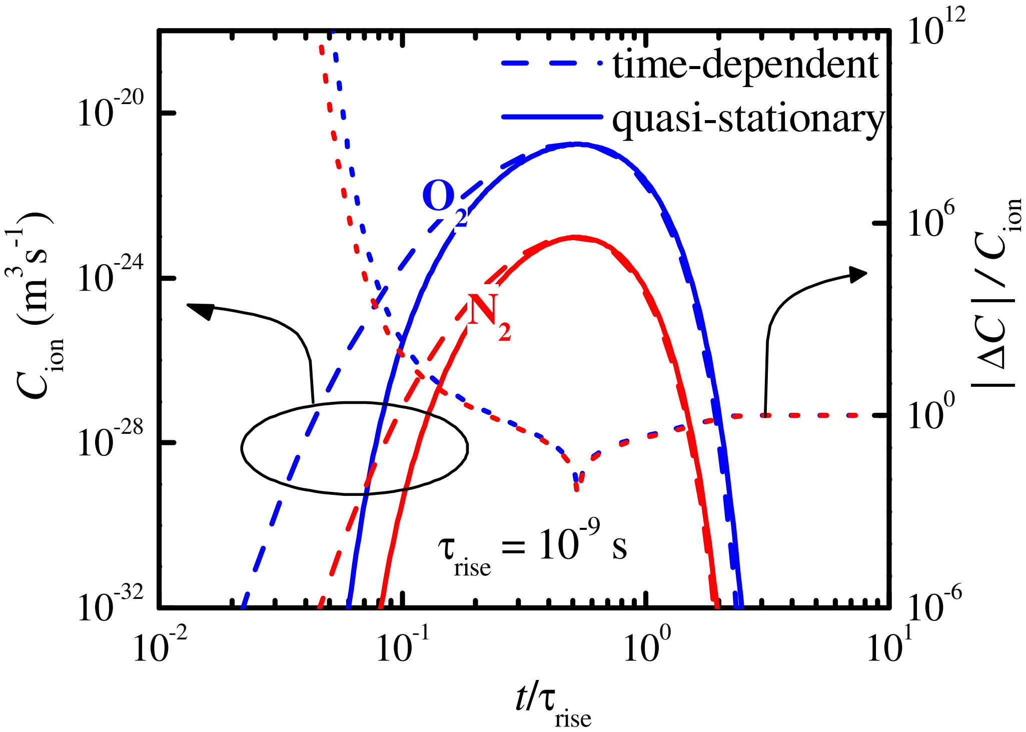
Ionization rate coefficients

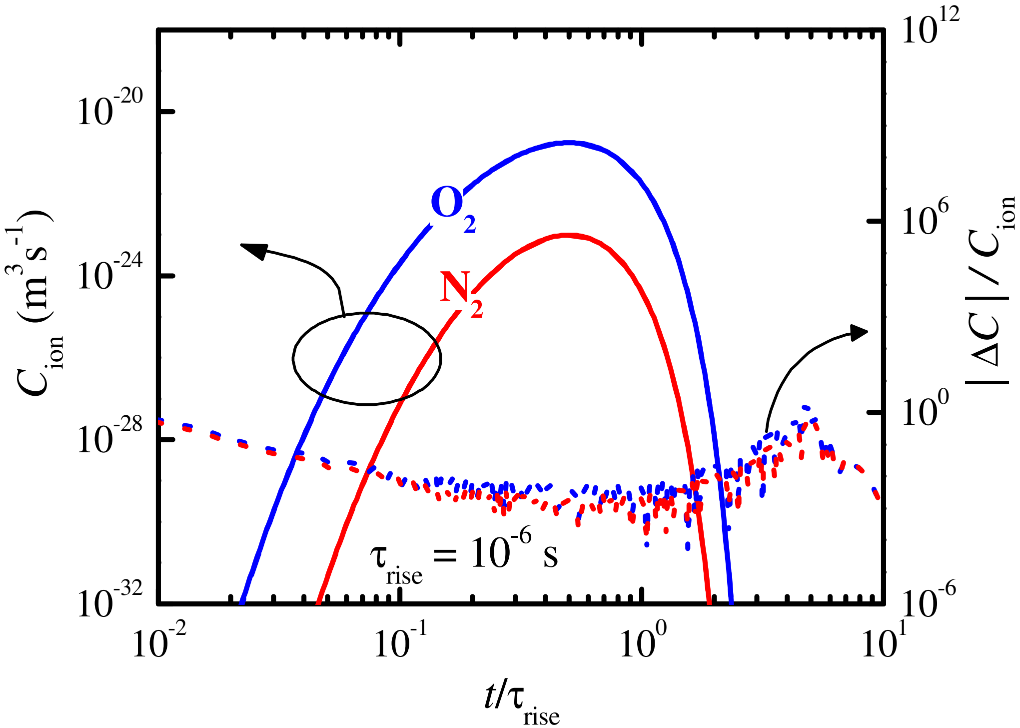


$p = 10^5$ Pa

$\tau \sim 2x10^{-8}$ s

$E_0/N = 100$ Td





Similar observations for other (excitation) rate coefficients

Formulation adopted – I (complement)

Time-dependent electron Boltzmann equation

$$\frac{1}{N}\sqrt{\frac{m_e}{2e}}\sqrt{u}\frac{\partial f(u,t)}{\partial t}+\sqrt{\frac{m_e}{2eu}}\frac{\langle\nu_{\text{eff}}\rangle(t)}{N}uf(u,t)+\frac{1}{N}\sqrt{\frac{m_e}{2e}}\frac{\partial G(u,t)}{\partial u}=S(u,t)$$

$$f^1(u,t)=-\frac{(E(t)/N)}{\Omega_c(u,t)}\frac{\partial f(u,t)}{\partial u}$$

… steady-state form

The characteristic evolution time of the EEDF is much larger than the characteristic evolution time of the anisotropic component

$$\tau\simeq\frac{1}{\sum_k \frac{m_e}{M_k}\nu_{k,c}^{\text{el}}}\gg\frac{1}{\sum_k \nu_{k,c}^{\text{el}}}$$

$G(u,t)$ … *upflux* function (e.g., ohmic heating, elastic, rotational, Coulomb **continuous** operators)

$S(u,t)$ … inelastic / superelastic collision **discrete** operator

$$\Omega_c(u,t)\equiv\sigma_c(u)+\sqrt{m_e/(2eu)}(\langle\nu_{\text{eff}}\rangle(t)/N)$$