Power Manipulation & Laser Agitation
Relaxation Experiments on Plasmas

Joost van der Mullen

Université Libre de Bruxelles B
Fontys University, Tilburg NL

Cordoba; 7 September 2015

Creating
- New projects
- New insights
- New Doctors & Masters

Breaking
Conservative Academic Forces

STW
Philips
Draka
ECN
ASML

TU/e

Vimeiro: Iberia Spring 1992

NATO ASI series Carlos Ferreira and Michel Moisan.
Microwave Discharges; Fundamentals and Applications

Eindhoven big delegation
No MW plasmas: mainly Big DC machines Cascaded Arc,
ICP exception

Selling PLASIMO to Thorn EMI **Graem Lister**
Learning Microwave Discharges
Meeting Cordoba Group: Los Sabios

jvdM termonology
pLSE
EEK
etc.

Un Holandes perdido en Cordoba

Month later: Visit to Cordoba: (Sevilla)

Exchange of Students

Develop/improve Methods

Projects

Bilateral Collaboration Framework Cordoba <-> Eindhoven

Profesor Invitado $\rightarrow$ Thesis Director of own projects.

Exchange of Students

Eric Timmermans
Jeroen Jonkers
Frank Fey
Harald Vos
Dany Benoy
Harm van der Heijden
Bart Hartgers
Marco van de Sande

Jesus Torres
Antonio Jurado
Manuel Fernandez
WillemJan van Harskamp
Nienke de Vries
Manuel Jimenez
Katia Iordanova
Jose-Maria Palomares

Cordoba Eindhoven
Sofia

→

Mariana Atanasova
Thesis 2013
Gerard Degrez
Evgenia Benova

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Manuel Jimenez
Katia Iordanova
Jose-Maria Palomares

Almost Dutch

Methods

Absolute OE S Continuum

Absolute OES lines

H- Line shapes Widths - Peaks - Calderas

Stark Intersection Method

TS with iCCD detection

Projects

Plasmas for environment (Jean Bacri; Toulouse)

AVR Chemie (on-line monitoring waste destruction incinerator)

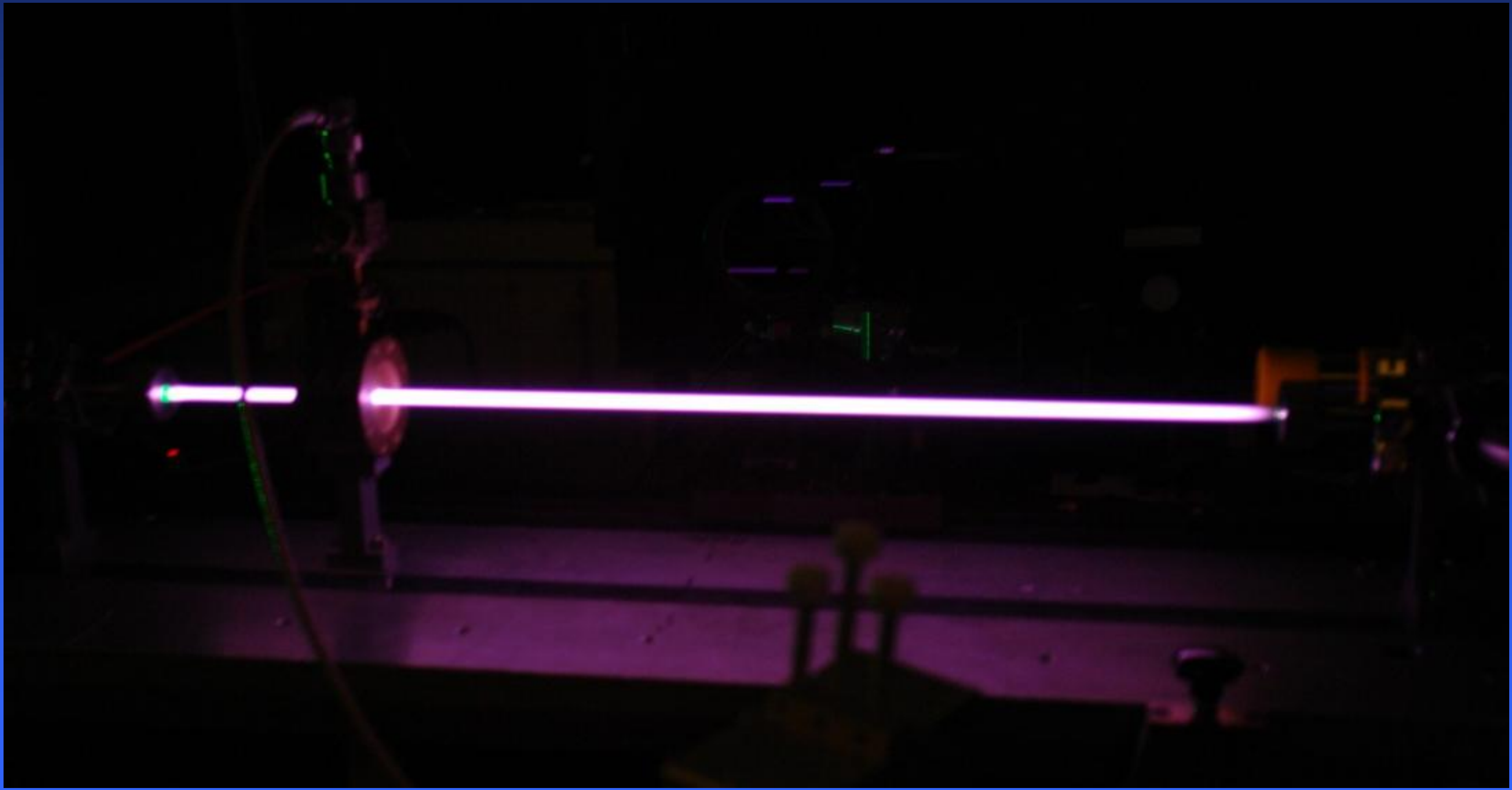
COST on lighting

Optical Fibres (Draka company)

Solar cells   (ECN)

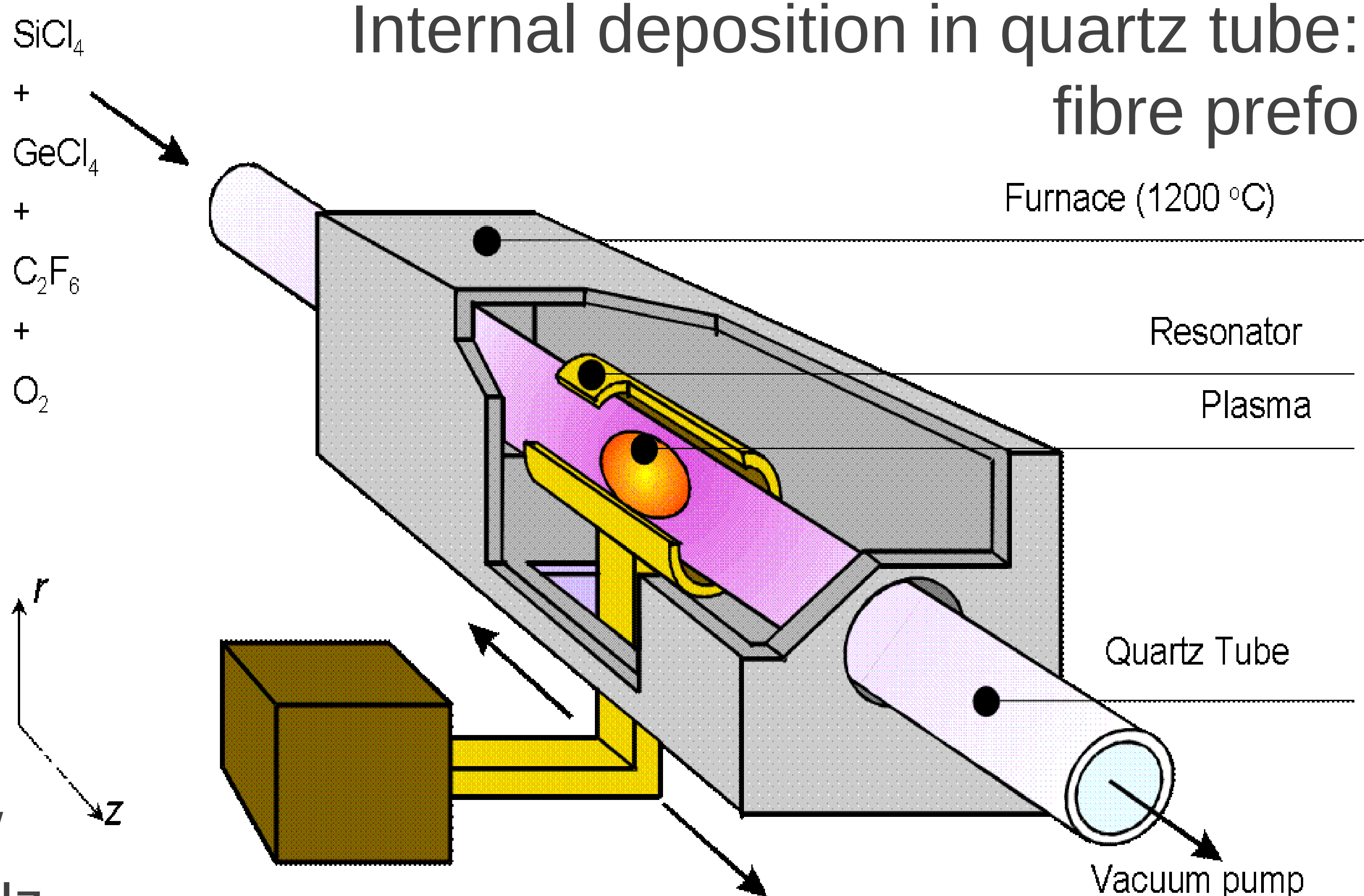
CO_2 valorisaion

The plasma source: a low-p SIP



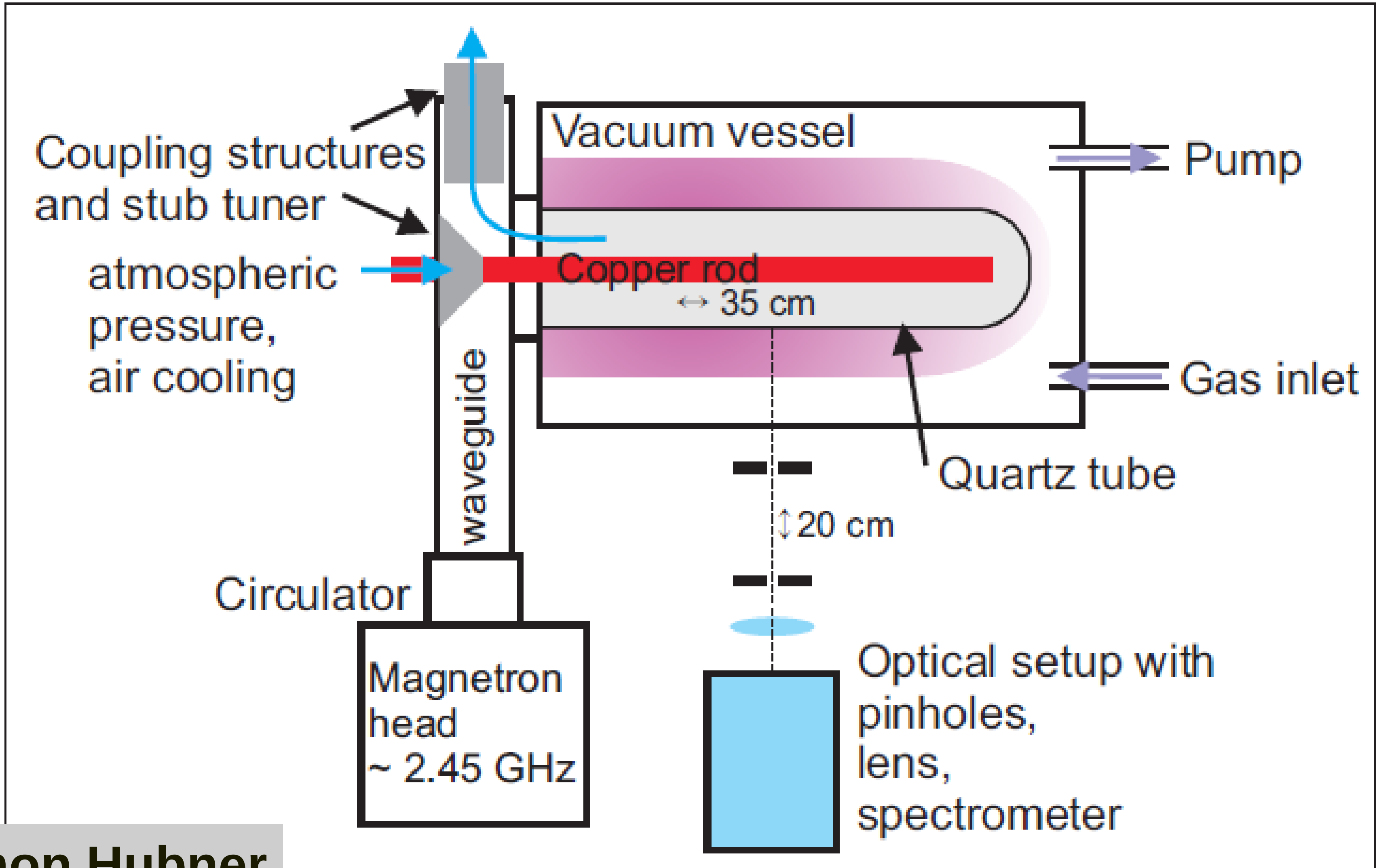
Inspiration form industry: Travelling MIP

Internal deposition in quartz tube: fibre preform



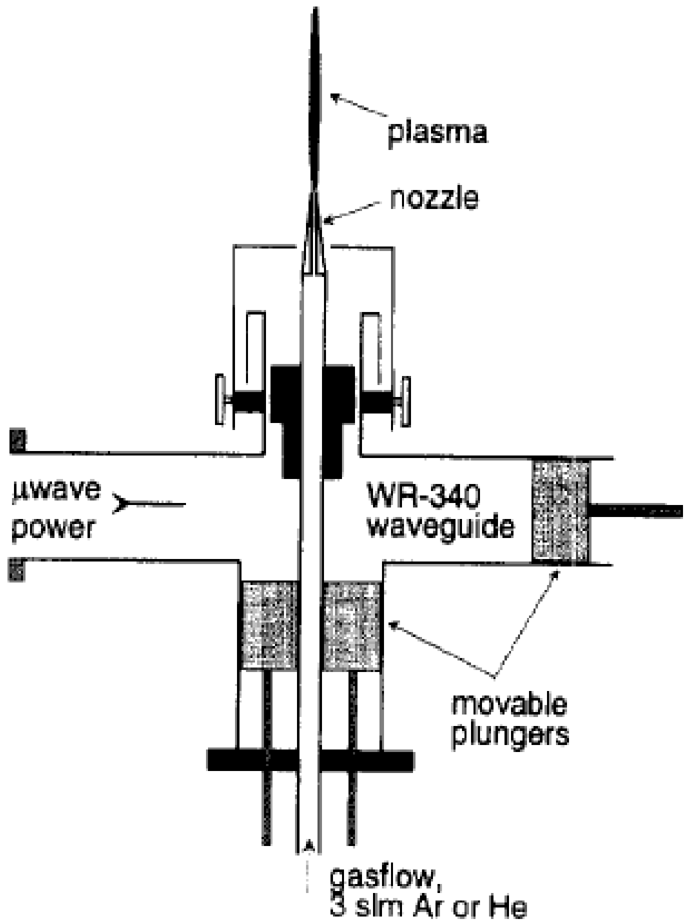
P = 1-4 kW
f = 2.45 GHz
p = 10mbar

The coaxial system

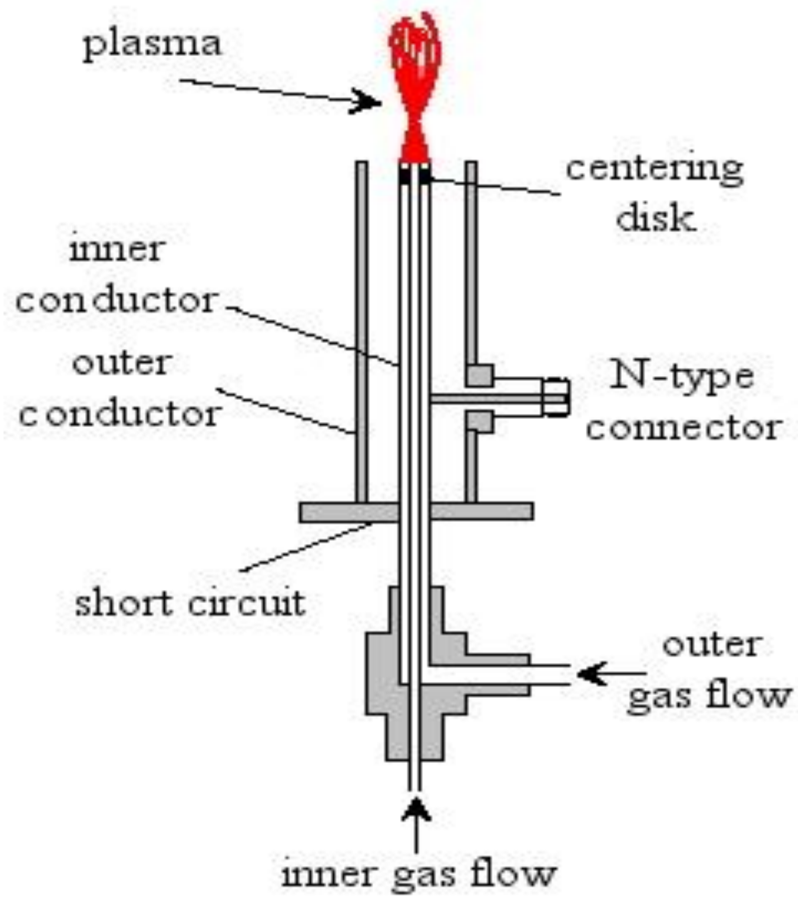


Simon Hubner

Atmospheric sources I

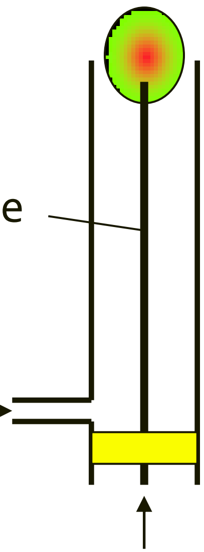


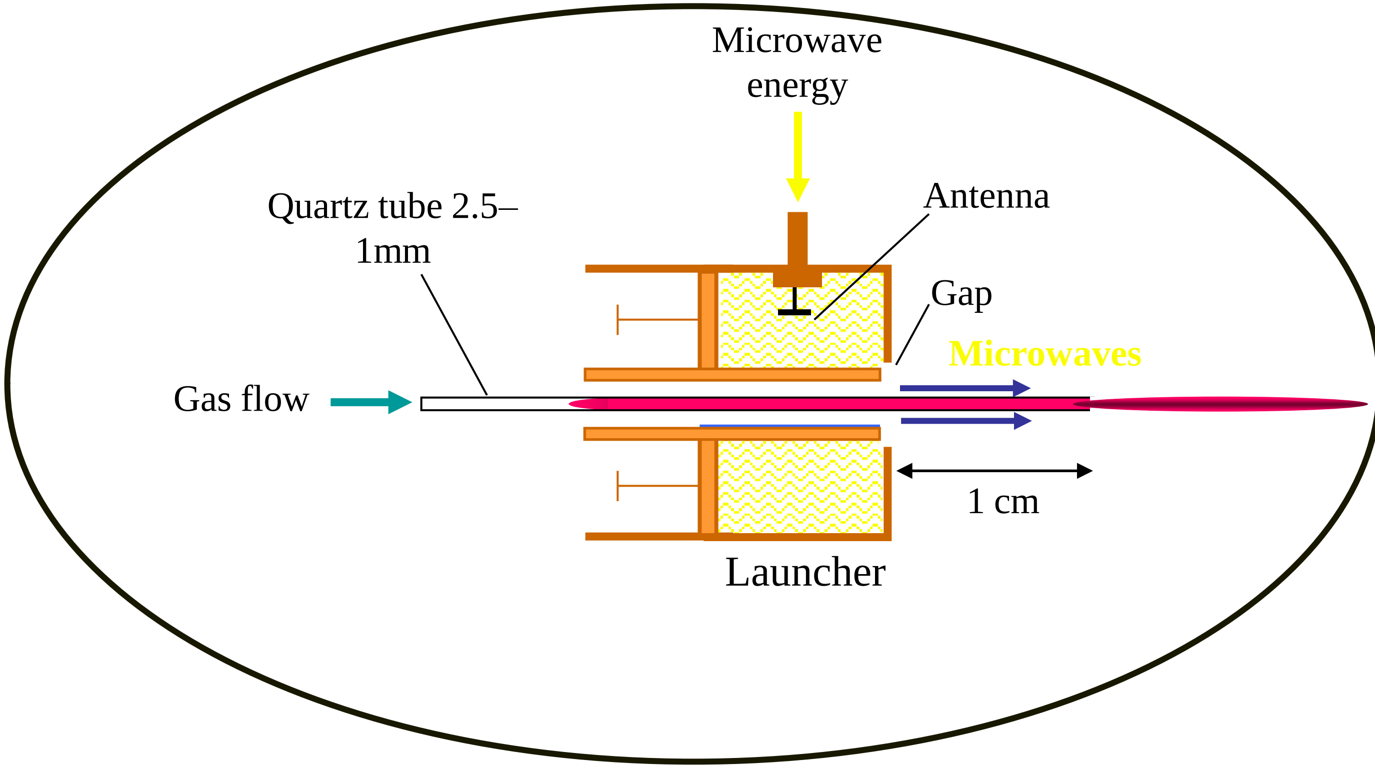
TIA



MPT

Atmospheric sources 2

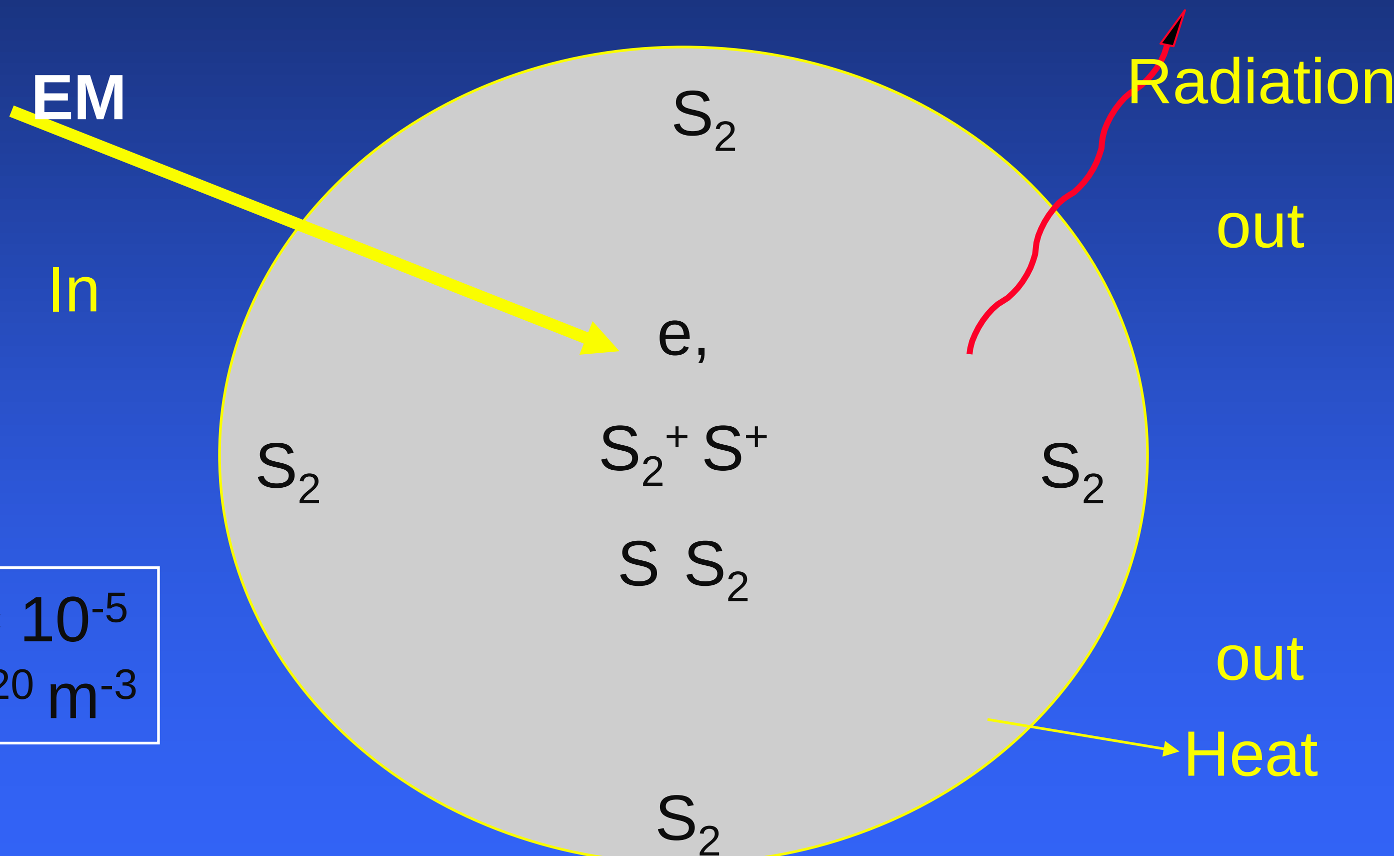




Gdansk jet

Surfatron

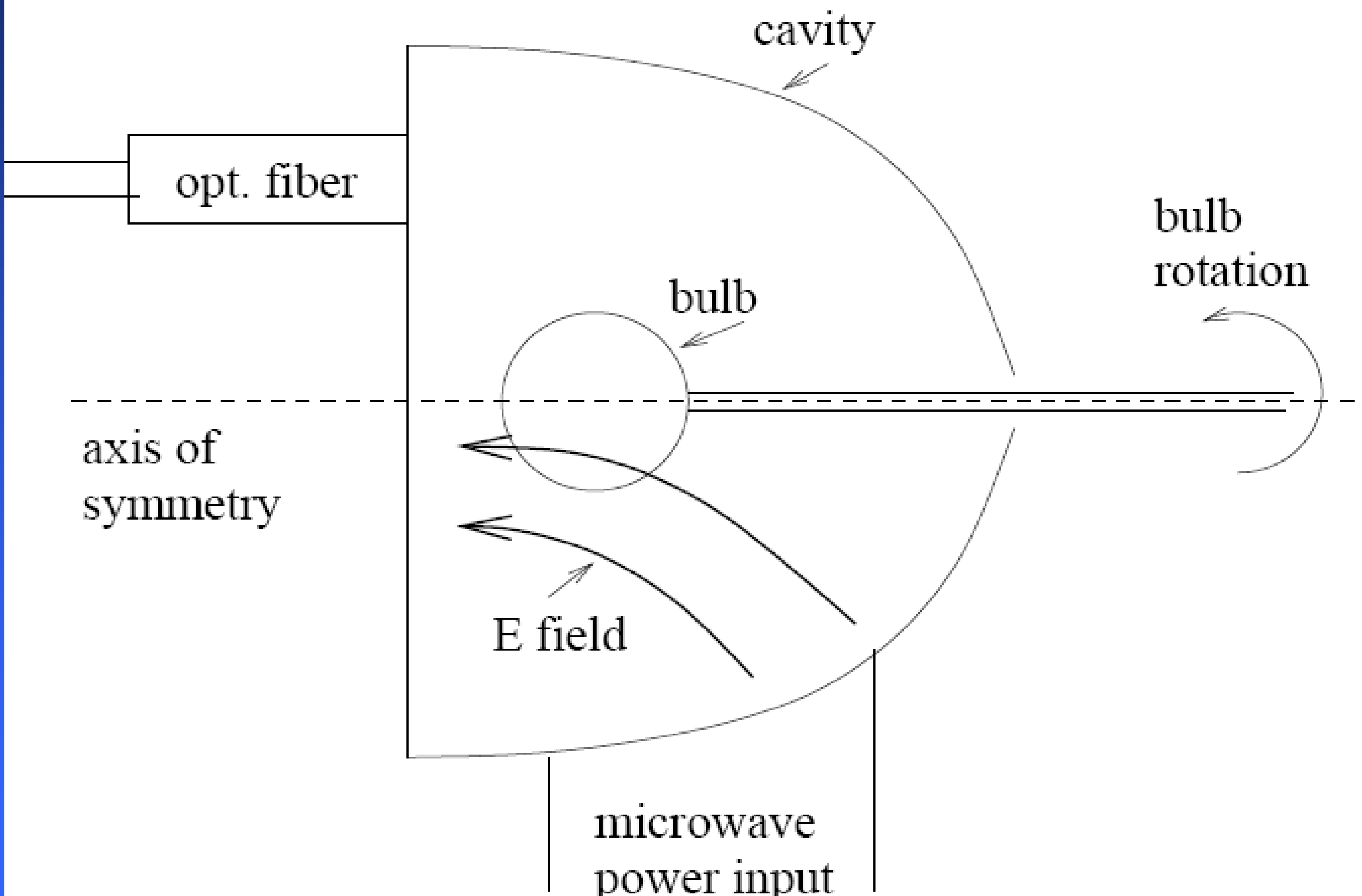
The Sulfur lamp



$n_e / n_1 \approx 10^{-5}$

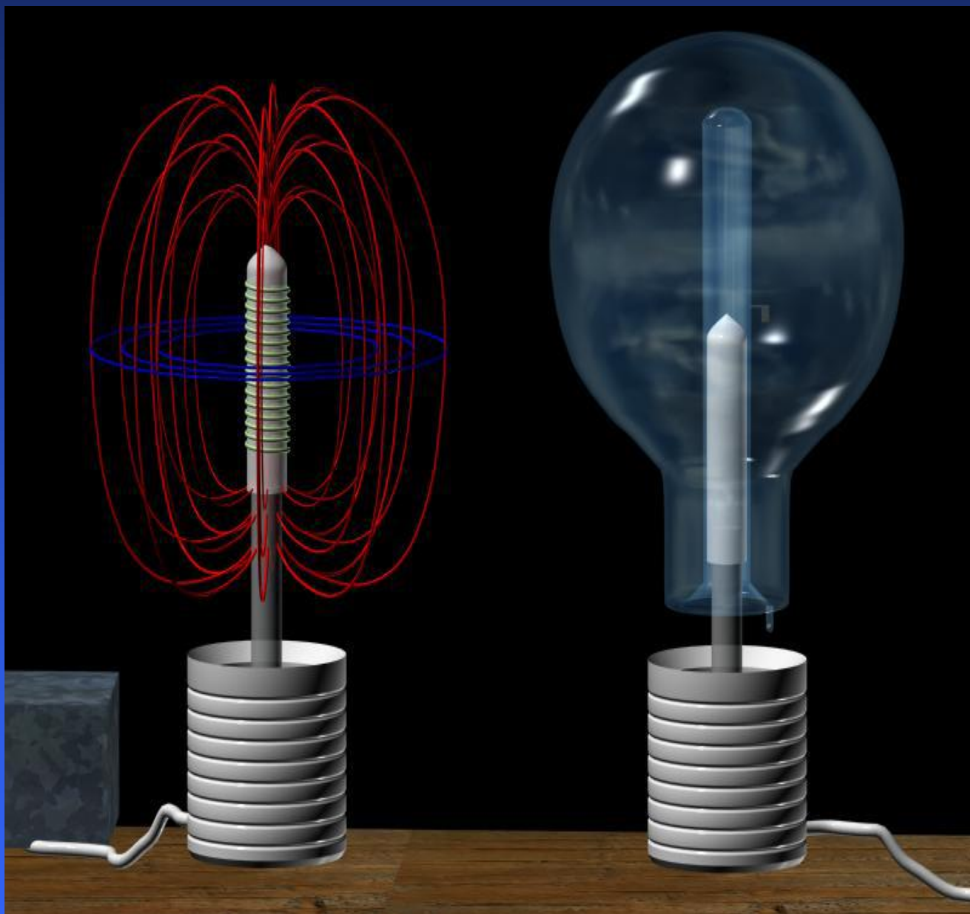
$n_e \approx 10^{20}\ m^{-3}$

In 1992 a candidate for the illumination Sidney 2000



U/e

The 2.45 GHz driven QL lamp



Inductively

Microwave induced

Relaxation

Time lag: application of an external stress to a system
and its response.

Nobel Prize for Chemistry in 1967.
For studies of extremely fast chemical reactions,
effected by equilibrium disturbance by very short pulses of energy.

Manfred Eigen:
Equi-Disturbance: rapid changes in temperature or pressure
Power manipulation: follow the passage to a new equilibrium.

Ronald Norrish and **George Porter**
flash photolysis, i.e. by short light flashes.

Relaxation Applied to plasmas

Power Interruption

D.B. Gurevich & I.V. Podmoshenskii,
Opt. Spectrosc. 15 (1963) 319

E.I. Bydder, G.P. Miller SAB 43 (1988) 819

F.H.A.G. Fey, W.W. Stoffels, J.A.M. van der Mullen,
B. Van der Sijde, D.C. Schram; SAB (1991) 885

t-Laser induced Fluorescence : t-LIF (not n- LIF nor v-LIF)

N. Omenetto, O.I. Matveev,
reservoirs, Spectrochim. Acta Part B 49 (1994) 1519–1535.

J.M. Palomares, W.A.A.D. Graef, S. Hübner,
J.J.A.M. van der Mullen SAB 2013

Relaxation Techniques in Plasmas

Aim: Understanding Equilibrium (departure)
Get rate coefficients

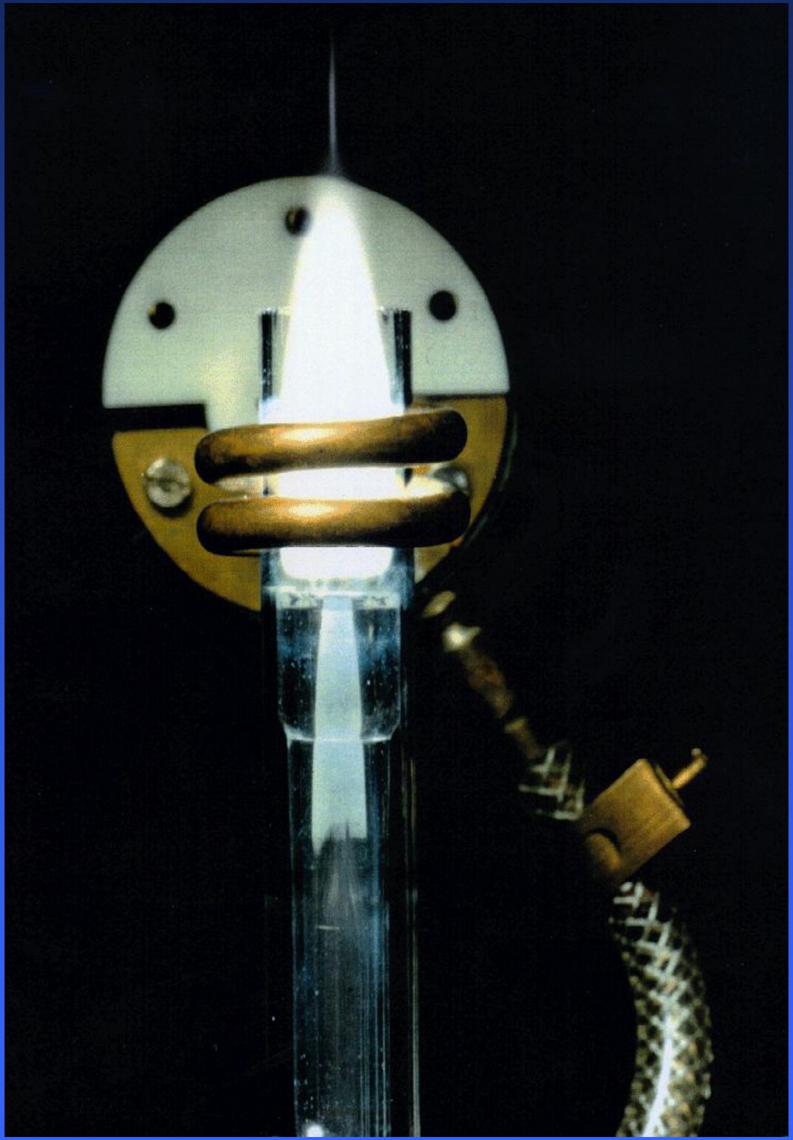
Method **Kick-up & Cool-down**

Two approaches

1) Power Interruption and Re-Ignition — **Global** $\Delta n_e \neq 0$ $\Delta T_e \neq 0$

2) t-resolved LIF — **Specific** $\Delta n_e = 0$ $\Delta T_e = 0$

The atmospheric Inductively Coupeld Plasmas



p = 1 atm

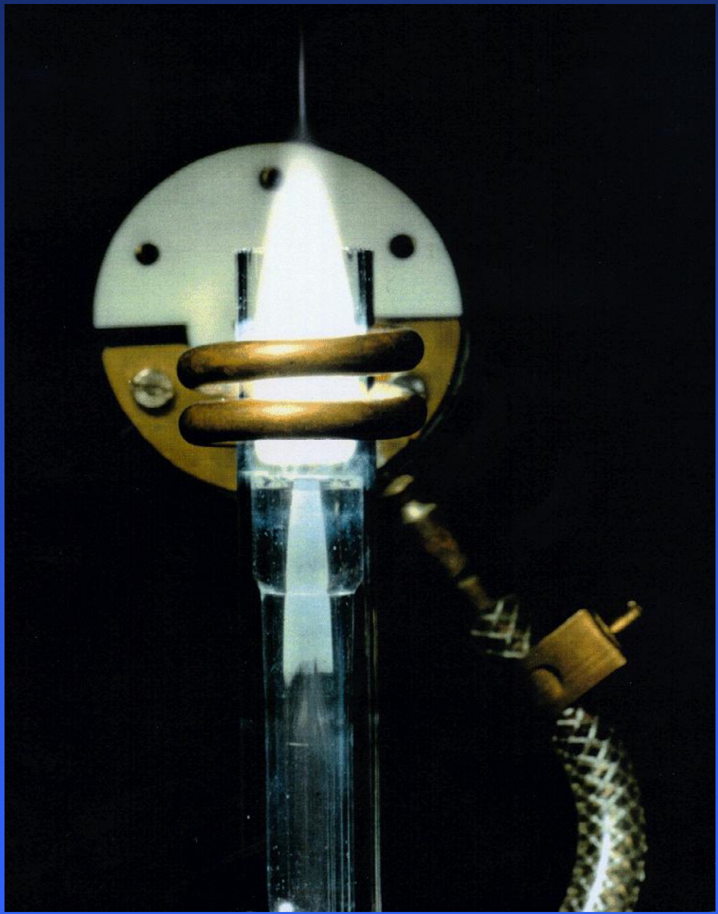
P = 1 kW

Φ= 14 slm

Argon + (Water + Analytes)

Mg
Fe
Li
Etc.

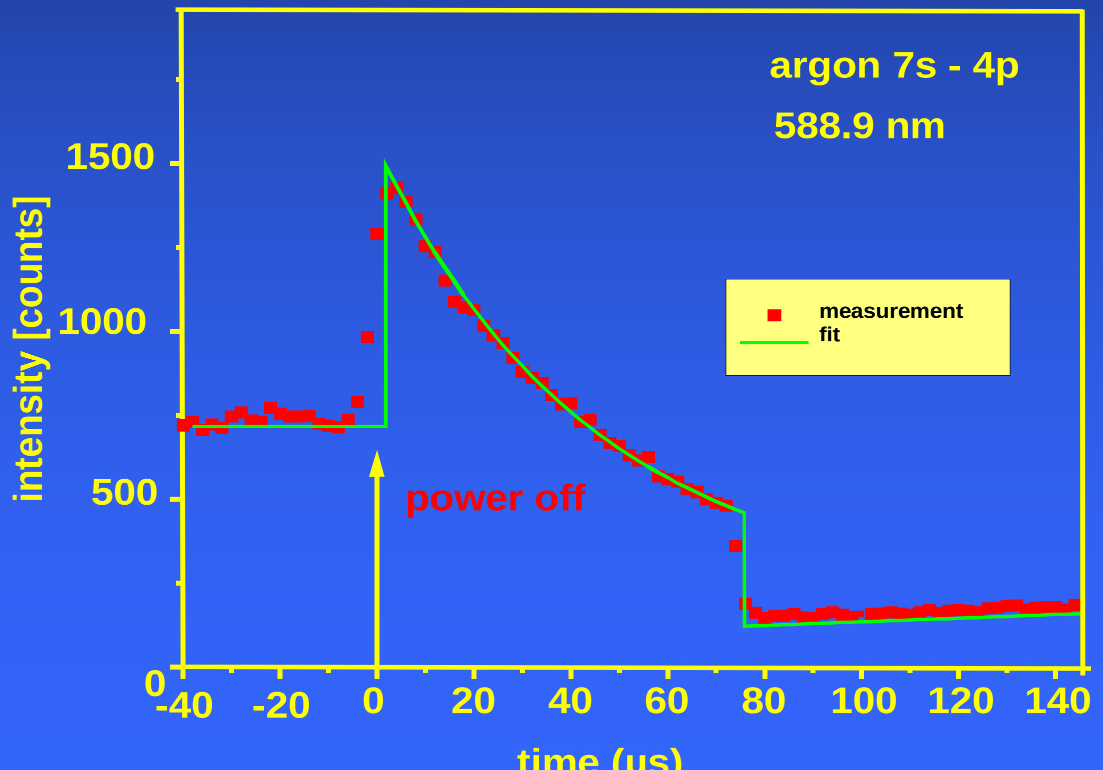
Two Atmosperic Plasmas



Wound healing

Wound creation

Power Interruption on ICP



Why is the Line Emission going **up** At switch-**off** ??

TU/e

Jump at cooling

Saha (like) balance

$e(\varepsilon_{fast}) + Ar(4p) \leftrightarrow e(\varepsilon_{slow}) + Ar(4p) + e(\varepsilon_{slow})$

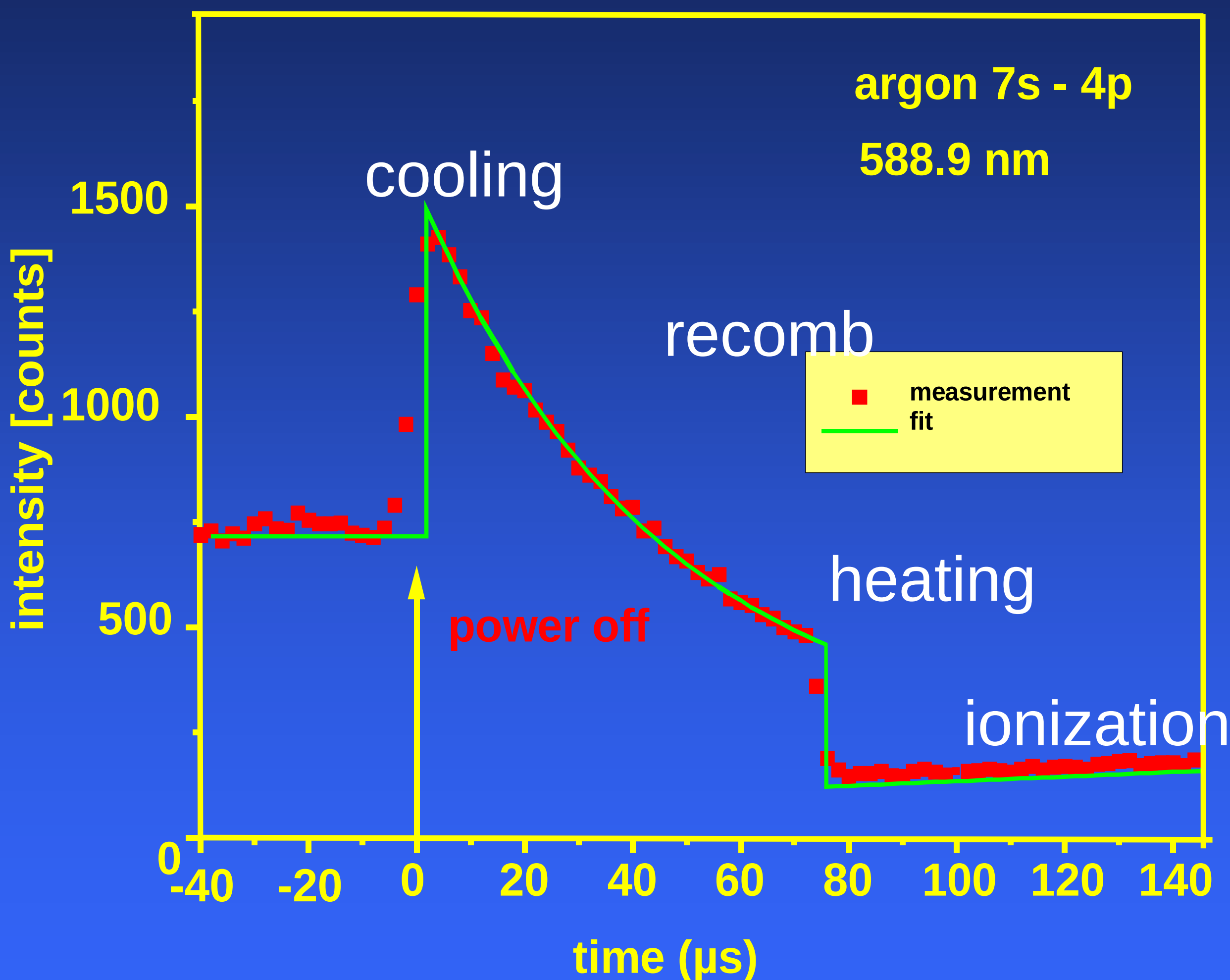
Power switch-off: population of $e(\varepsilon_{fast})$ goes down:

ionization stops while recombination continues.

After that new situation based on electrons of lower T: T_e^*

Presumably $T_e^* = T_h$

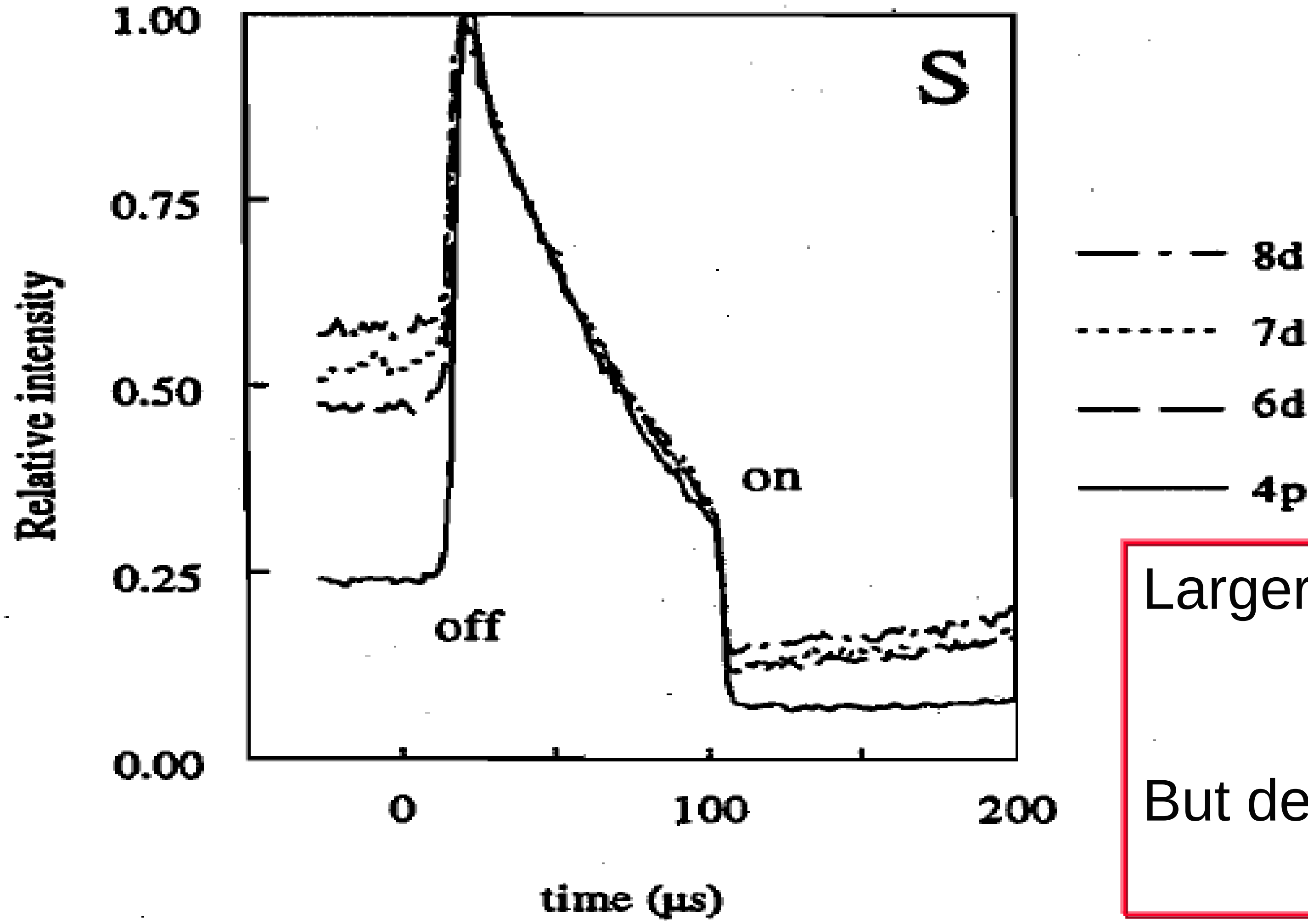
Power Interruption



Separation between

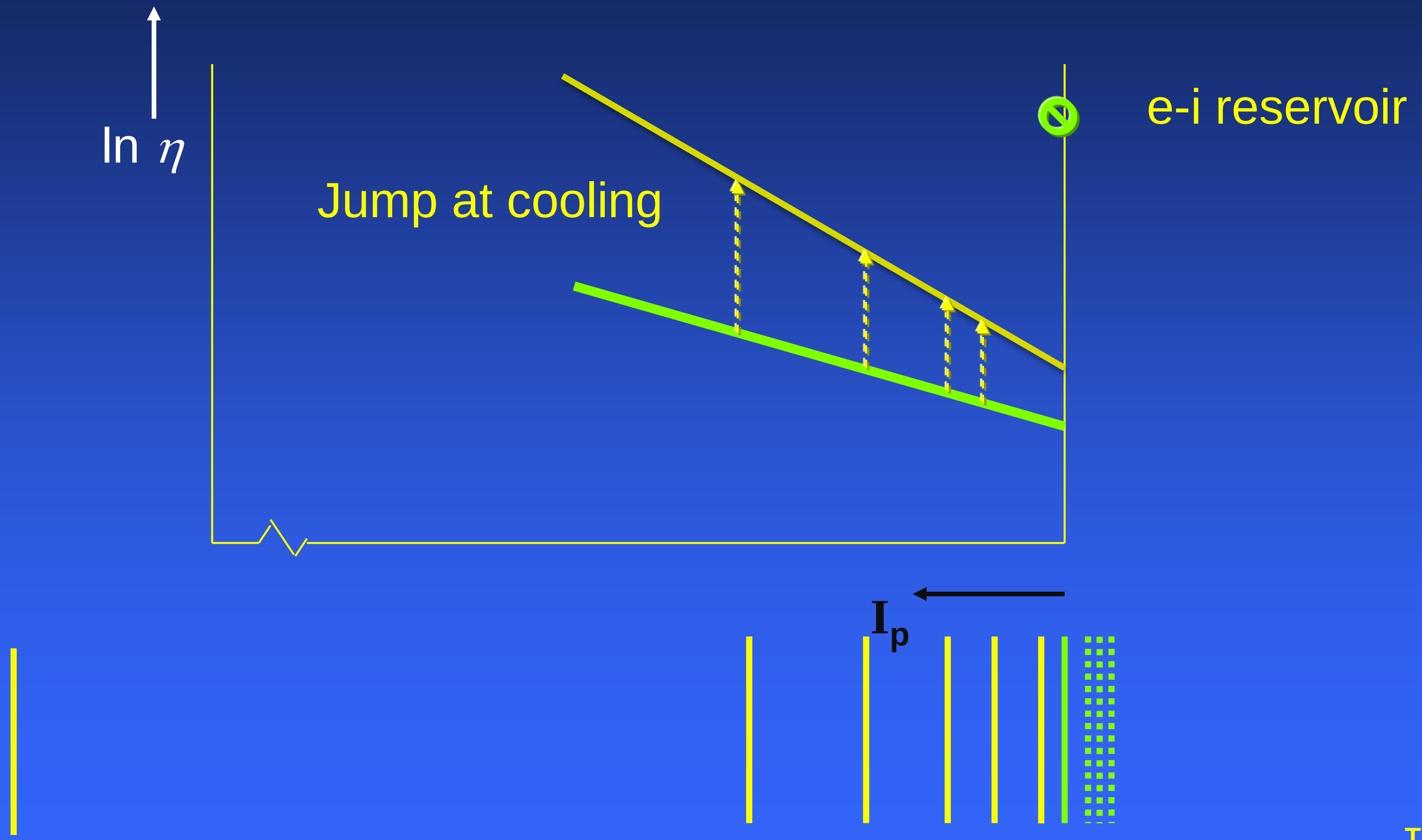
Fast Physics (ΔT)
&
Slow Chemistry (Δn)

For several Ar lines

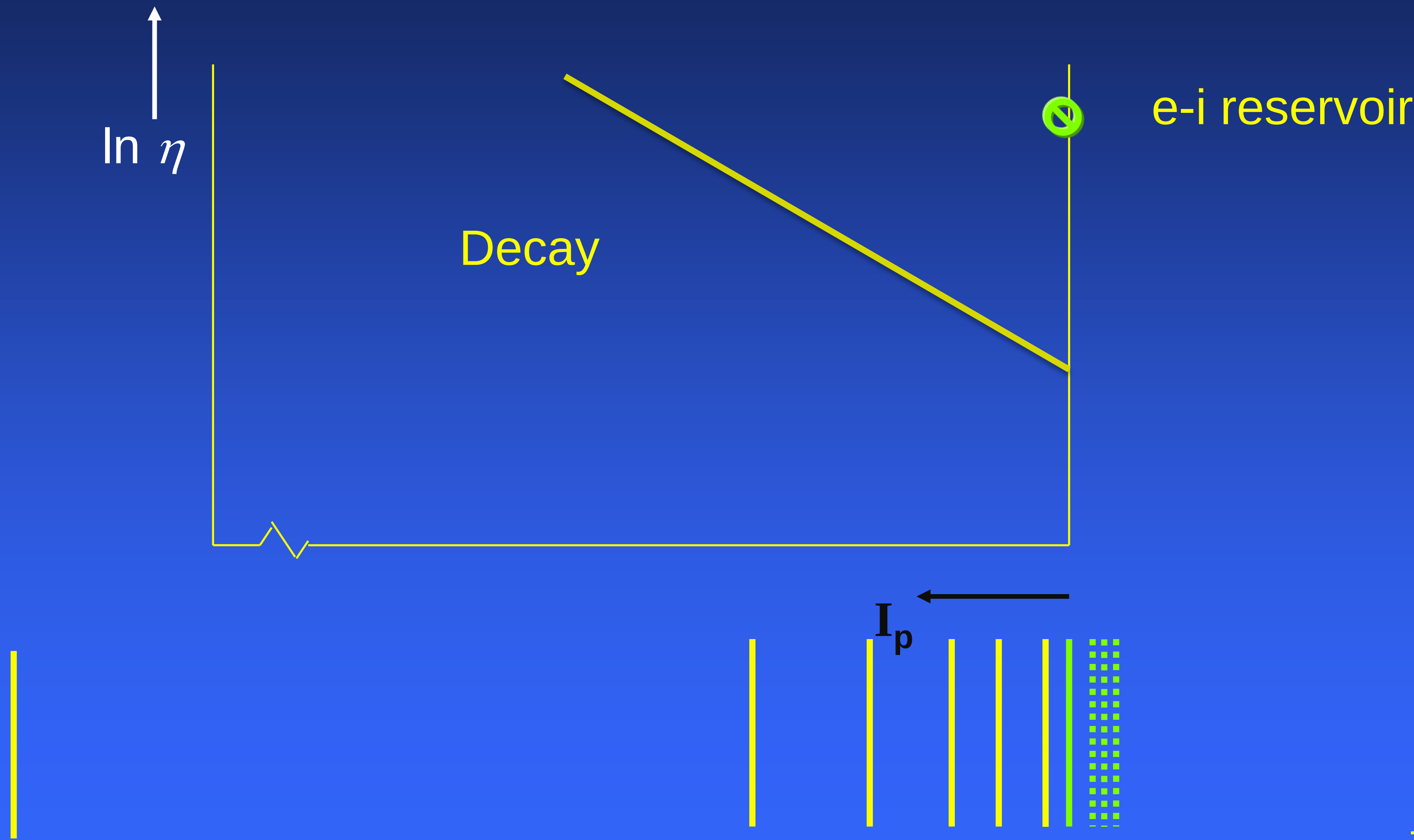


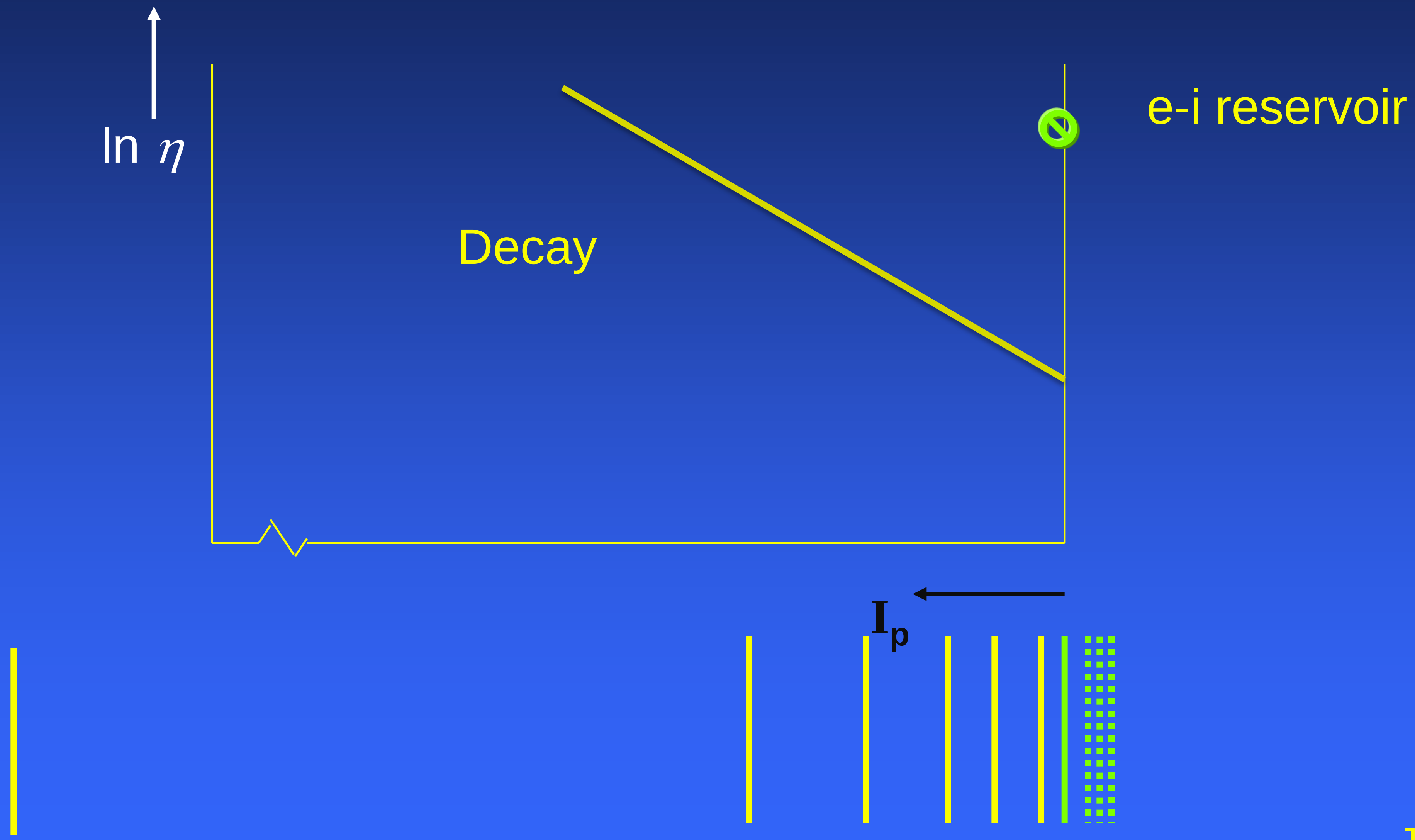
Larger Jumps
Lower levels

But decays
The same

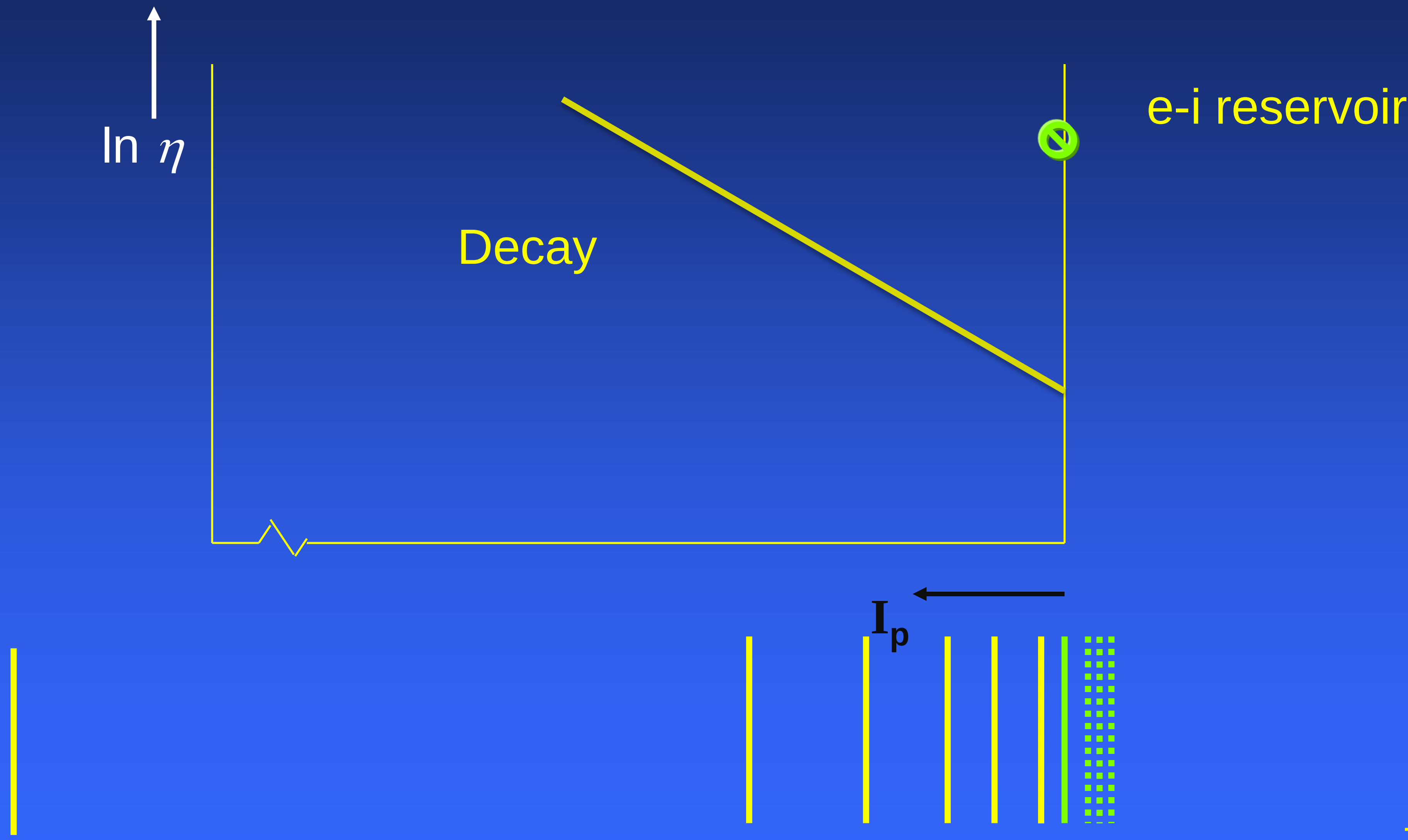


ln η
Jump at cooling
e-i reservoir
I_p

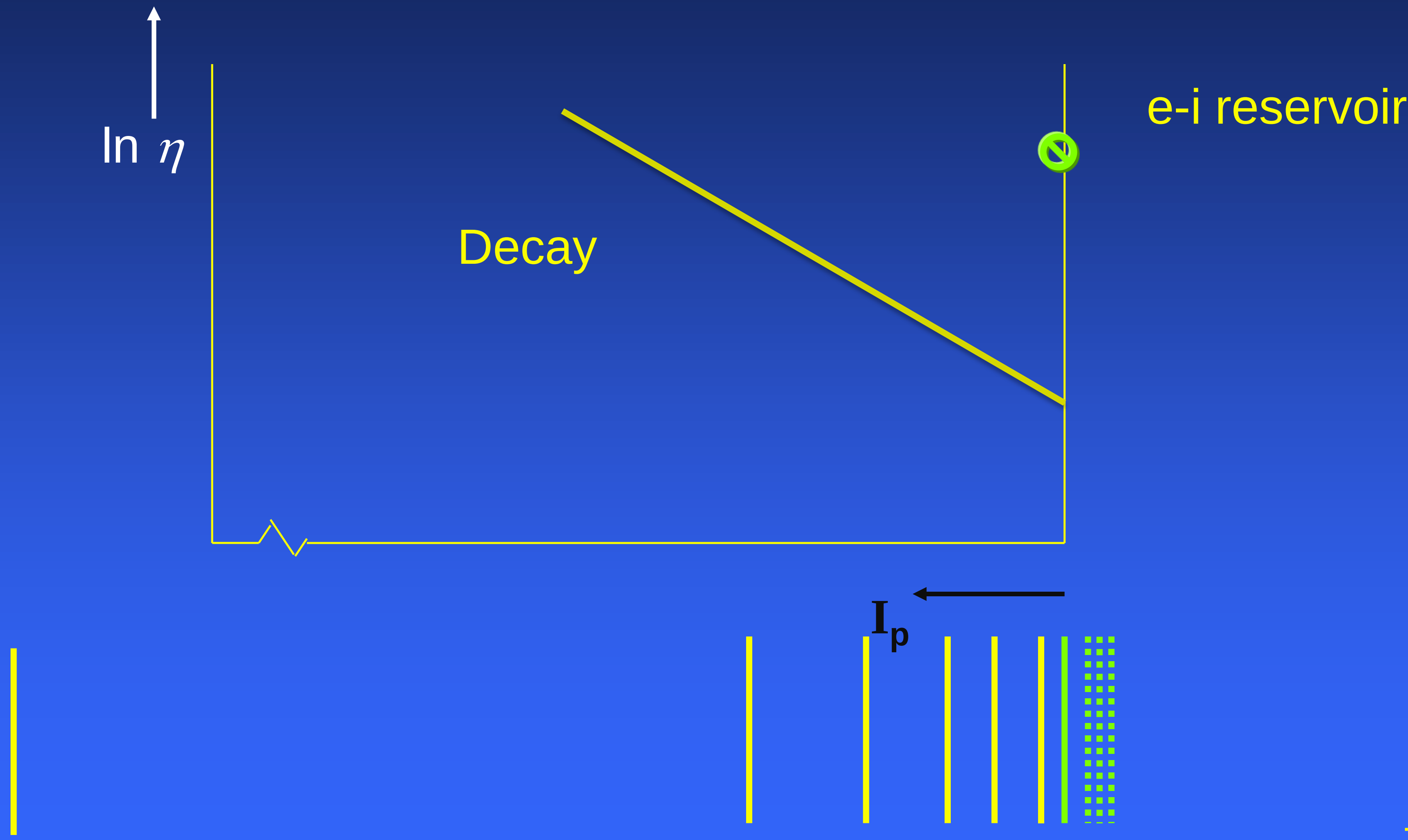

ln η
Decay
e-i reservoir
I_p



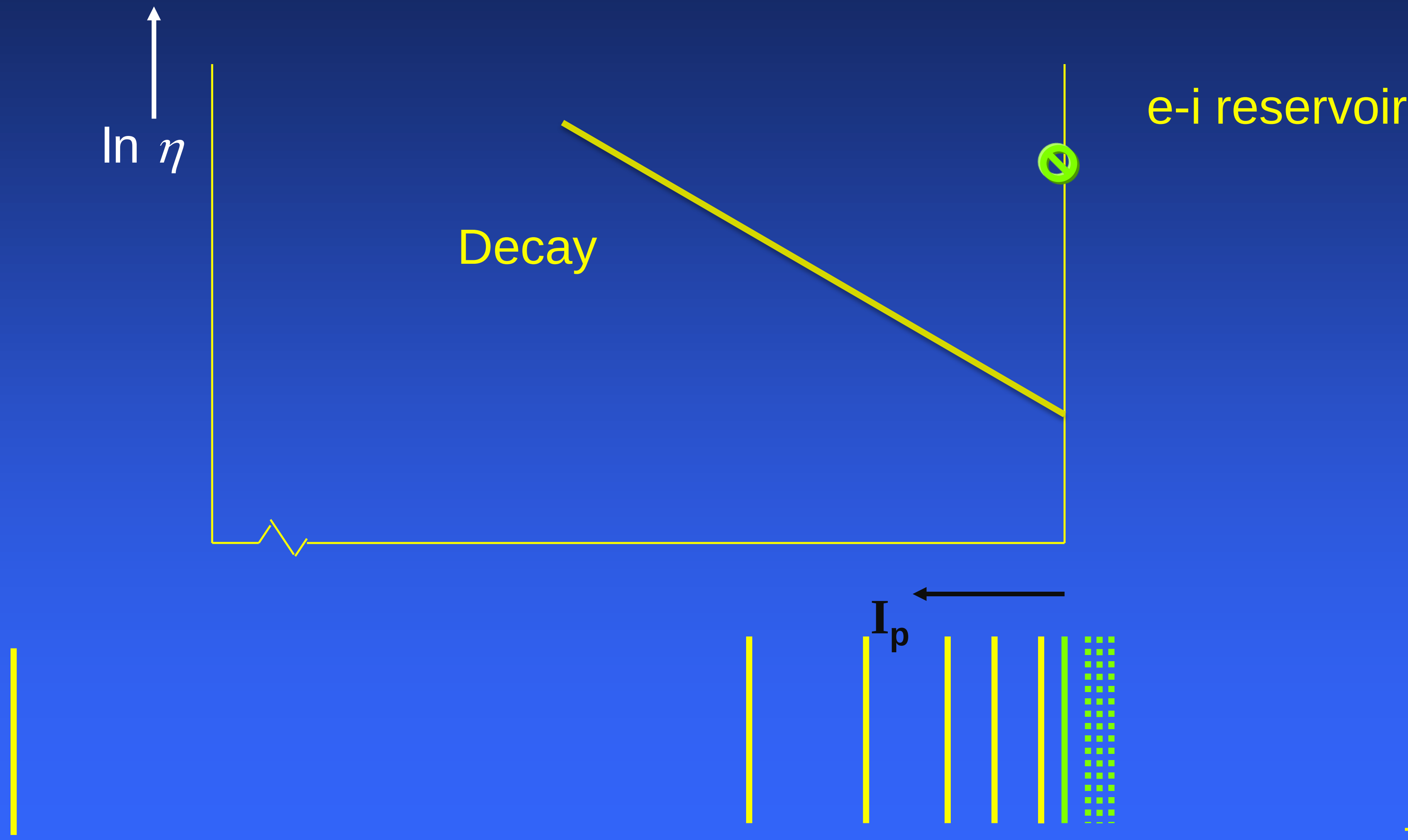
TU/e

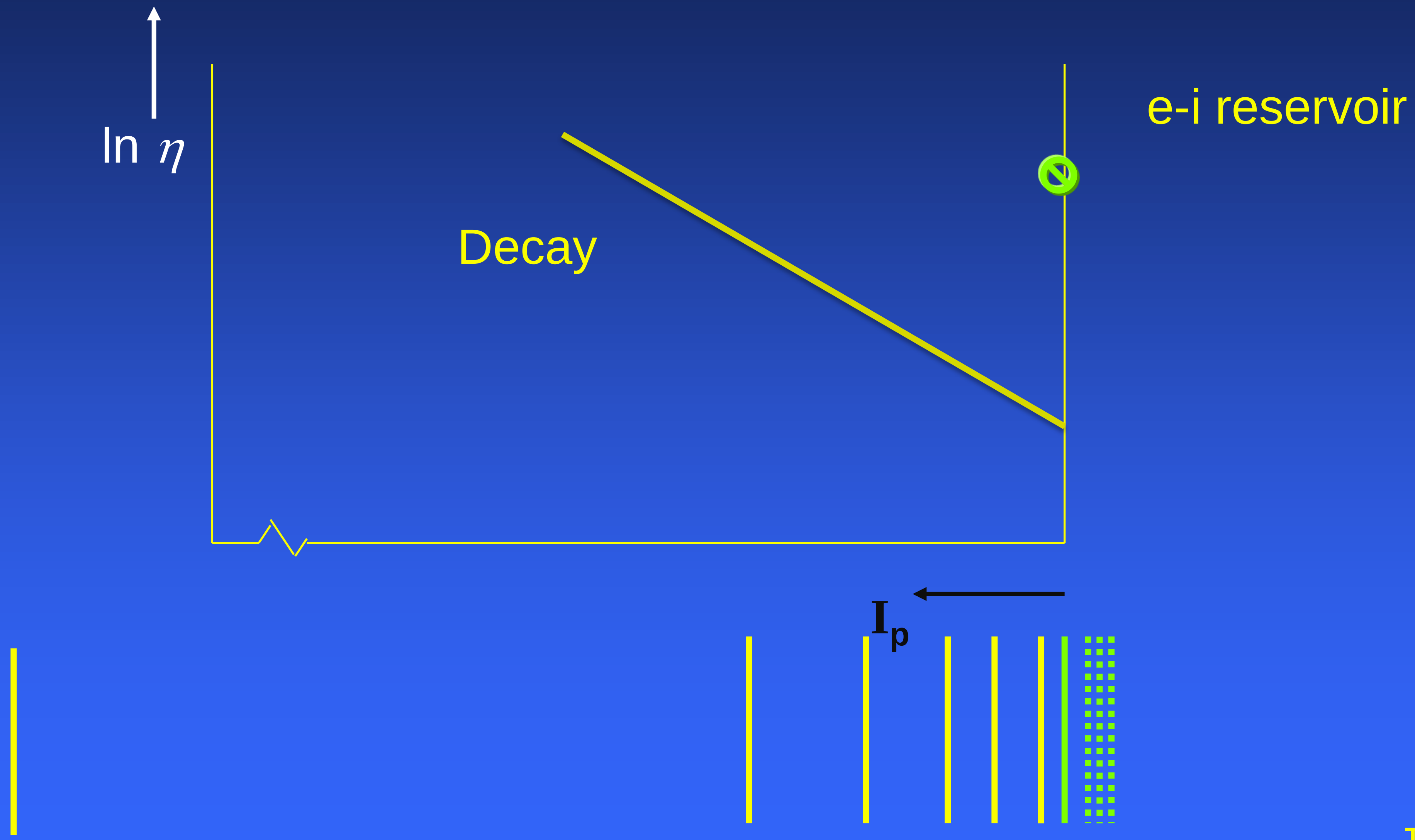


TU/e



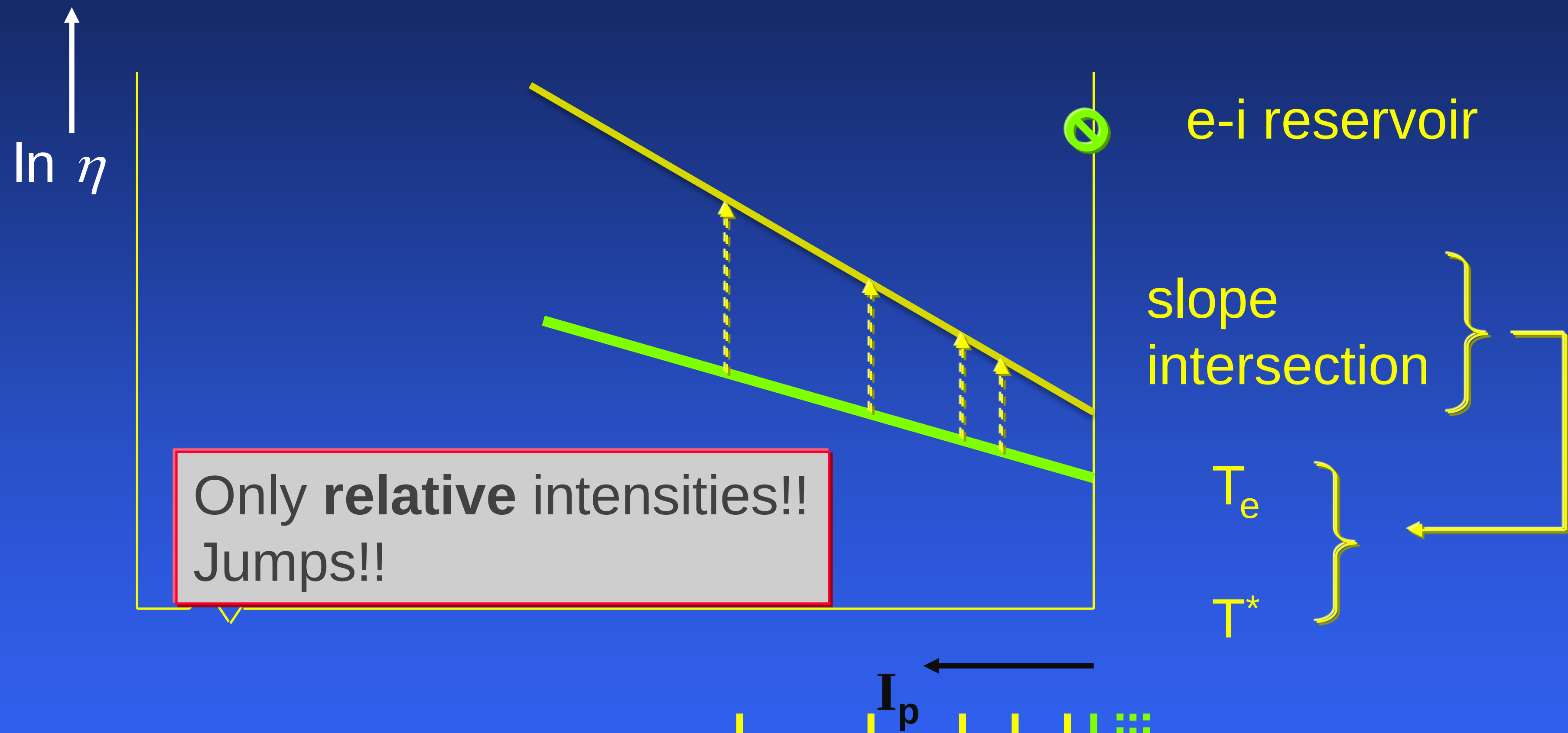
ln η
Decay
e-i reservoir
I_p


ln η
Decay
e-i reservoir
I_p

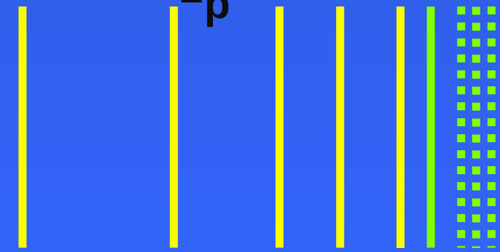


ln η
e-i reservoir
Decay
I_p

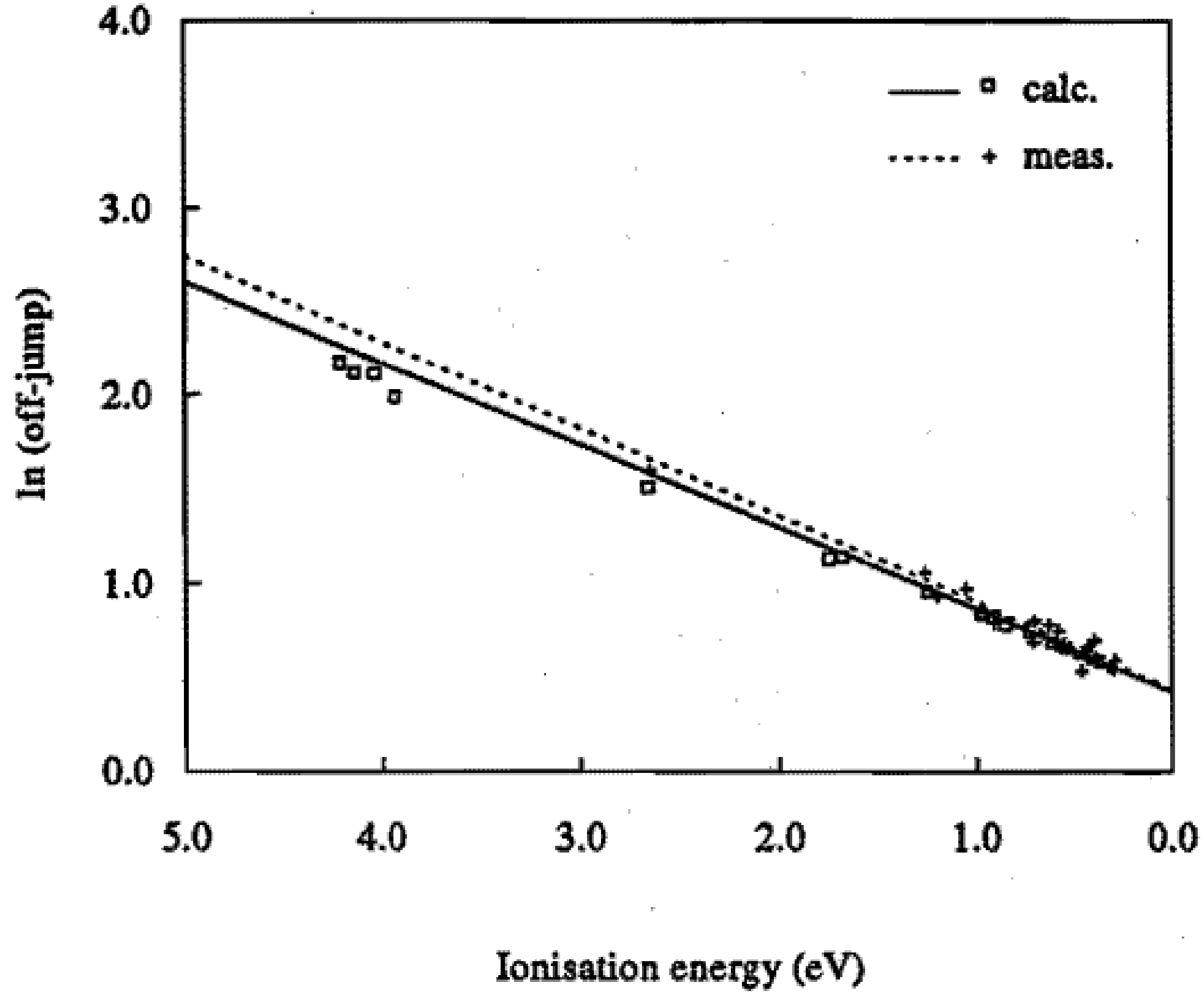
T_e and T_h deduced from Jump (?)



Does it work ??



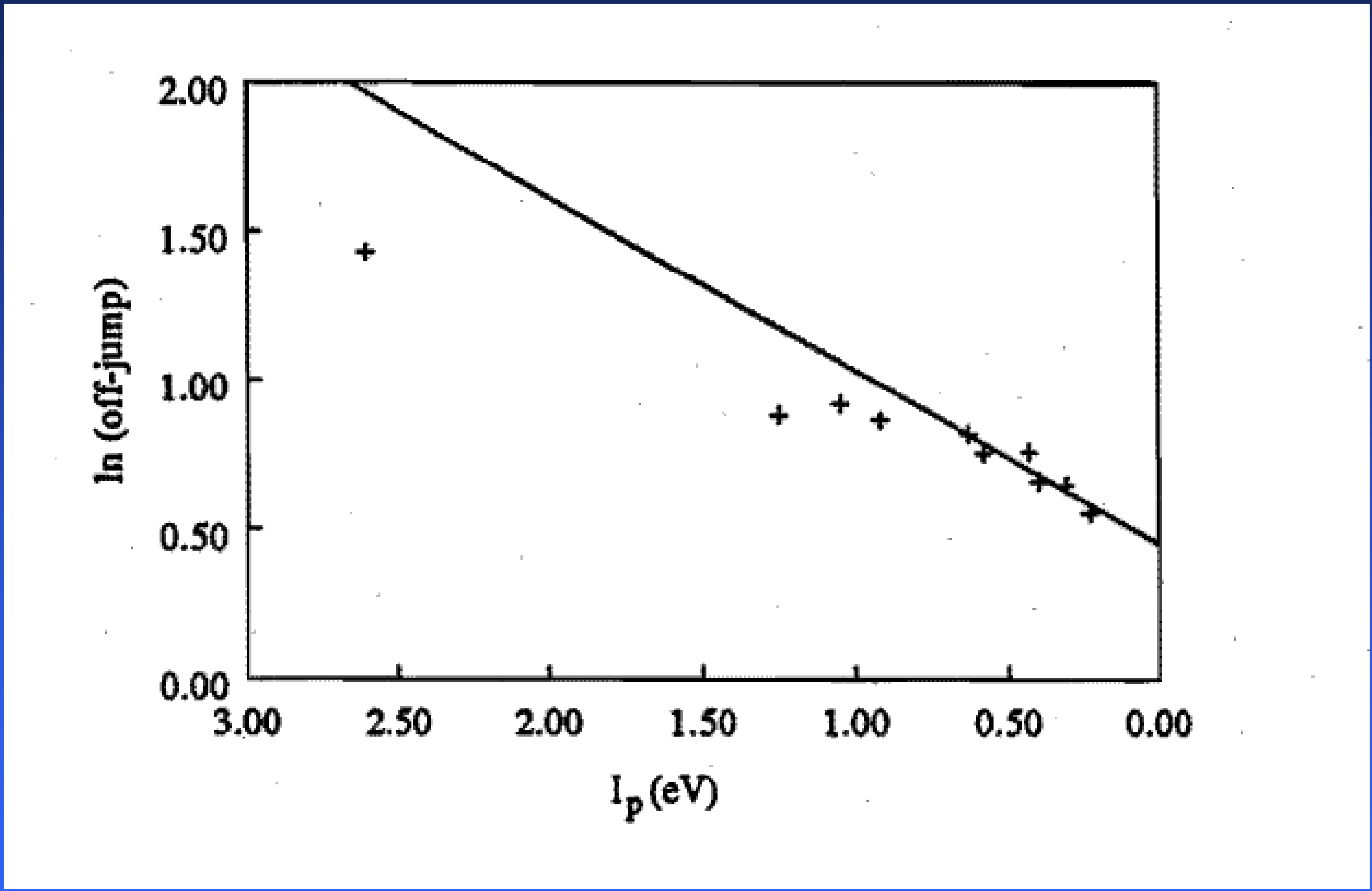
ICP at high power



Thesis Frank Fey

Exp <-> Model

ICP at lower power



SIP at even lower Power

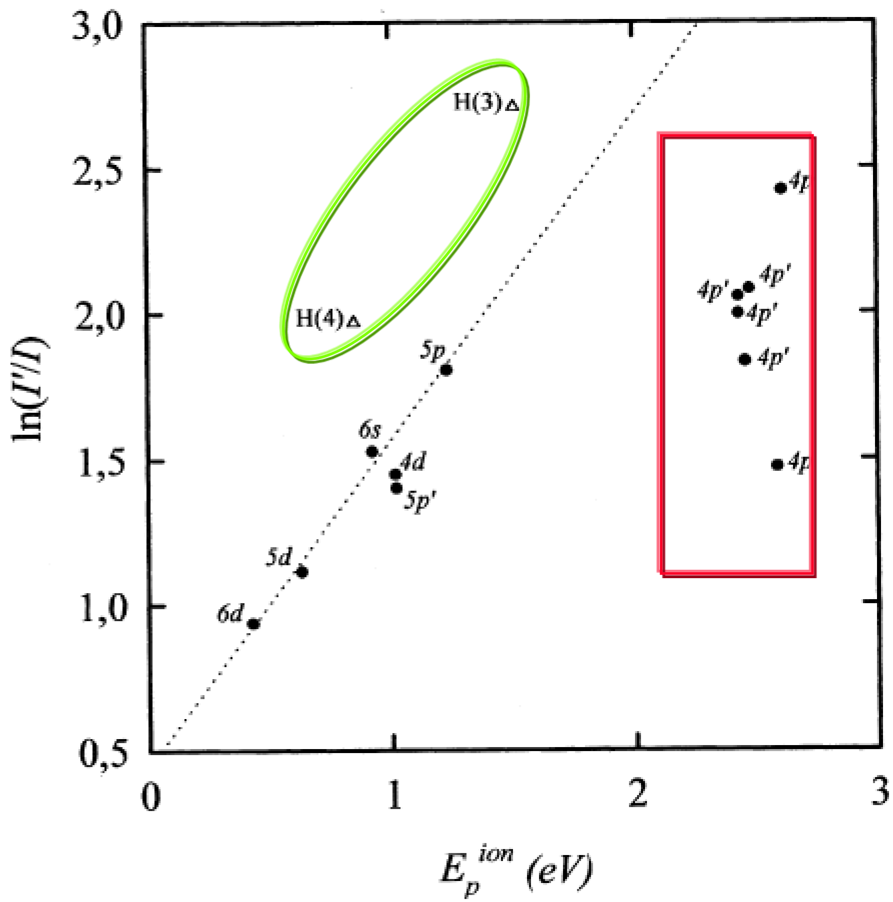


Fig. 4. Cooling jump of argon and hydrogen level population as a function of its ionization energy at $z = 13$ cm position (number of repetitions = 1000 times).

M.C. Garcia, A. Rodero &Sabios

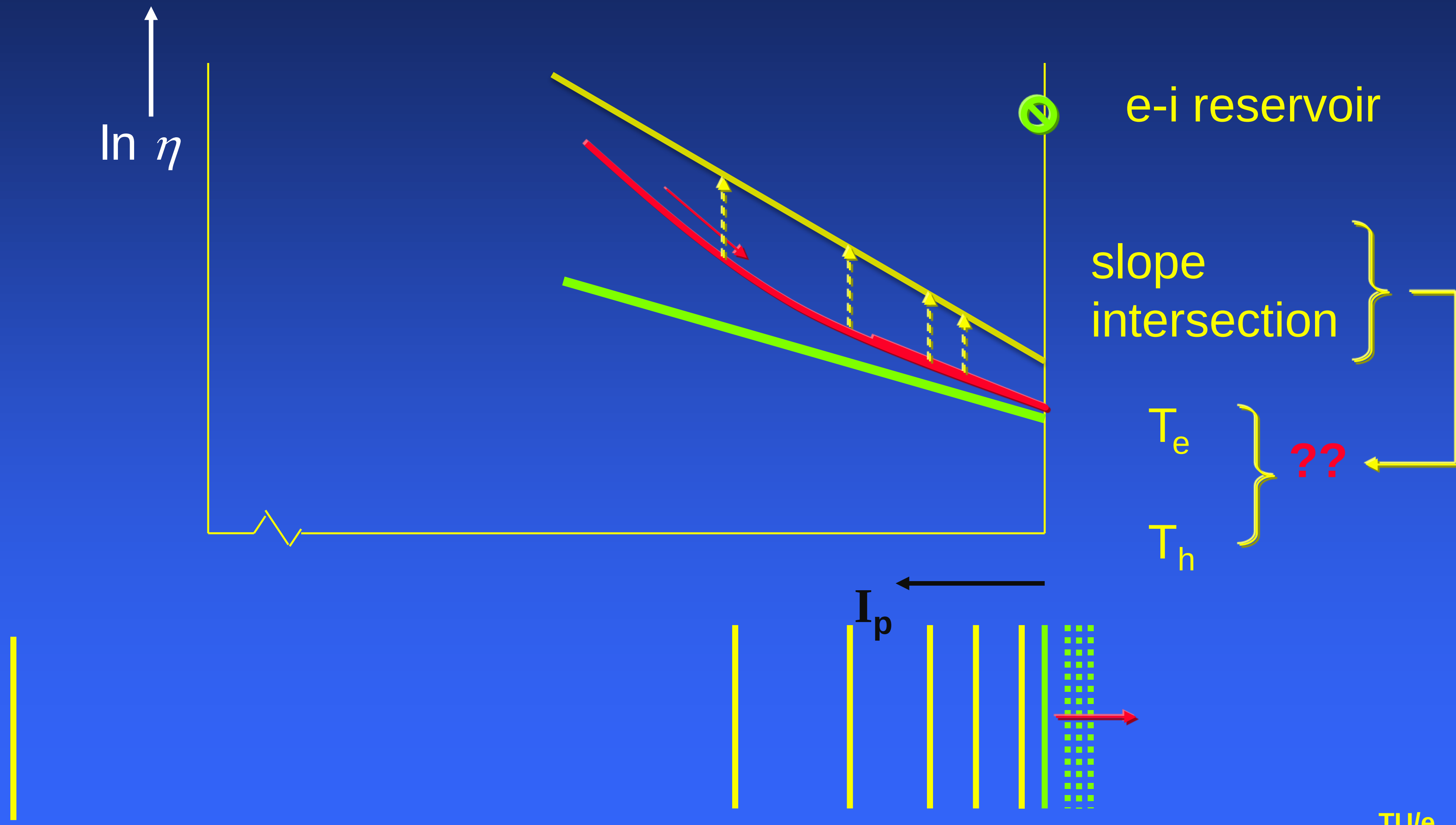
SAB 55 (2000) 1611

Low Ar lines: small jumps

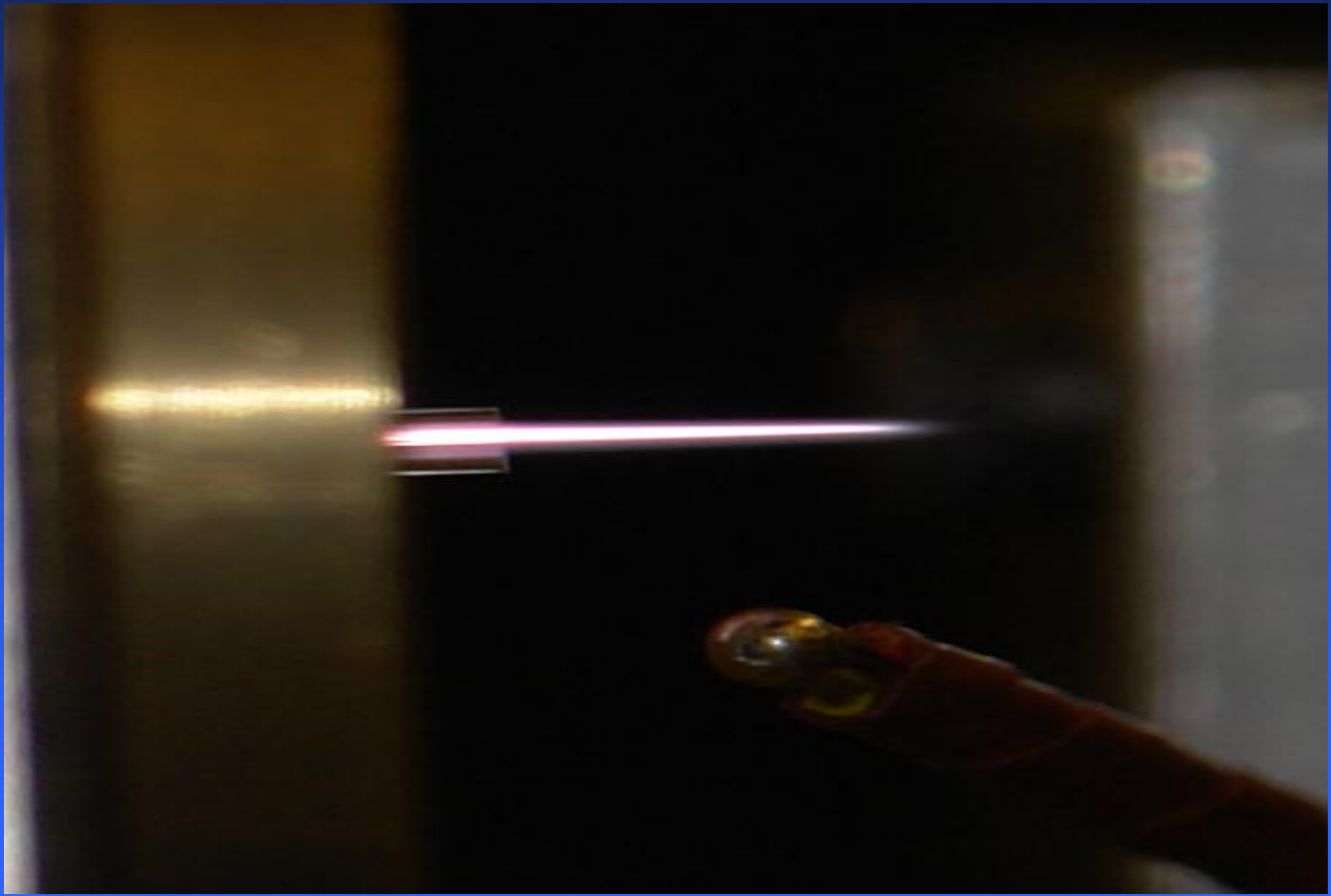
H lines: large jumps
Points towards Excitation Transfer

$Ar^* + H \rightarrow Ar + H^*$

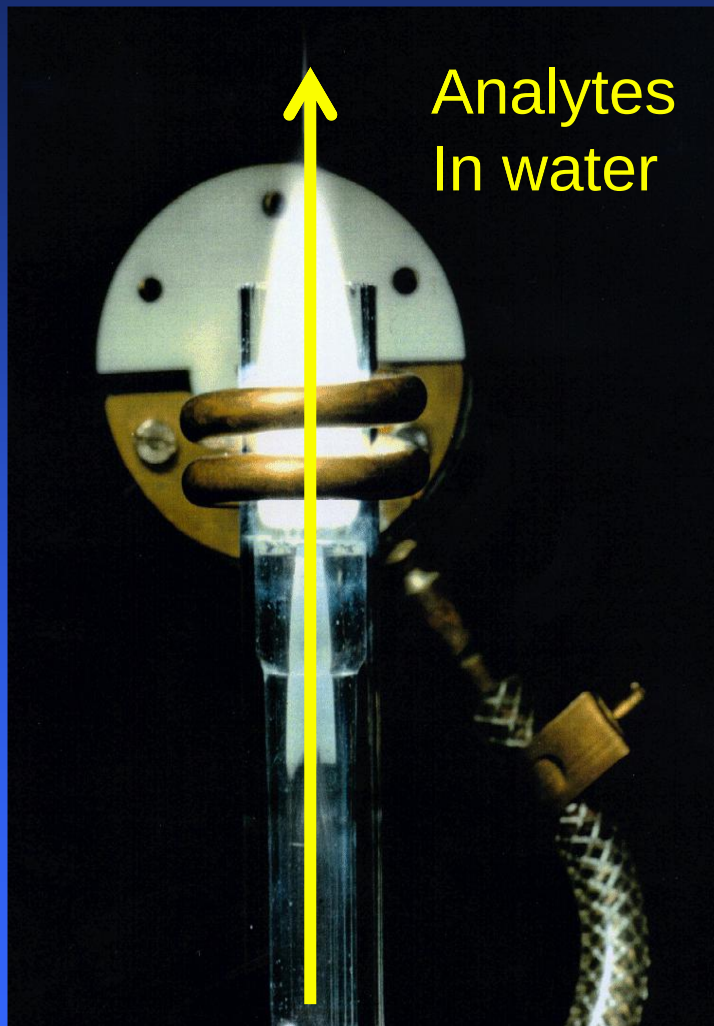
Influence of ei transport

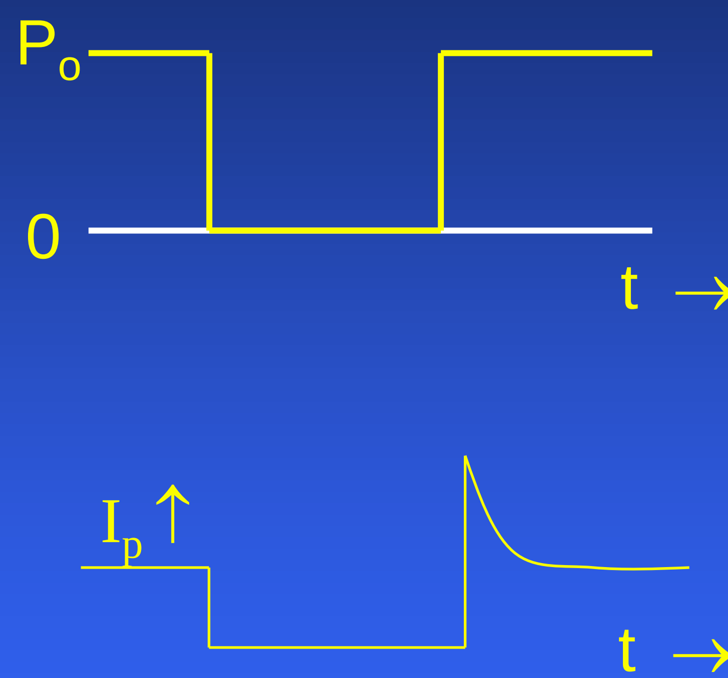


Surfatron Induced Plasma (SIP)



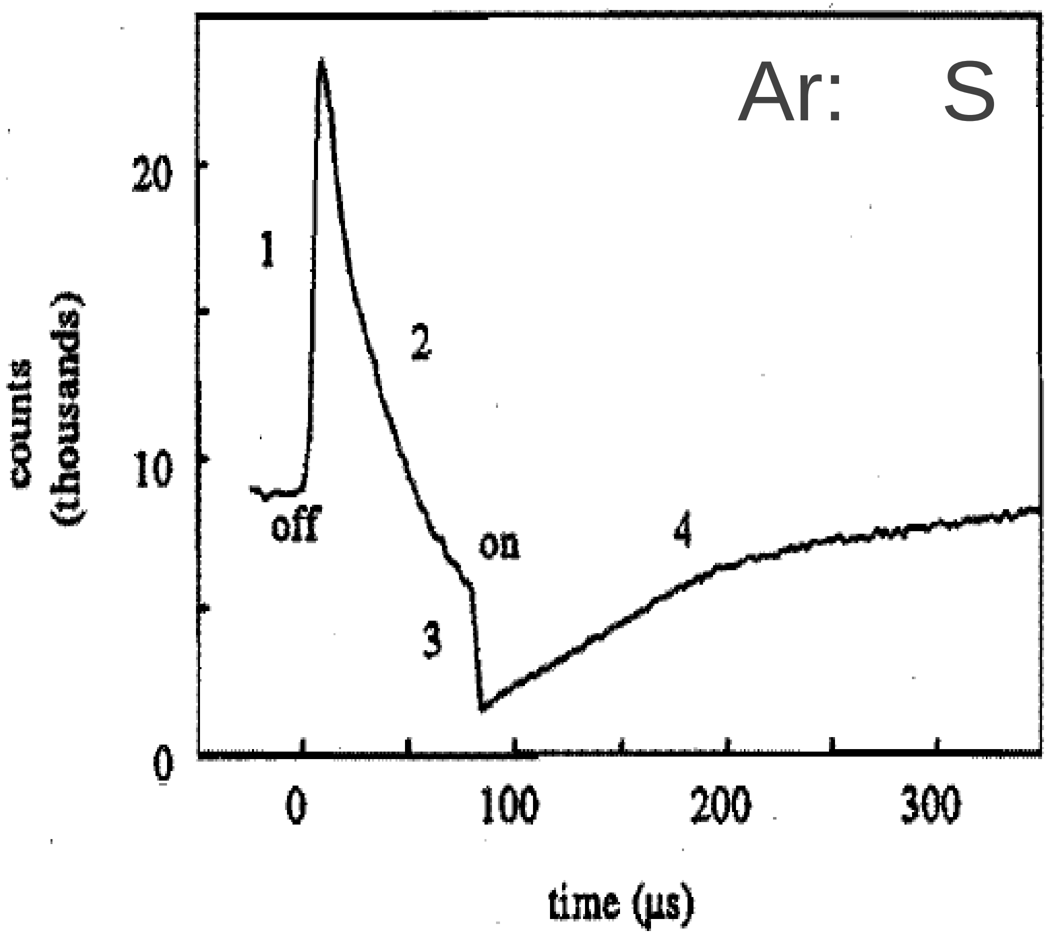
Response dependent on atomic system

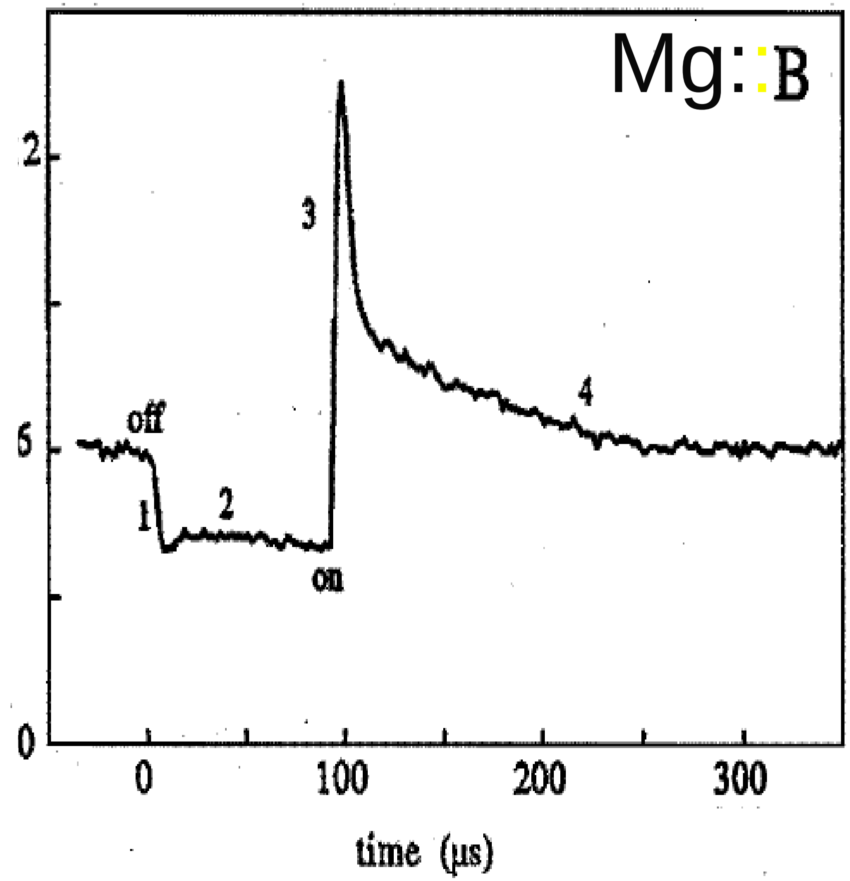




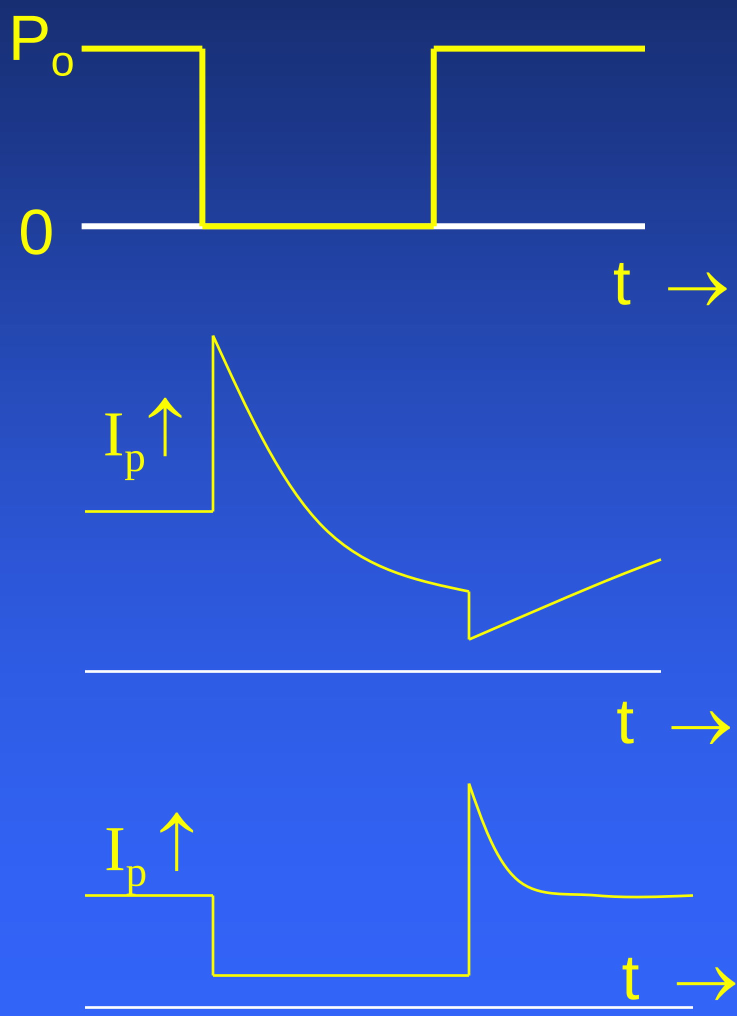
Typical Analyte Line Response

Saha versus Boltzmann





Each line its fingerprint



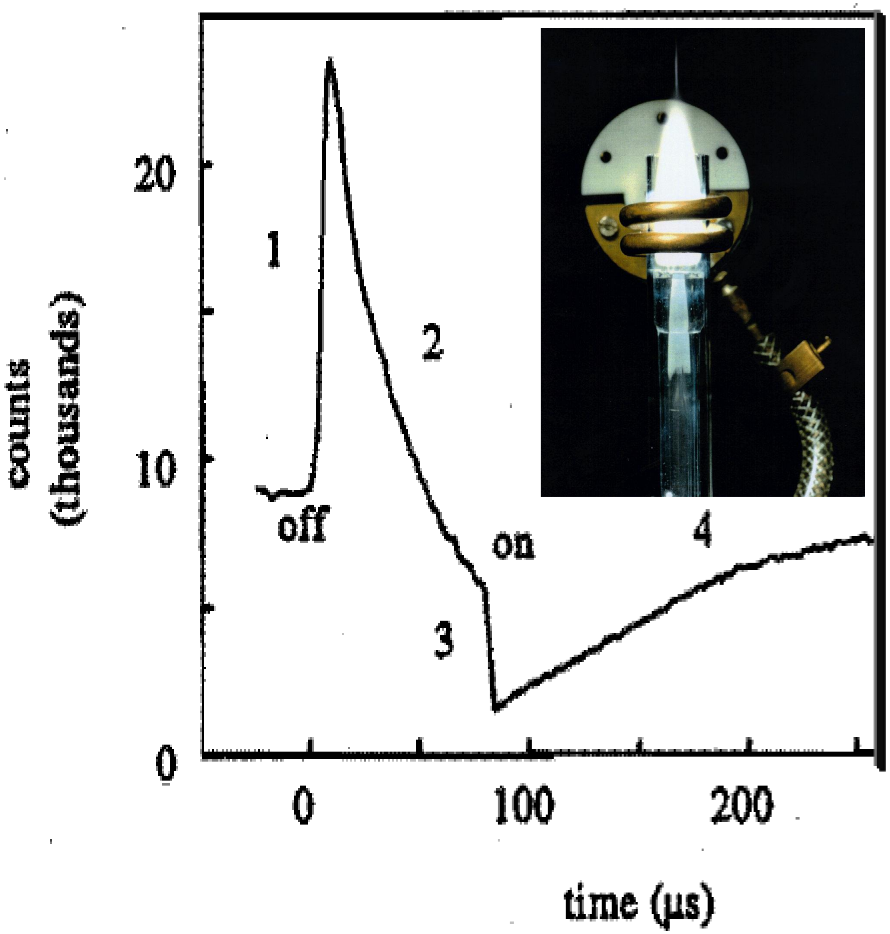
Saha-like response

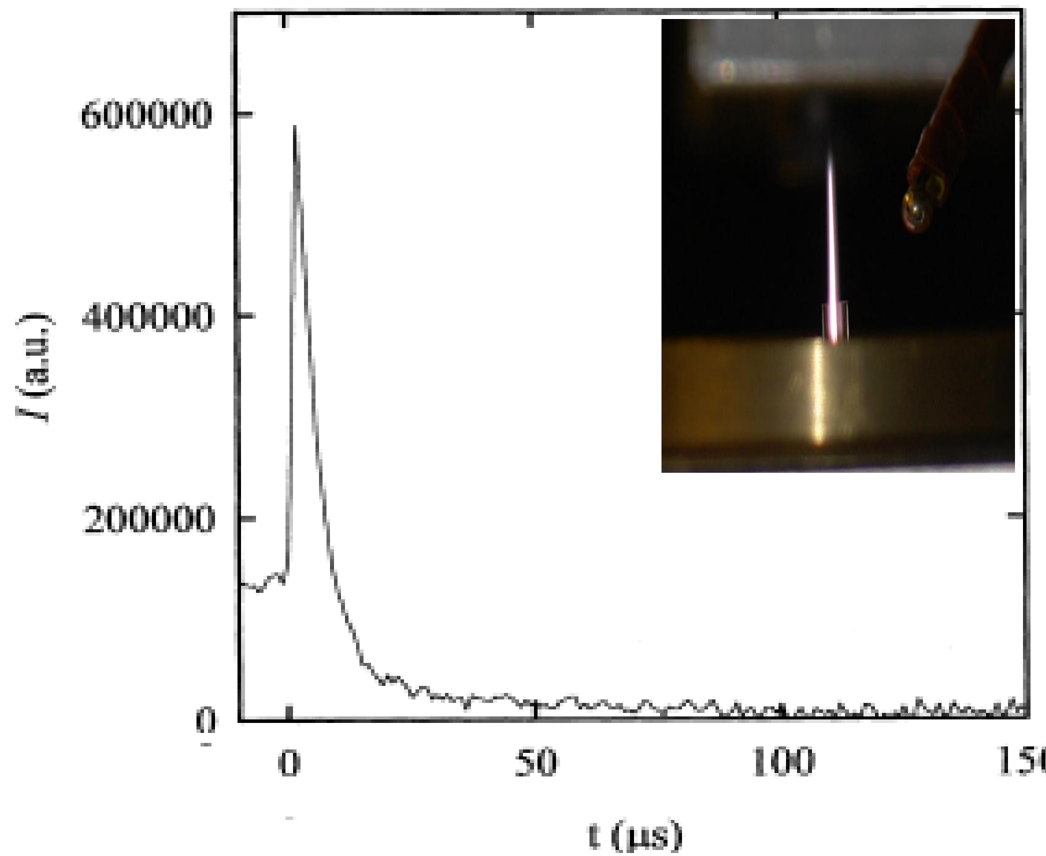
$$e_f + A(p) \leftrightarrow e_s + A^+ + e_s$$

Boltzmann-like response

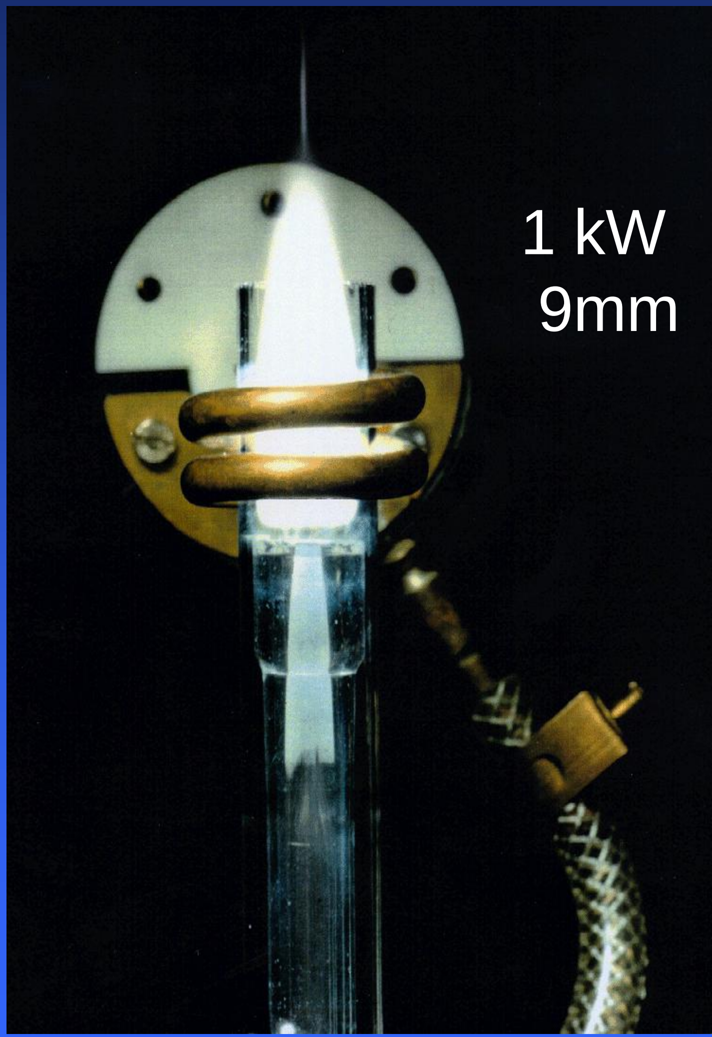
$$e_f + A(1) \leftrightarrow A(p) + e_s$$

Decay: Transport and Recombination



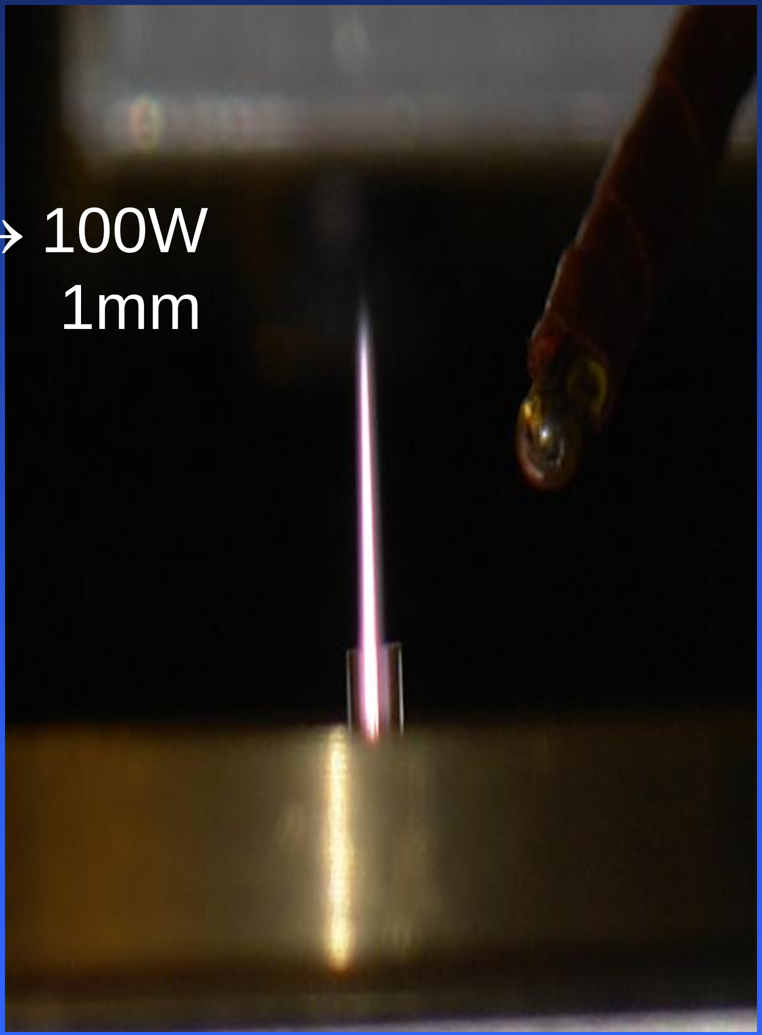


The ICP versus SIP



1 kW ↔ 100W

9mm 1mm



ICP $\leftrightarrow$ SIP compared

SIP known: T_e (10.000) nd T_h (1000K) known

T_e /T^*_e should be large ~ 10

Jump method: T_e* = 5000K; too high

T_e* >>T_h

How come??

Extra heating source??

Light is indirect

Light escape comes at the very end

Power Interruption gives Δn_e and ΔT_e

Δn_e and ΔT_e gives $\Delta n(Ar^*)$

light emission

Lets probe Δn_e and ΔT_e directly via **Thomson Scattering.**

Physics Versus Chemistry

Steady State:

$$EM \rightarrow \{e\} \rightarrow \{h, h^*\} \rightarrow \text{environment}$$

Two Links

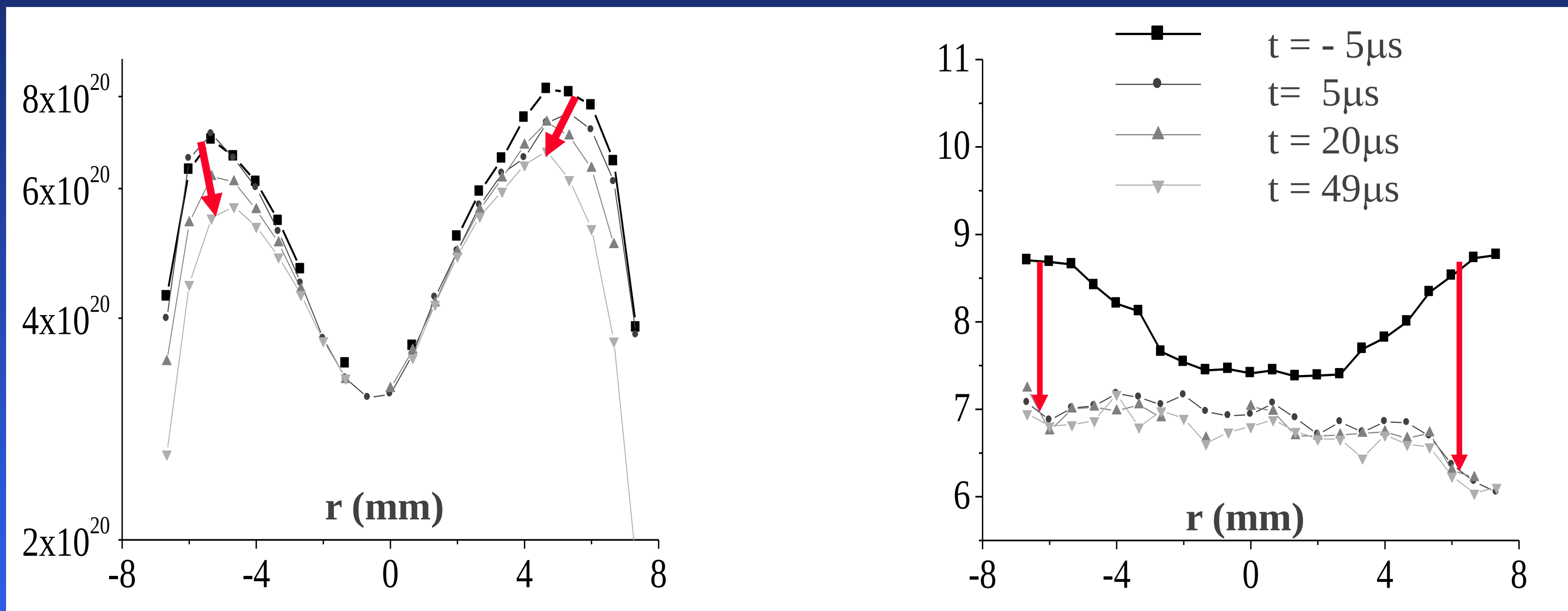
Analysis: Decouple Links

Probe {e} directly

With Thomson Sc

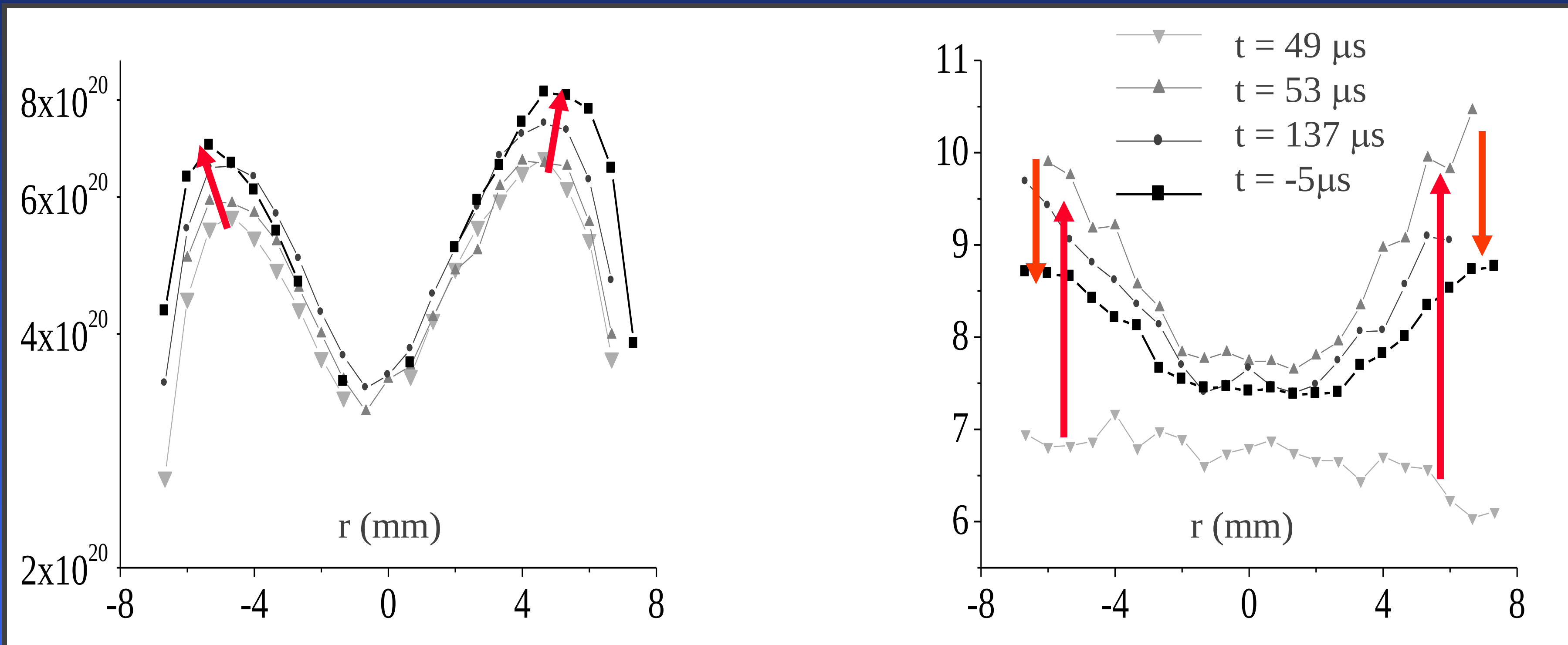
Change in T_e Physics
Change in n_e Chemistry

Cooling and Decay



Decay:	Cooling	$T_e \downarrow T_e^*$	$\tau_T \approx 2\mu s$
	Recombination.	$n_e \downarrow$	$\tau_n > 100\mu s$

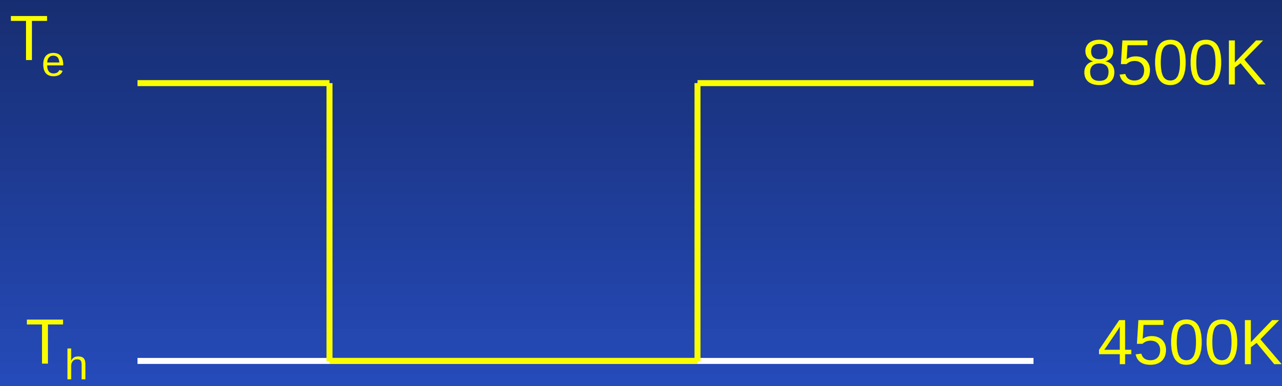
Heating and ionization



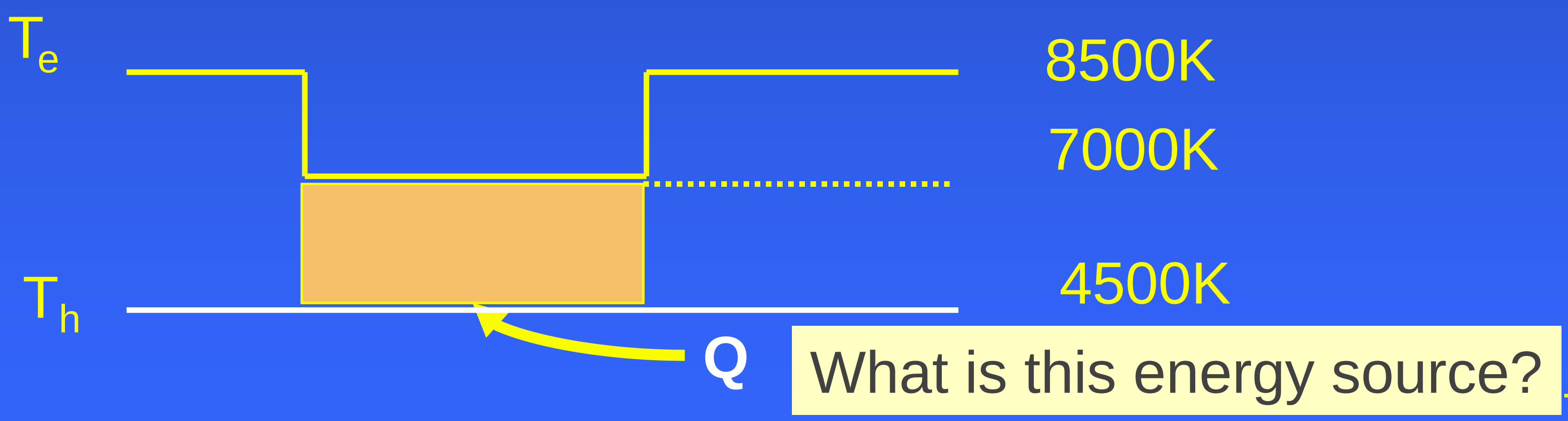
Re-ignition:	Heating	$T_e \uparrow T_e^{**}$	$\tau_T \approx 2\mu s$
	Ionization	$n_e \uparrow$ gradual	$\tau_n > 100\mu s$

Decay in T_e

What we expect



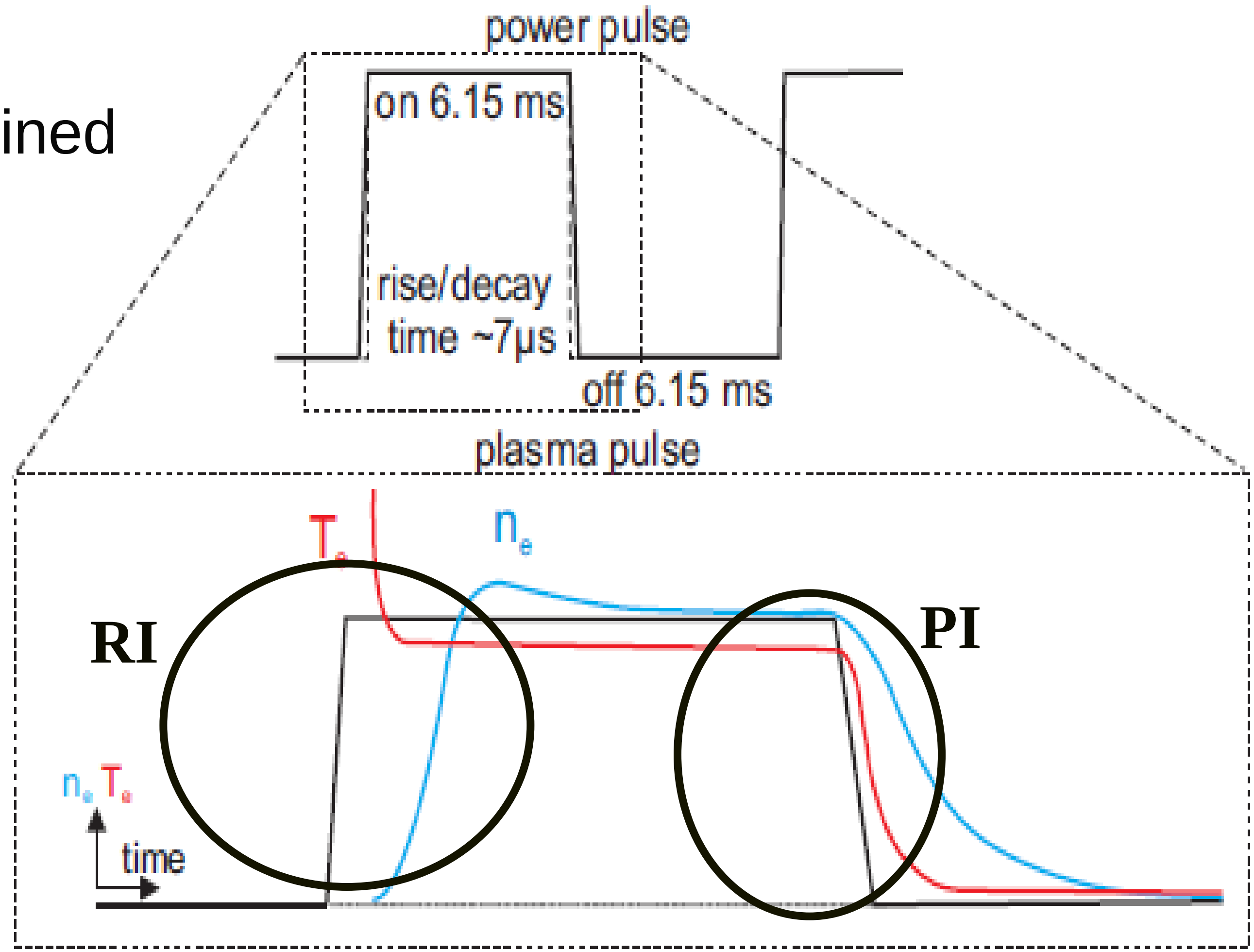
What we get



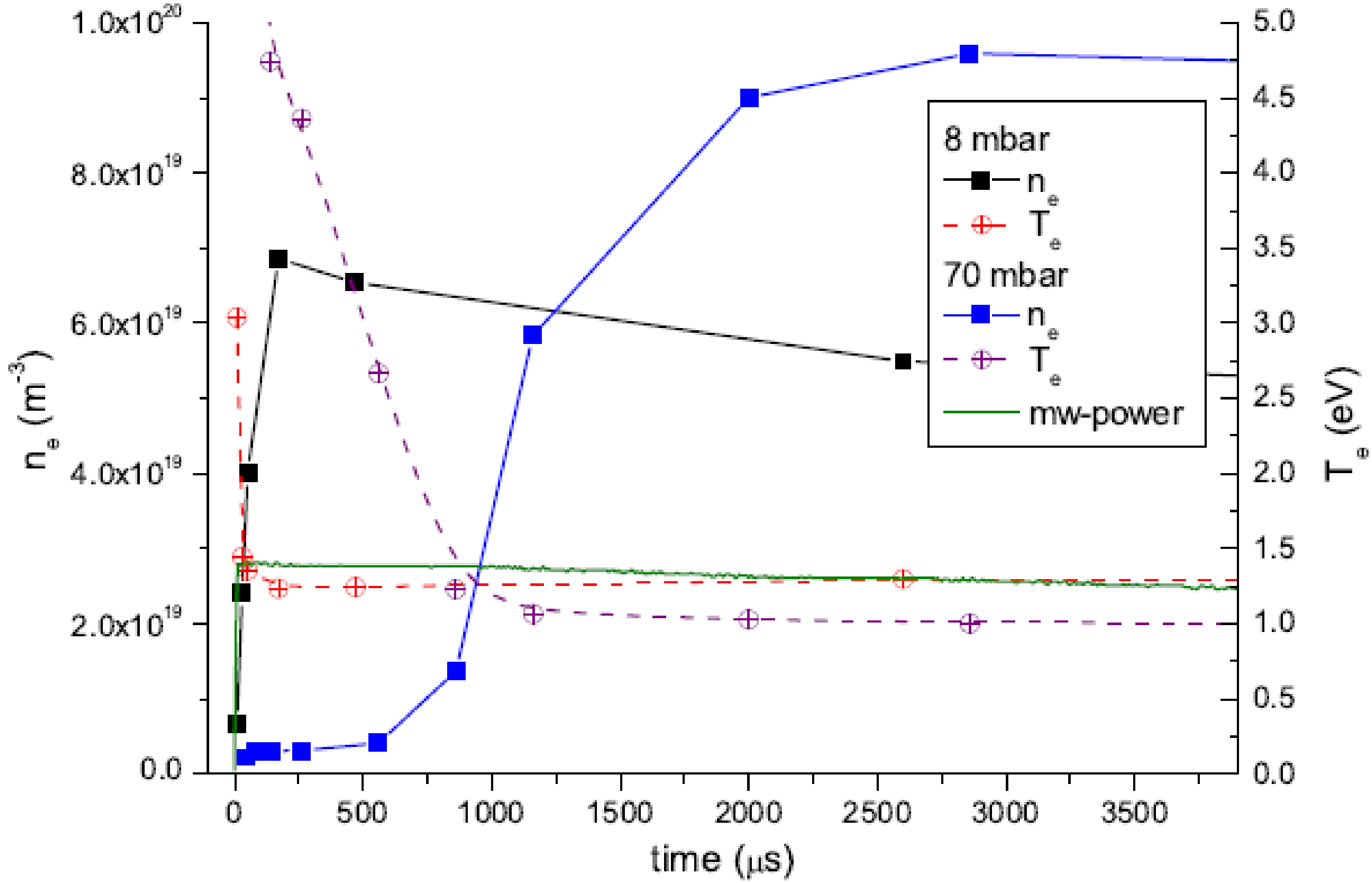
The plasma source: a low-p SIP

Power Pulsed low p SIP: on and off

Determined by TS



Effect of pressure



Solid state power supply

Critical in the study of temporal behavior: fast generator

Normal magnetron power supply:

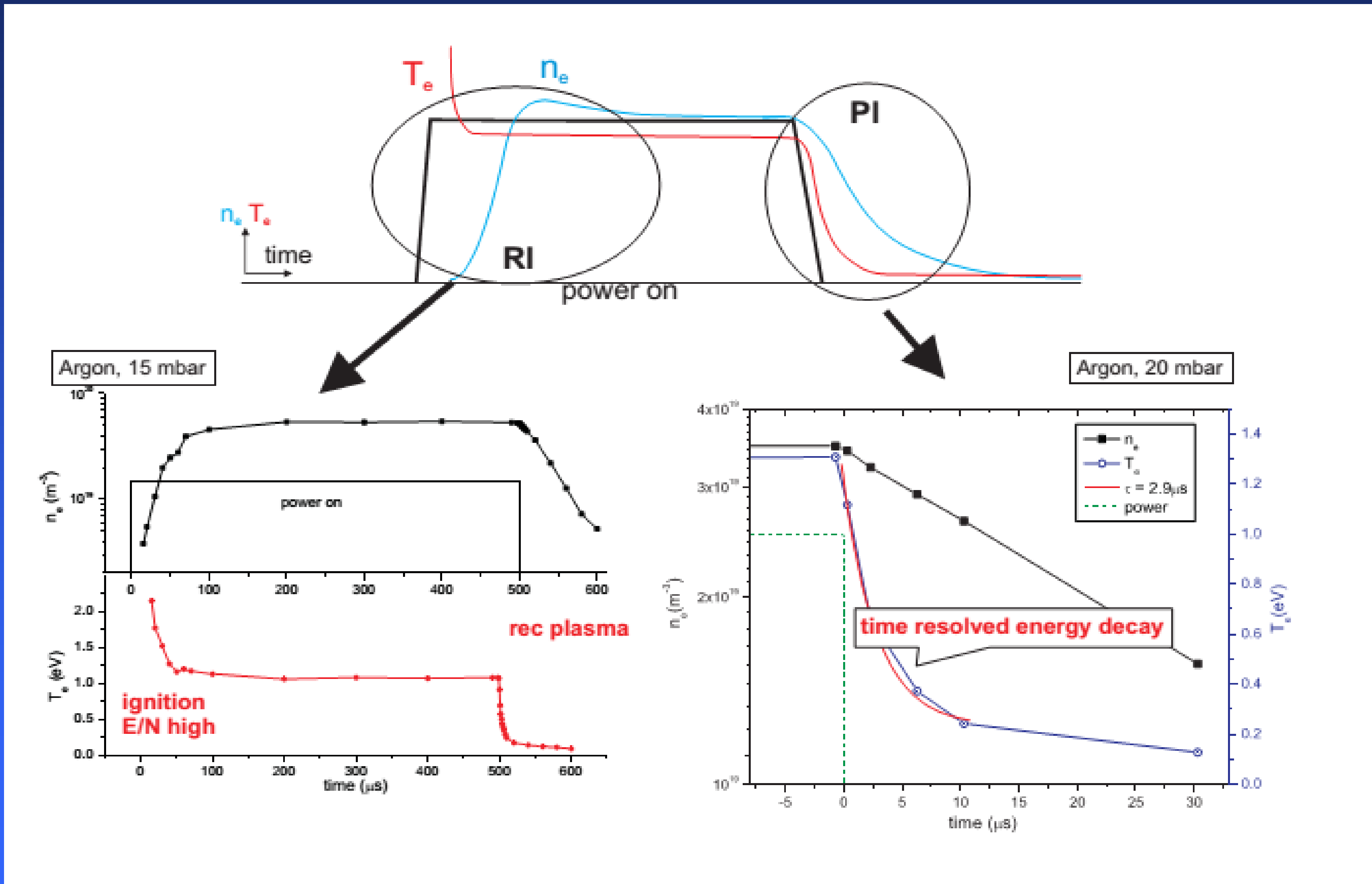
instable and $\Delta\tau$ >7 μs

Whereas $\Delta\tau(T_e)$ ~ 2 μs

↓

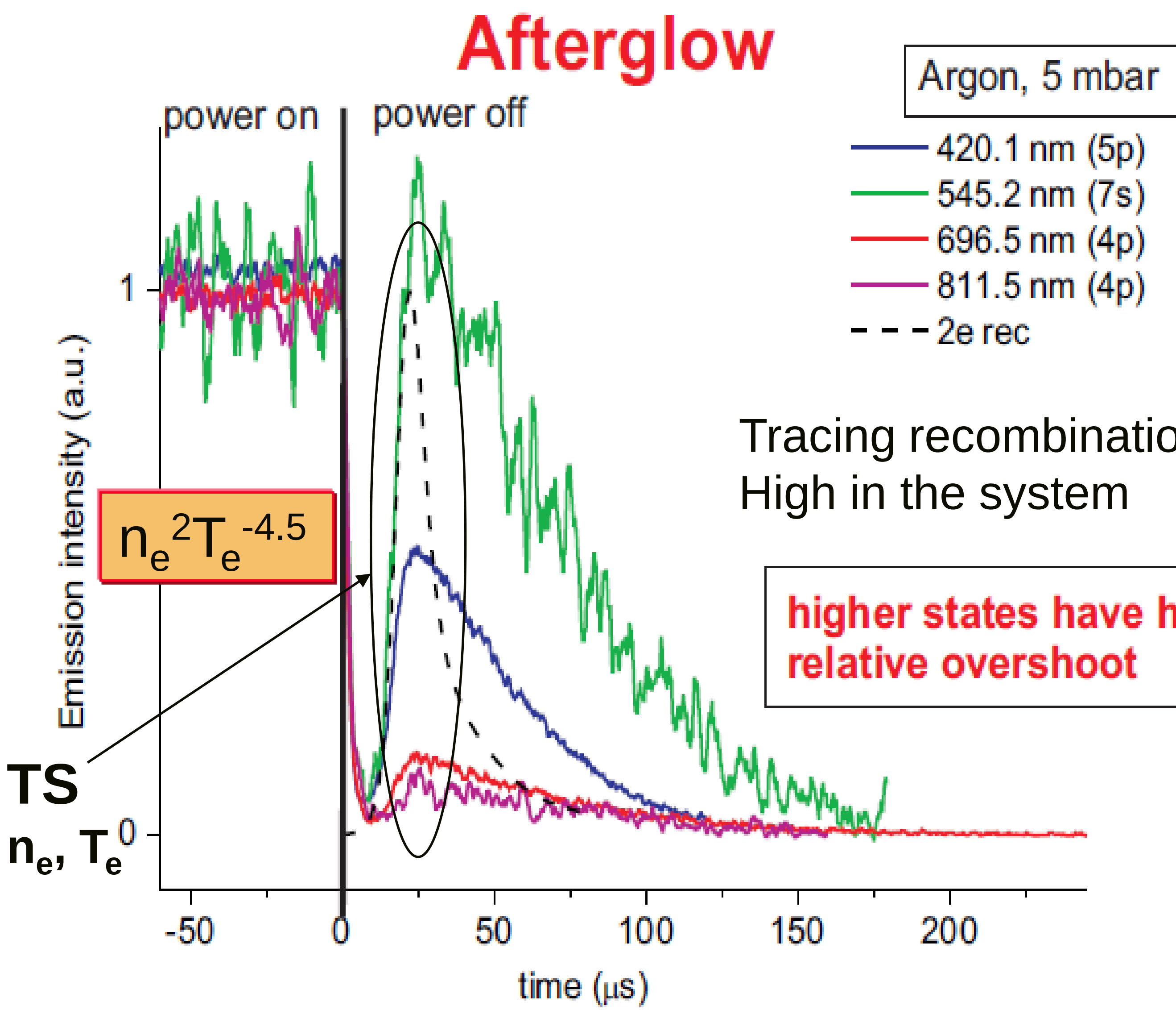
Solid state power supply τ(Power)~ 50ns!

Pure Ar plasma: RI and PI



TU/e

Saha remnants; again light



Tracing recombination flow
High in the system

higher states have higher relative overshoot

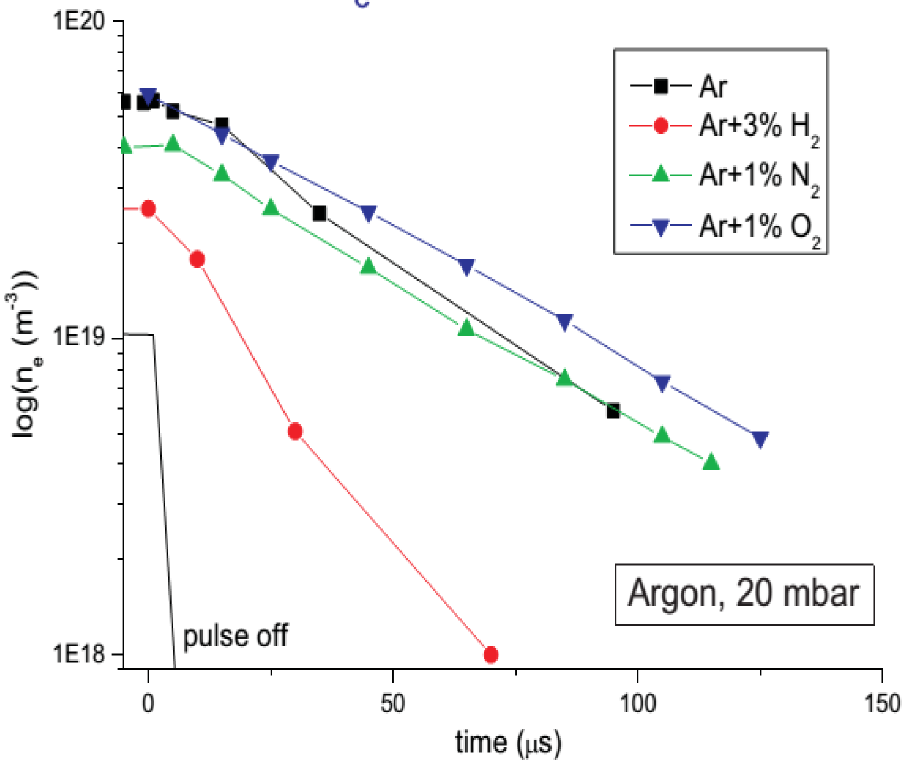
Confine to PI

Time scales $t_{off}(n_e) = 20 - 100\mu s$

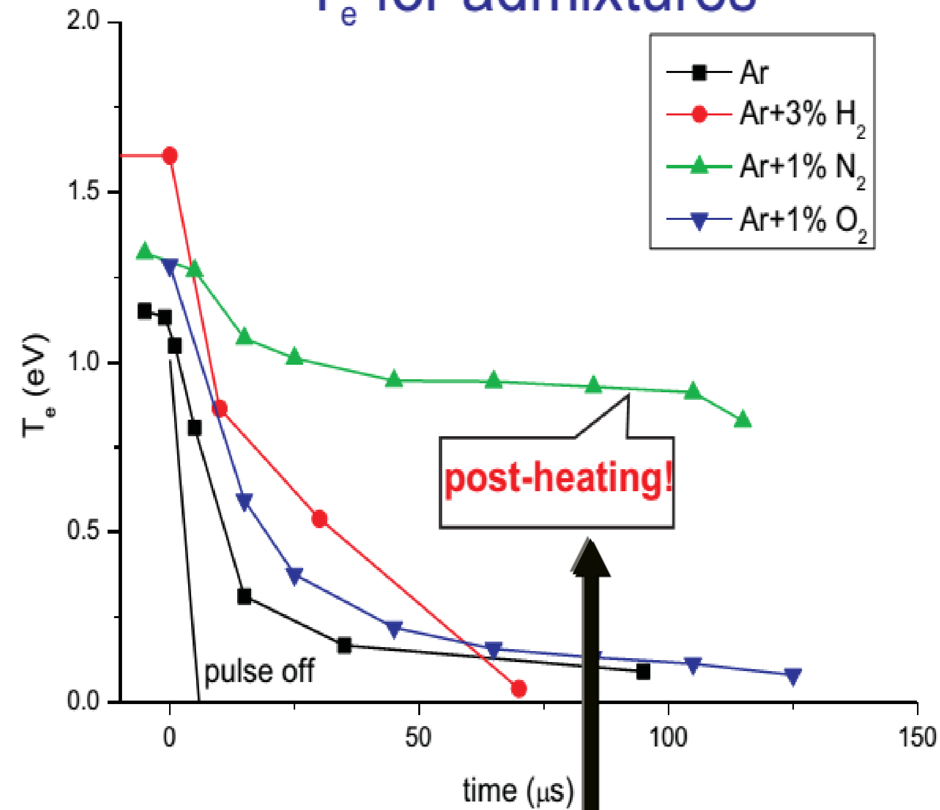
$t_{off}(T_e) = 1 - 5\ \mu s$

Depends on gas pressure and mixture

n_e for admixtures



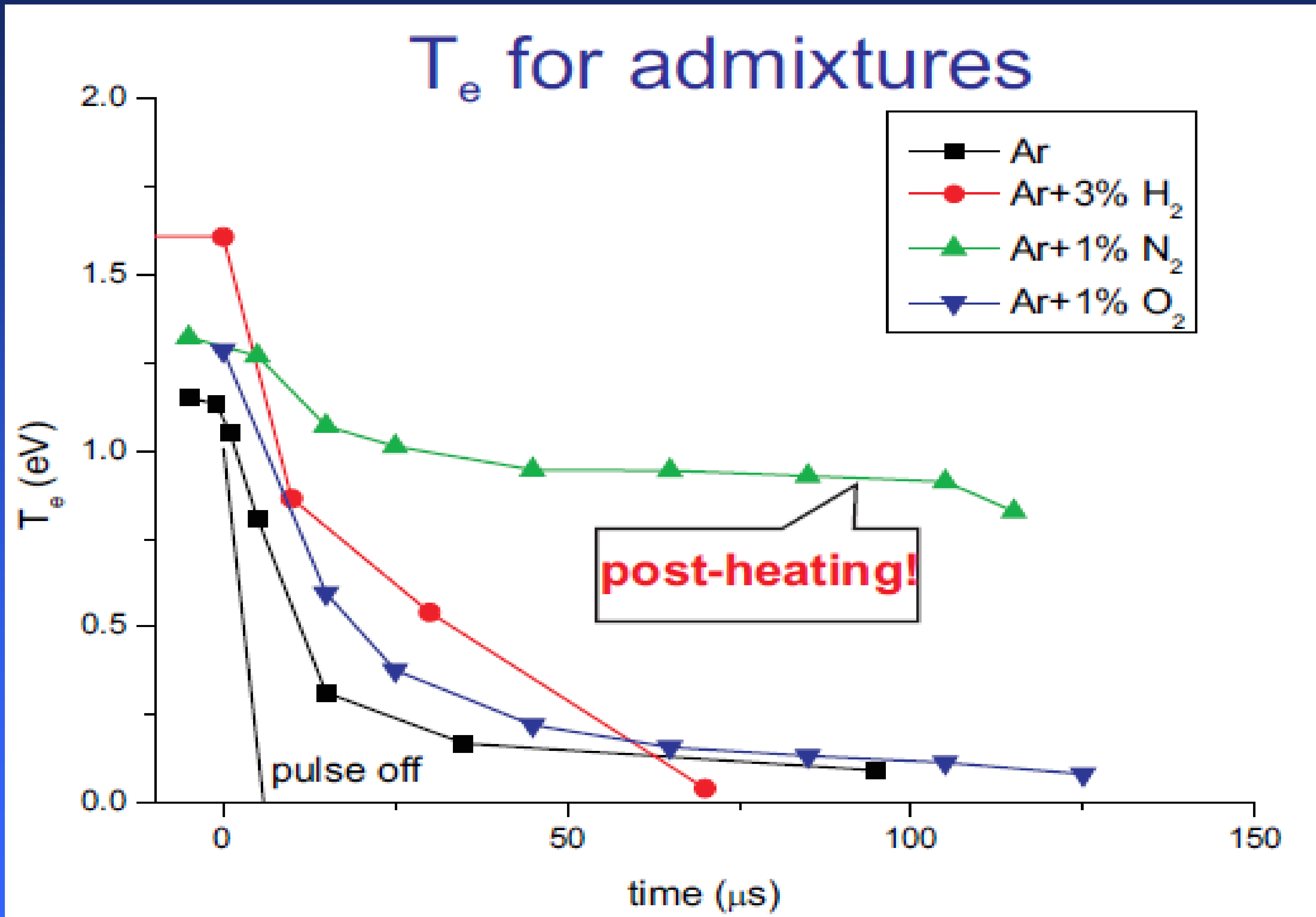
T_e for admixtures



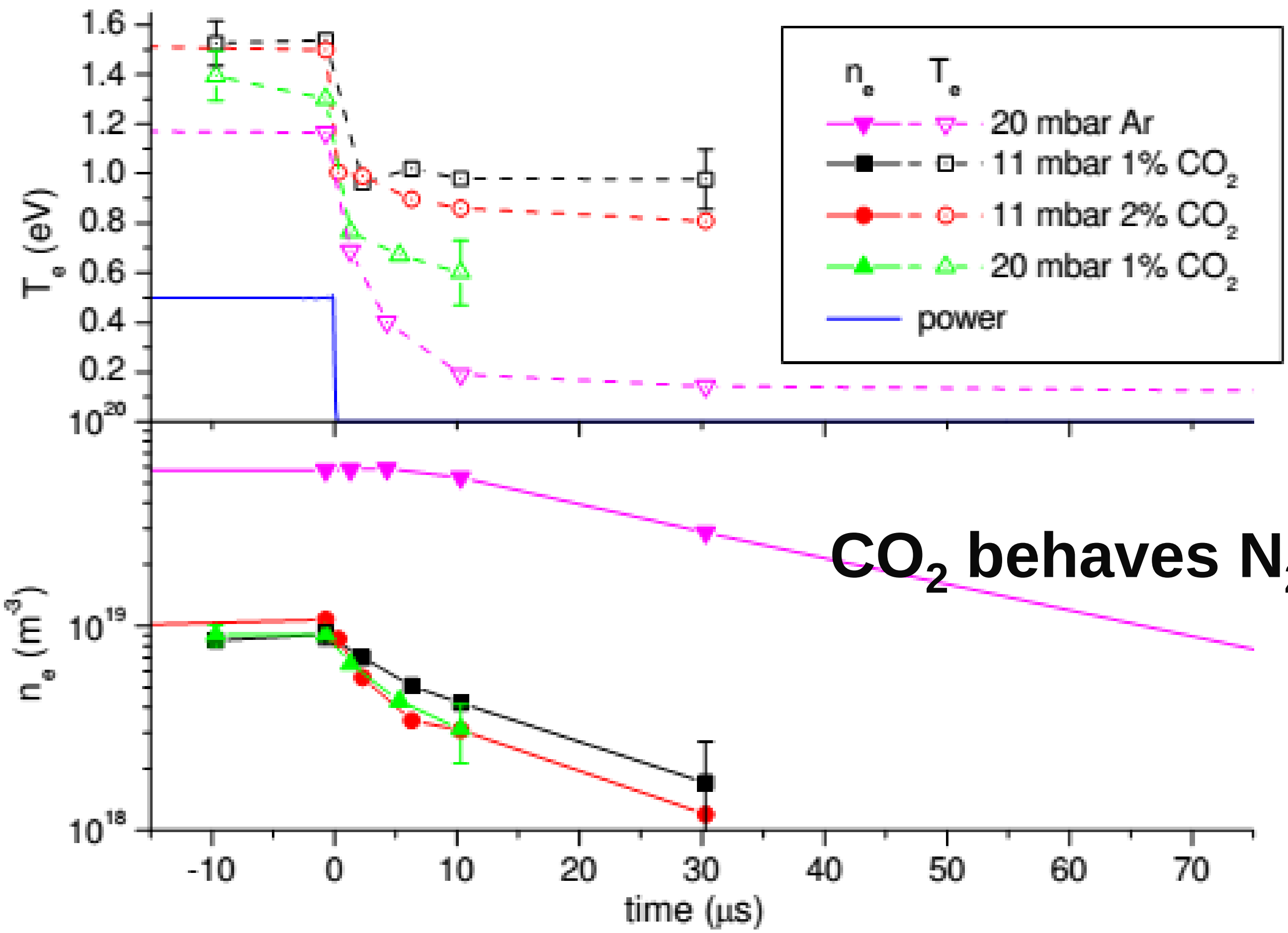
H_2 and O_2 behave Ar-like

For N_2 there is {e} **post-heating**

Strange T_e behavior in N_2 and CO_2



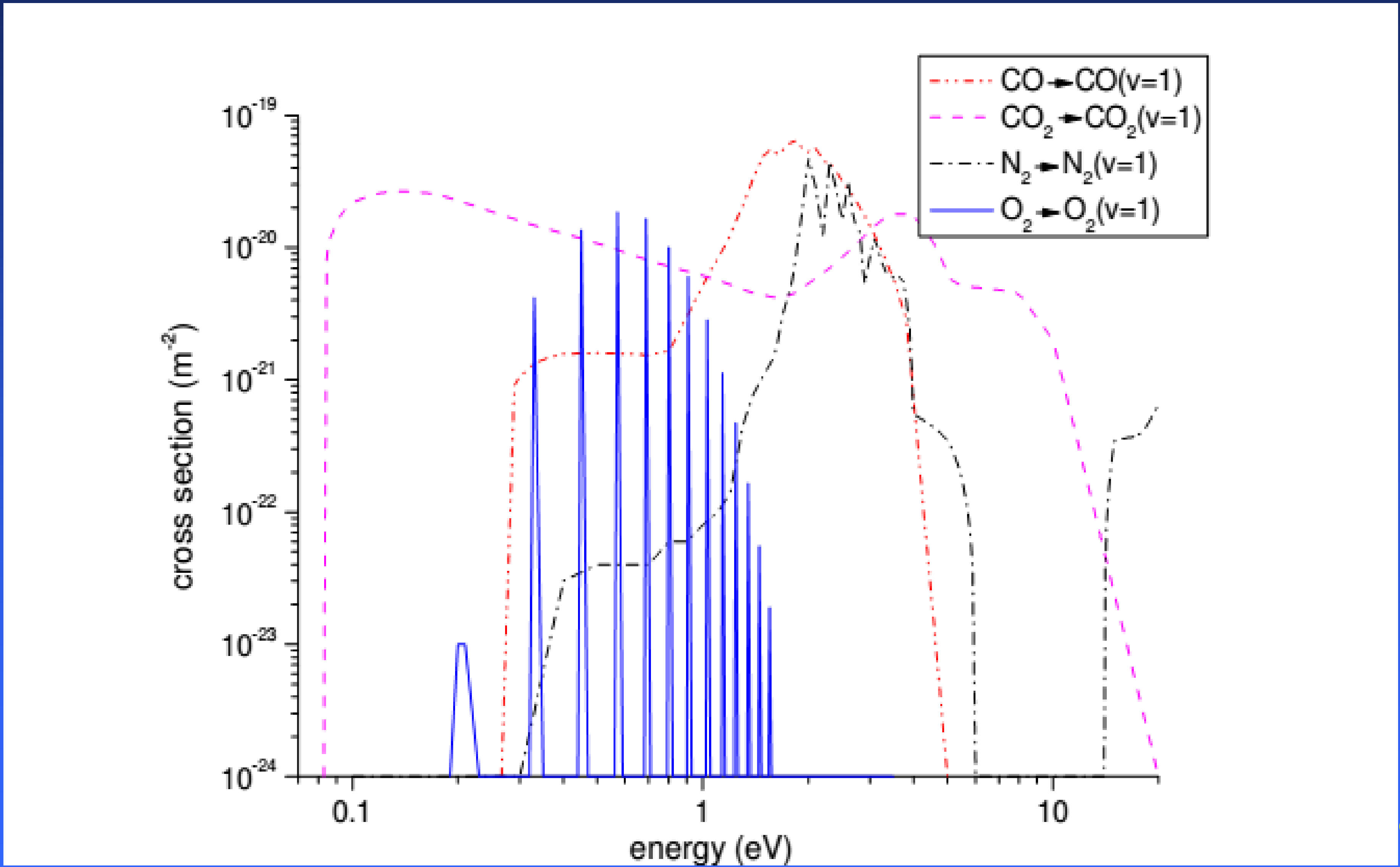
What about CO_2 ?



CO_2 behaves N_2 like!!

TU/e

Digging into cross sections



$CO_2 \rightarrow$ value added chemicals

B

Violeta Georgieva
Guoxing Chen
Nikolay Britun

Anemie Bogaerts
Antonin Berthelot

Shaoying Wang
Jose Palomares

NL

PV + Wind: $CO_2 \rightarrow$ fuels (Solar fuels)

Concluding PI for CO_2

e- CO_2 Vib cross section is large

Good energy-coupling inelastic- super-elastic e-CO_2(vib)

CO_2 dissociation most likely e-CO_2 ladder-climbing

T_{vib} (CO_2) must be large ~ 10.000K

T_{trans} (CO_2) is small ~ 1000 K (in this plasma)

T_{wall} is low ~ 1000K

Coupling vib-wall bad

A grand CO_2 plasma model must account for e-CO_2(vib) coupling

TU/e

Sub-conclusions

Power manipulation gives insight in

Plasma Transport

Recombination/Ionization

Cooling/Heating

Role of Molecules

Solid state power supply better

Best: Thomson Scattering during Power Manipulation
supporting light interpretation

Reaction dynamics

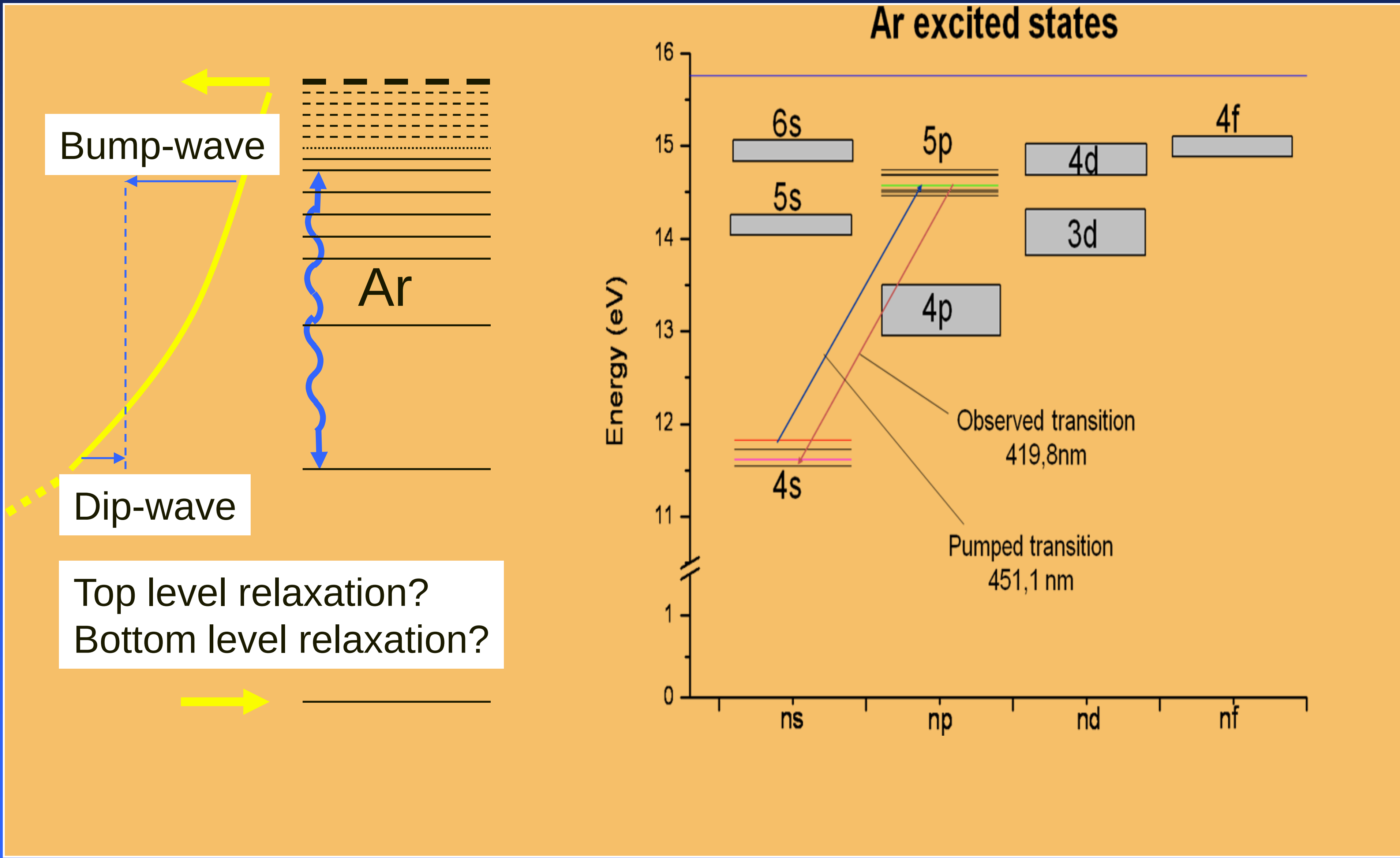
For knowing the reaction velocities; rates wanted:

Even shorter times

Fine tuned disturbances

$\rightarrow$ t-LIF

t-LIF in an ionizing Ar plasma



Laser: needed high rep rate

Classical	Yag-Dye	10 ns	100 mJ	10Hz
Novel High RR	Yag-Dye	10ns	4 mJ	10kHz

DP-SSL

1000 x more info per unit time

1000 days

PhD

1 day

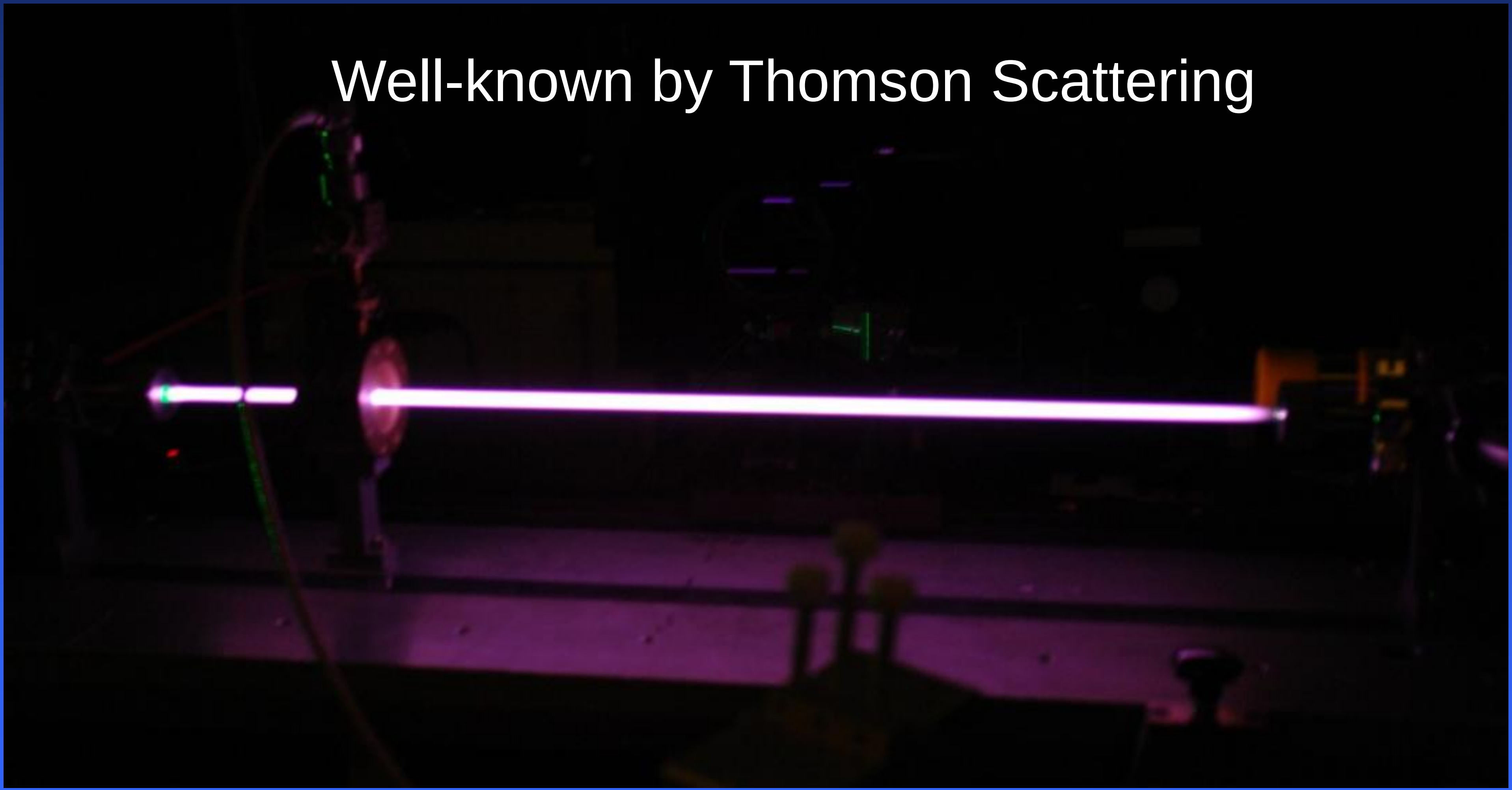
Yag+Dye = Edgewave+Sirah

Two systems

1) The "blue" 2f 355 nm pu

2) The "green" 3f 532 nm pumped

The plasma source: a low-p SIP



What's in a name

SA NI SaTiRe LIF @ Hrr

High Rep Rate: wanted photons
no pile-up

Laser induced fluorescence

Time Resolved: excitation kinetics

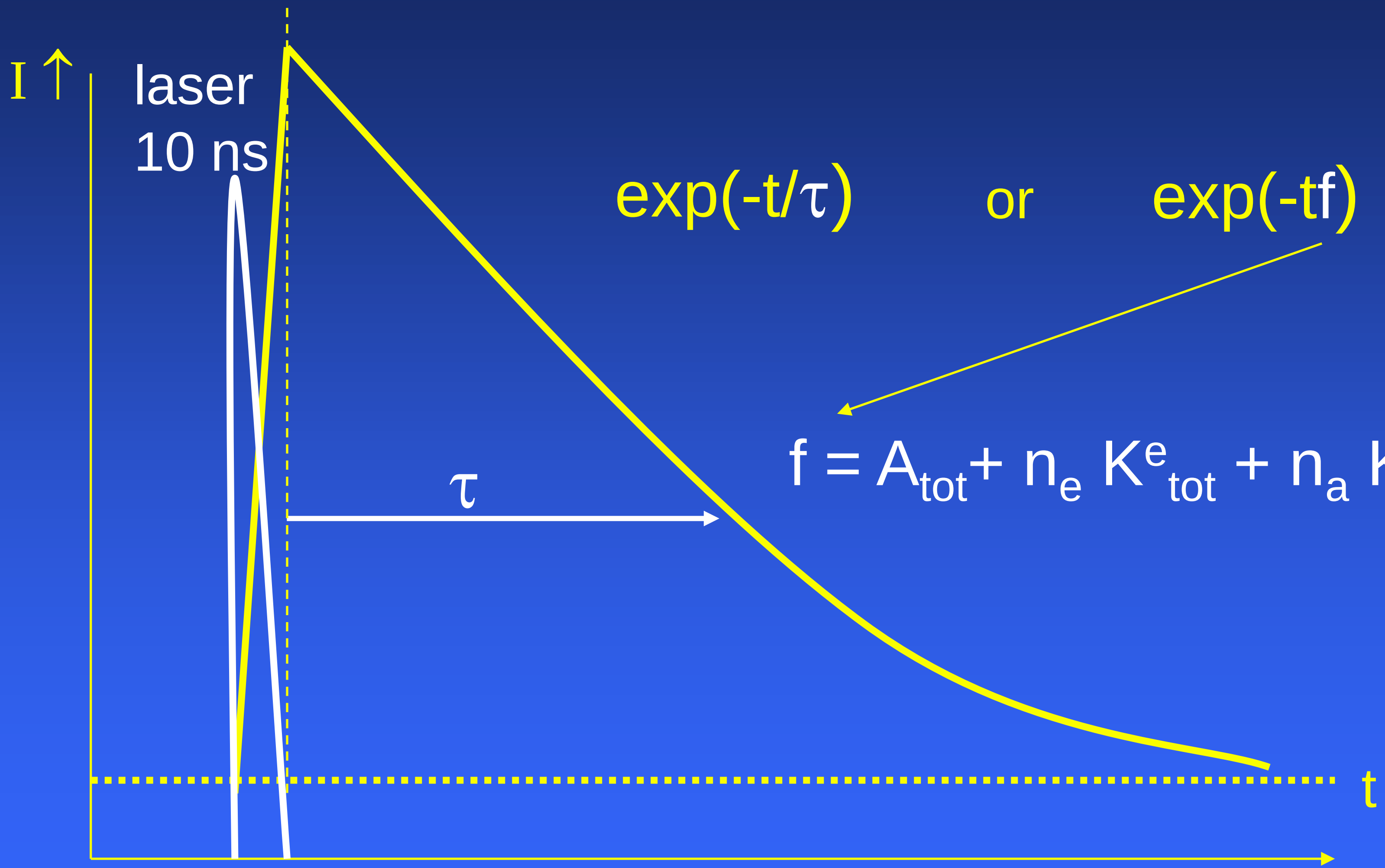
Saturation: reveals lower level

Non Intrusive: do not change plasma n_e and T_e

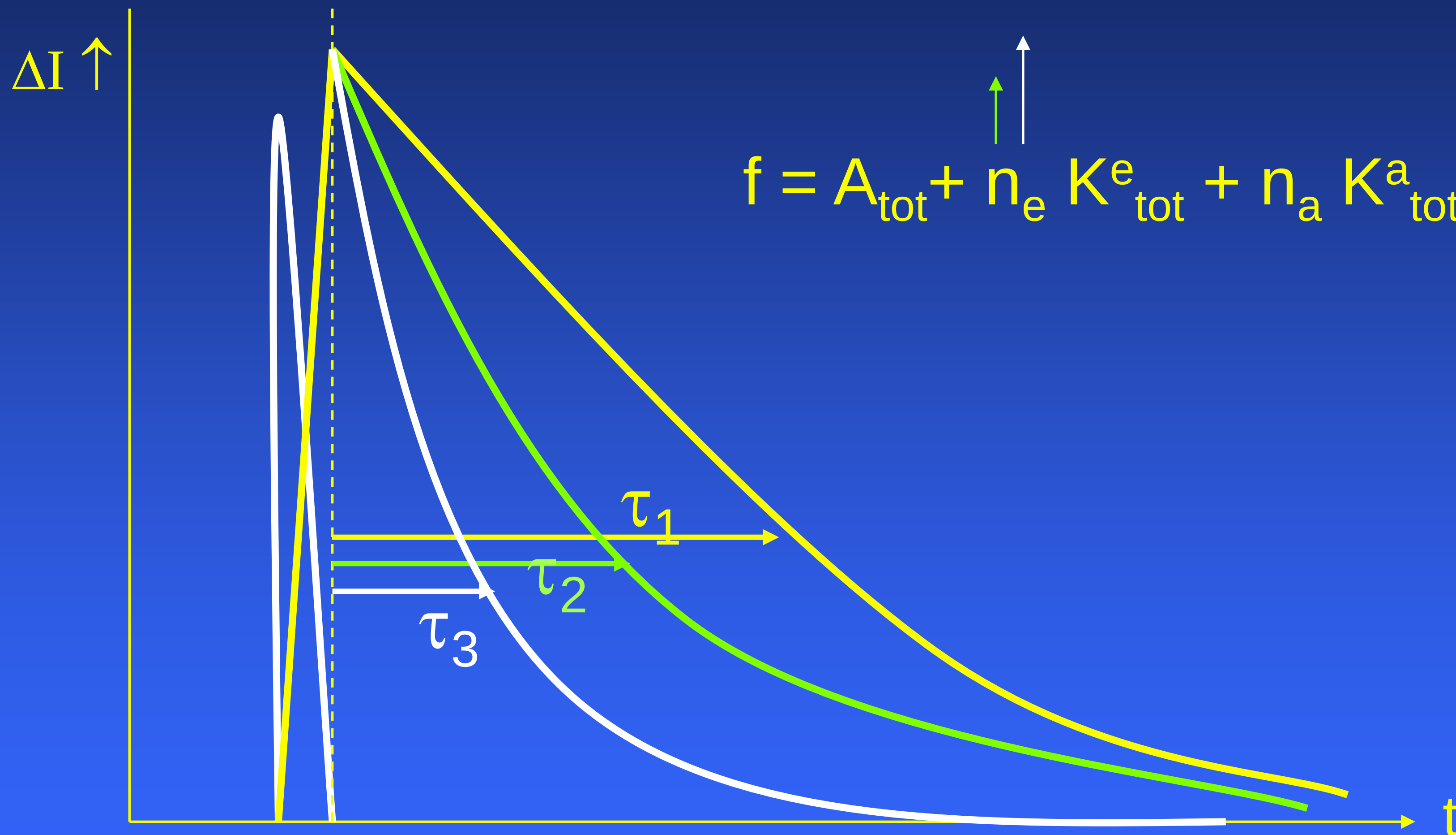
Short Activation: distinction instantaneous/delayed resp

Plasma dependent

The upper level: what we expect?

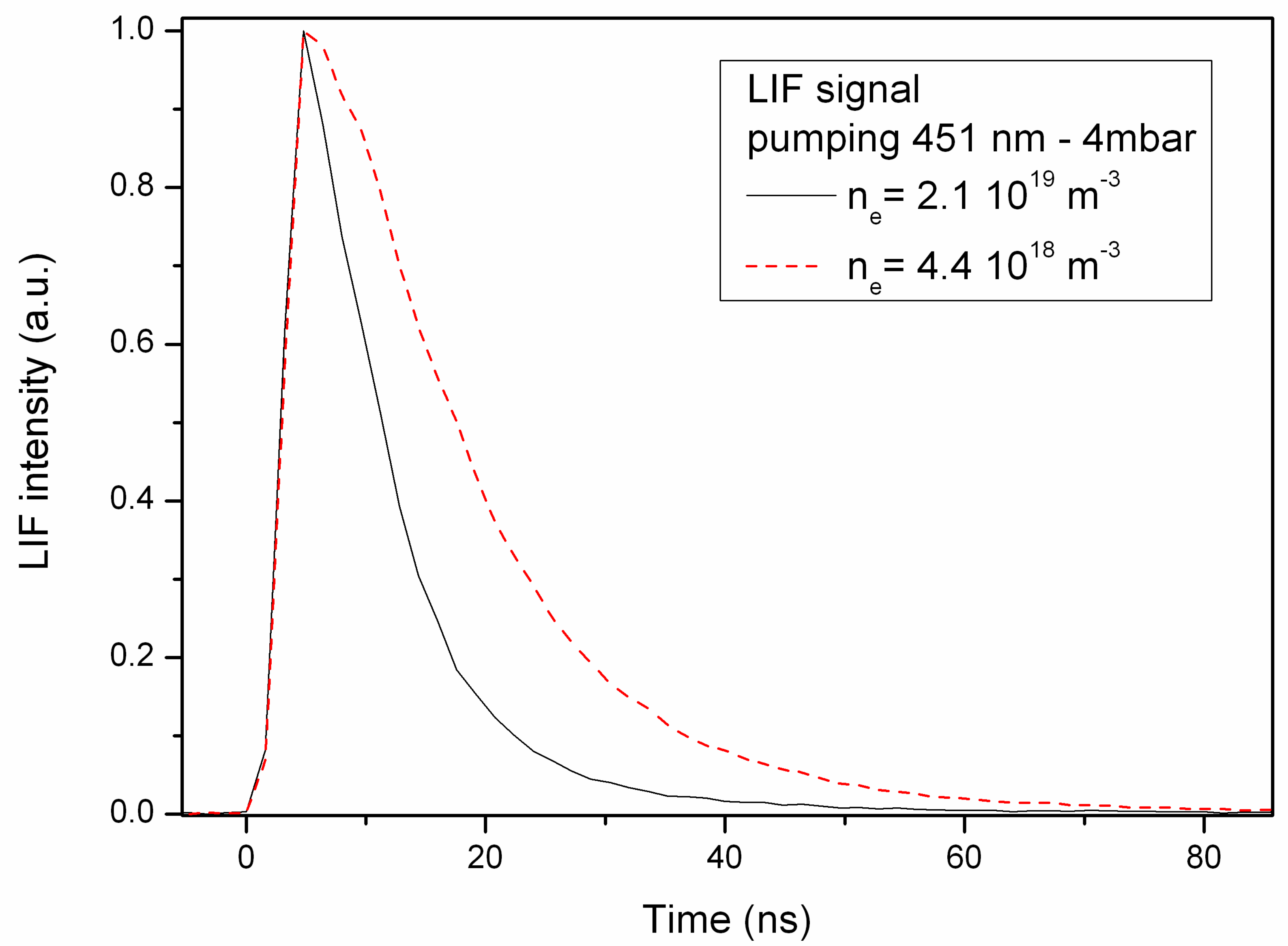


Total destruction frequencies

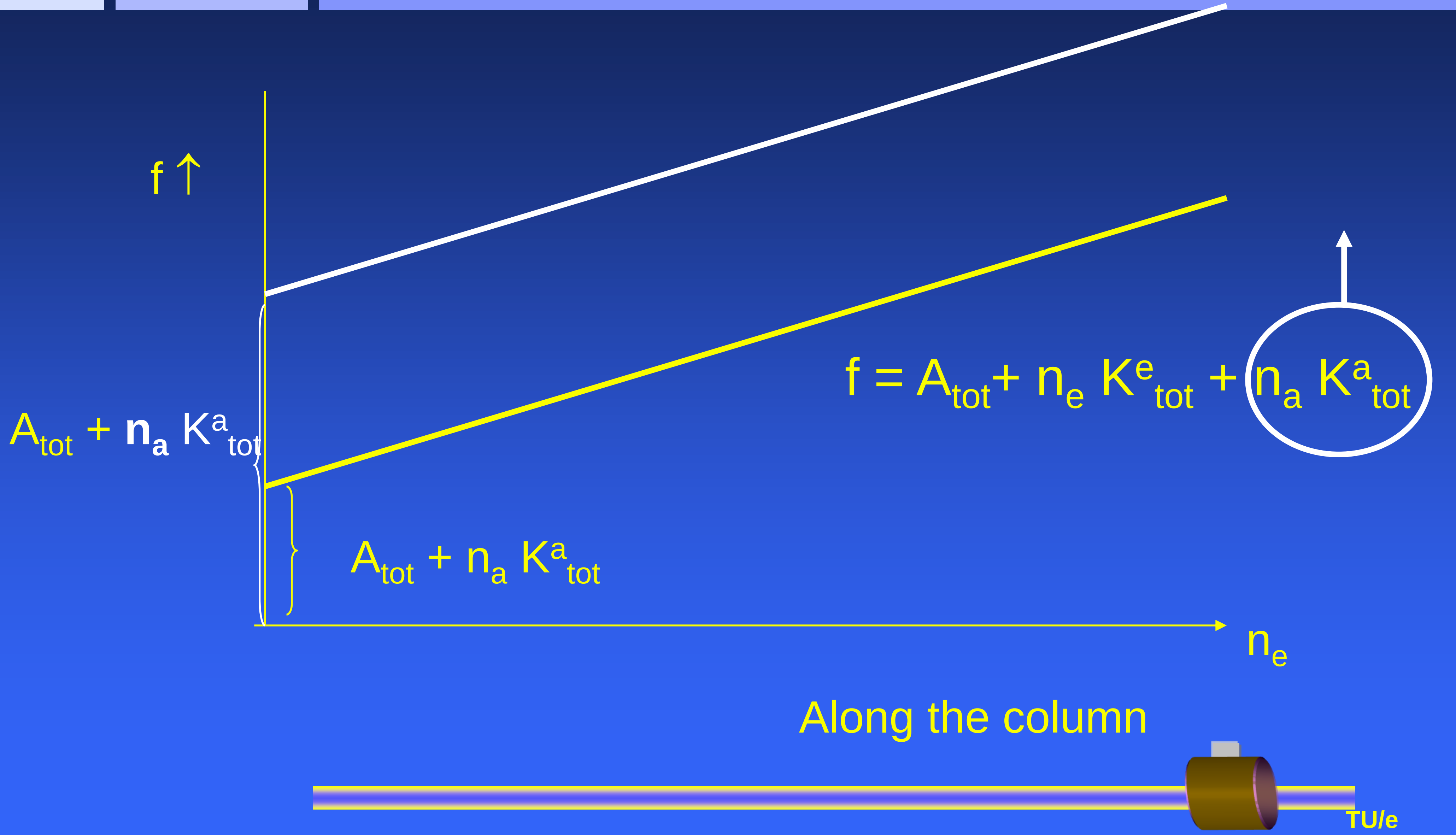


$$f = A_{tot} + n_e\, K^e_{tot} + n_a\, K^a_{tot}$$

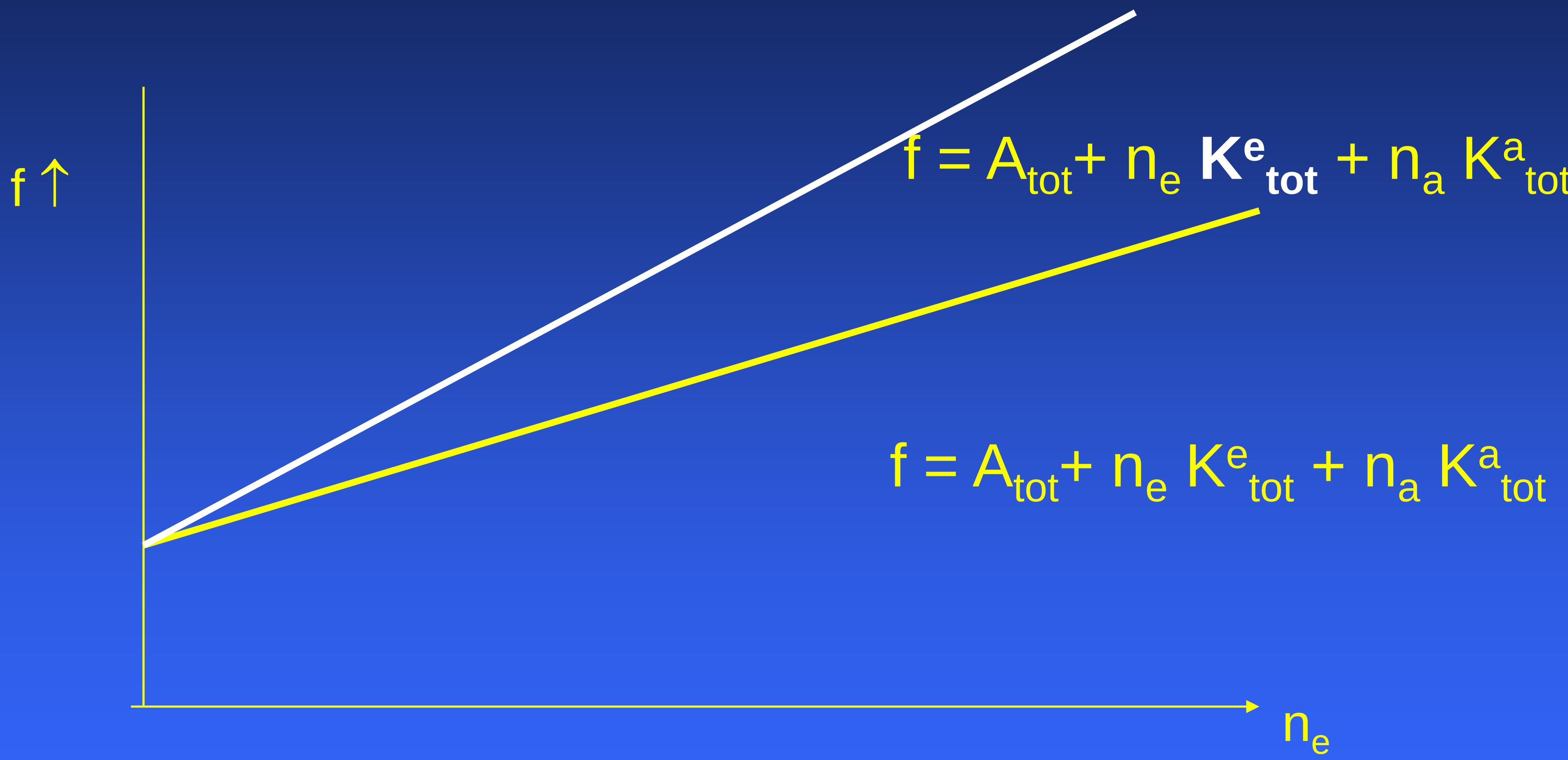
Example: Response of a 5p level



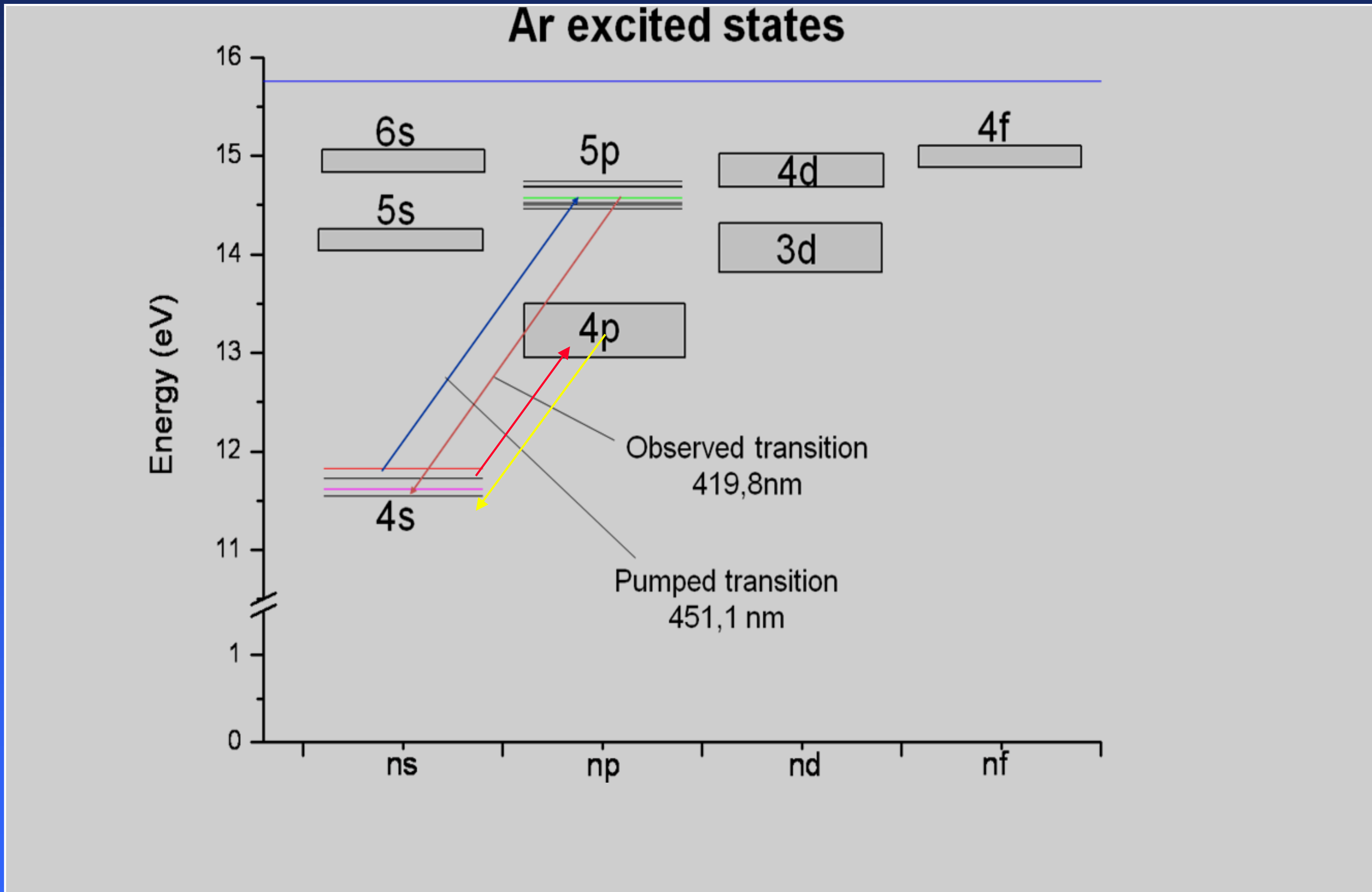
Influence n_e and n_a (gas density ~ pressure)



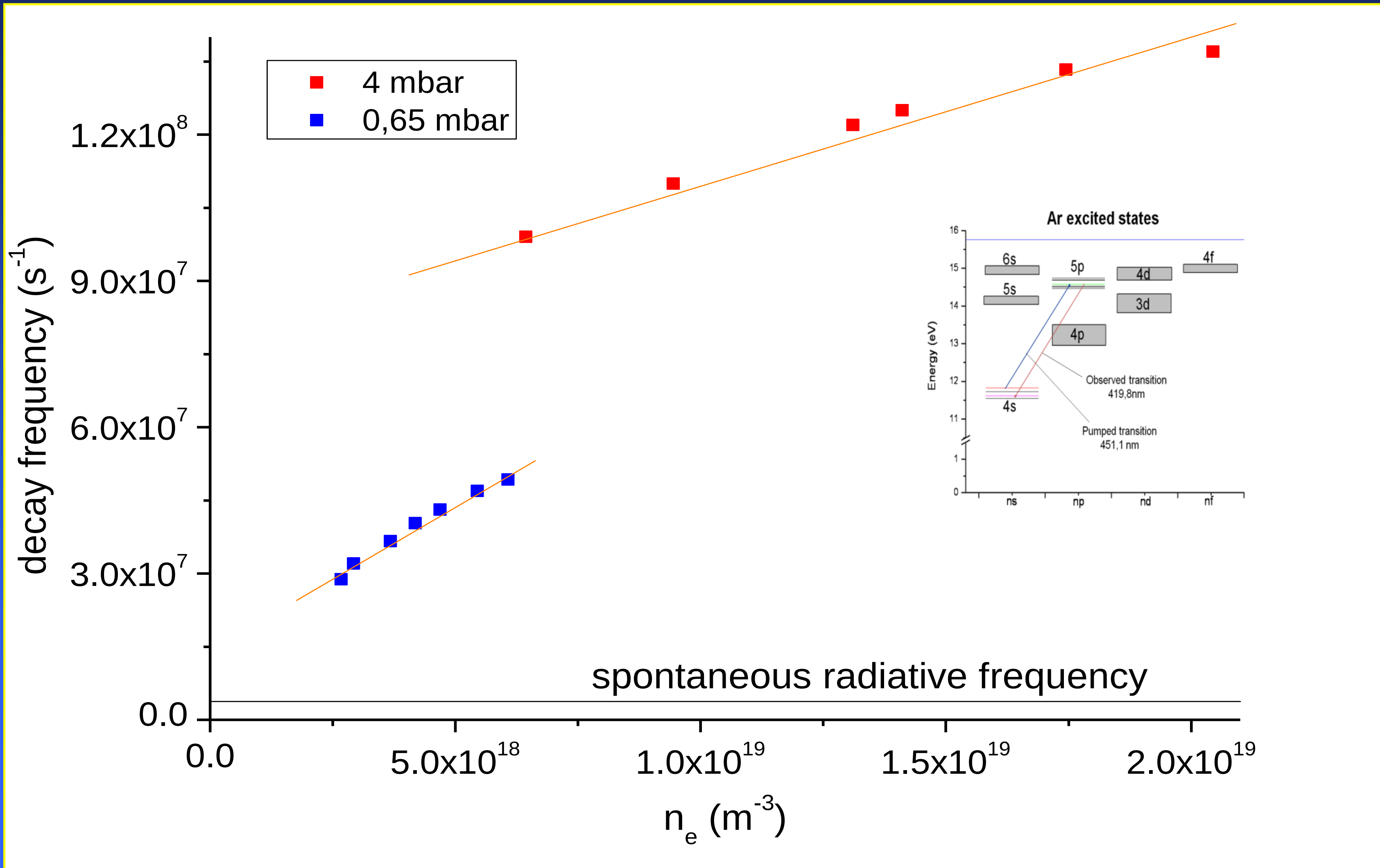
Higher rates; increase T_e



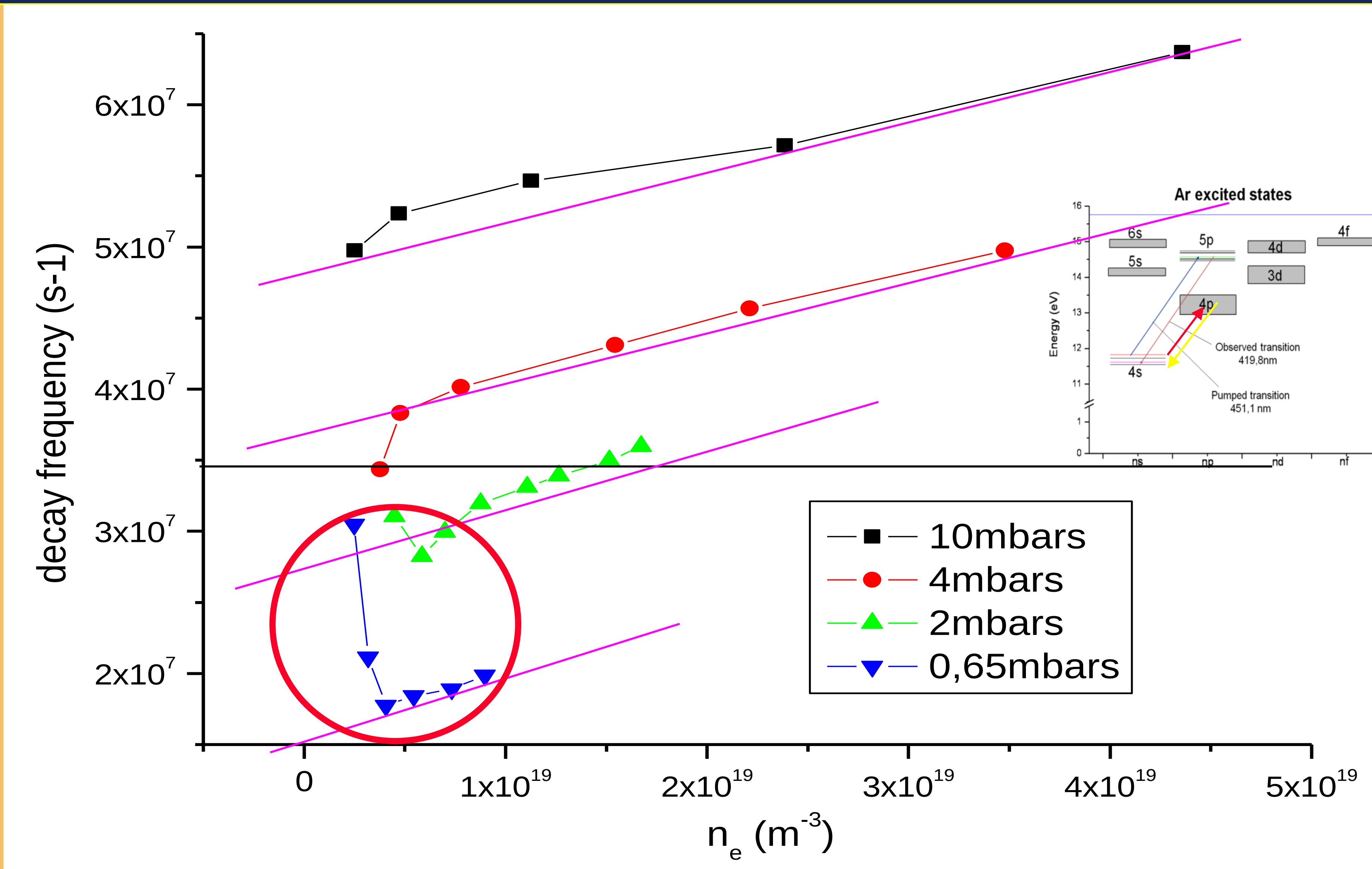
t-LIF in 4s-4p and 4s-5p



Fluorescence on 5p



Fluorescence of 4p



Decay lower than $A_{tot:}$ How come? Radiation Trapping

Delayed responses: the bump and dip

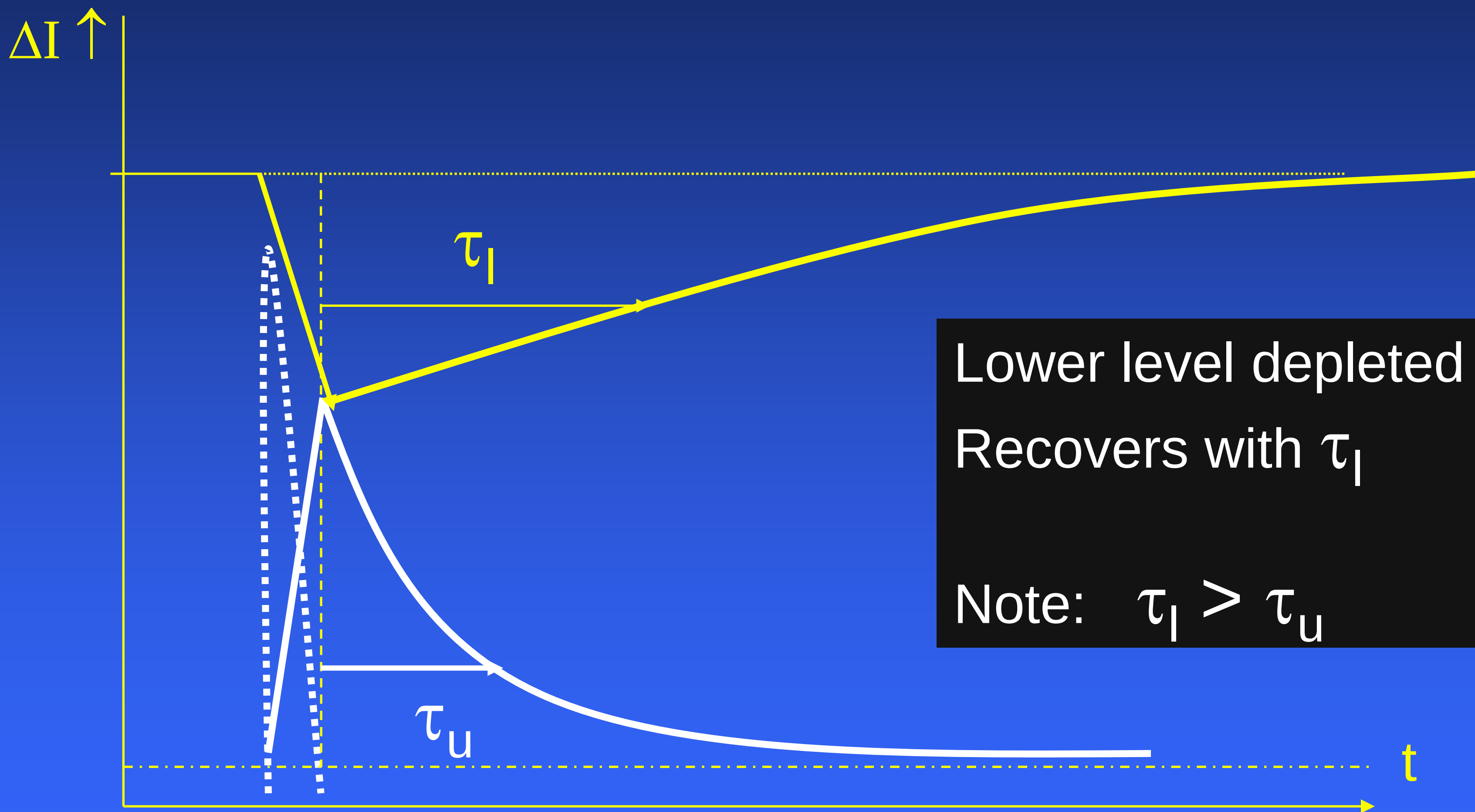
Total destruction rates can be determined

How are these composed?

Where is population surplus going to?

Redistribution	surplus	bump-wave
	depletion	dip-wave

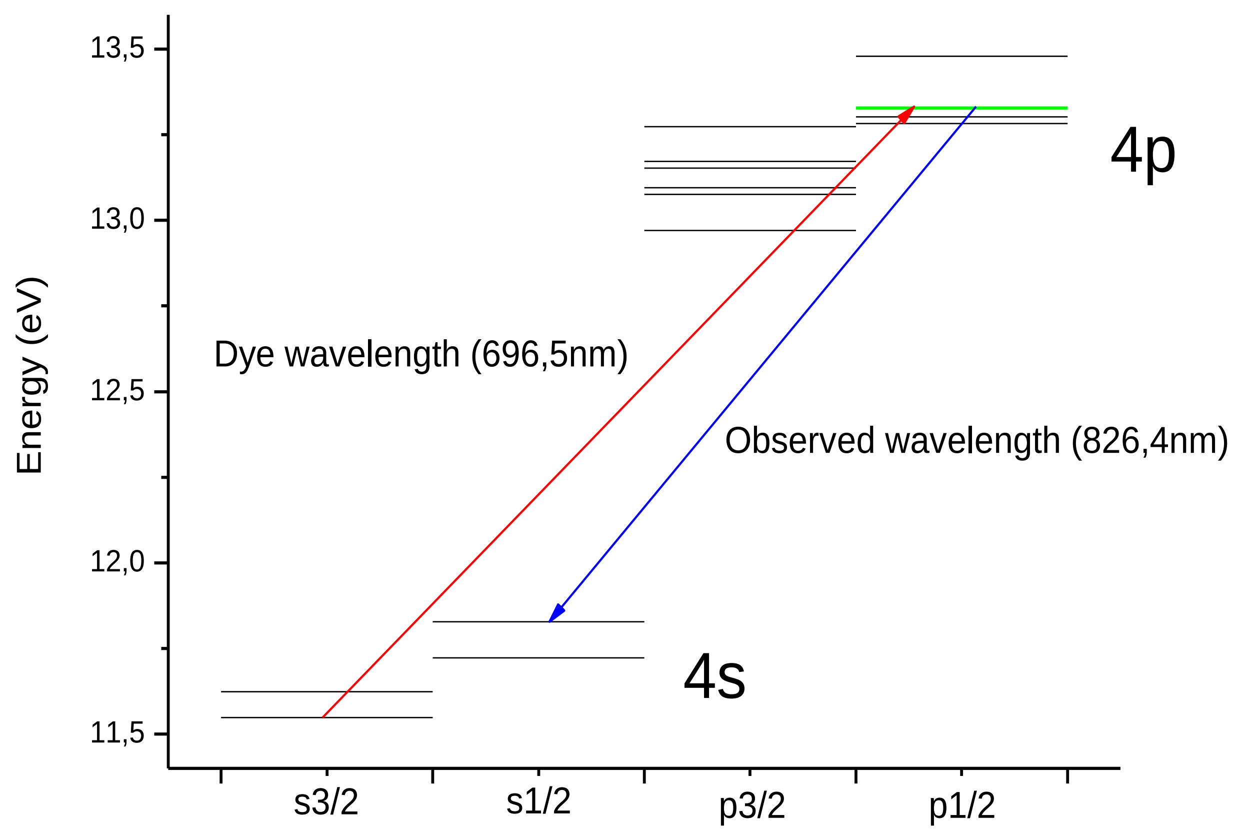
Pos and neg contributions



Lower level depleted

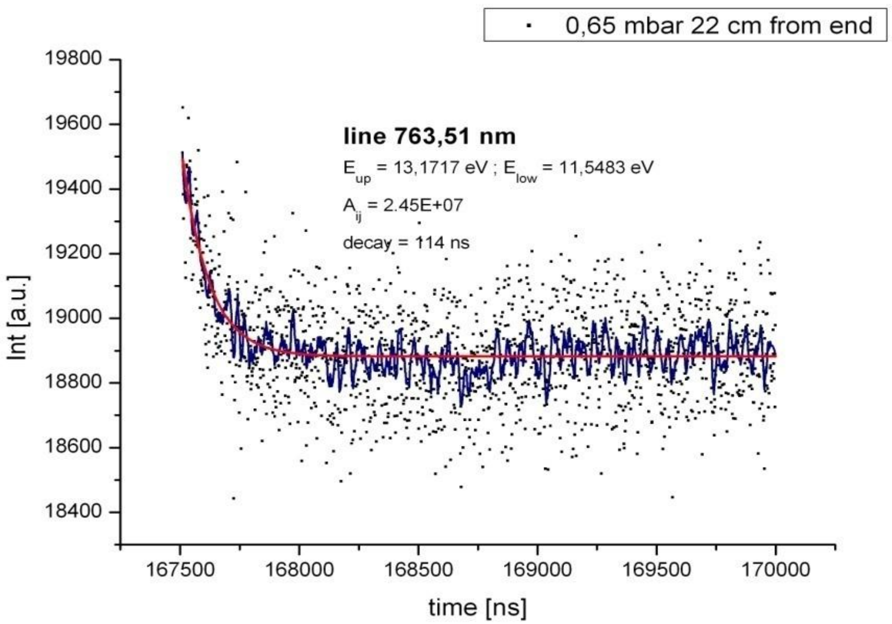
Recovers with τ_l

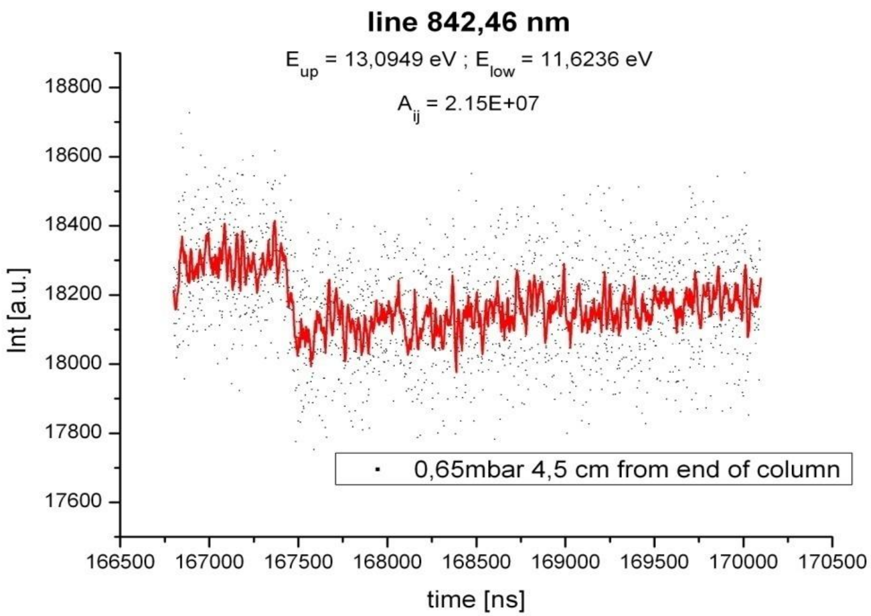
Note: $\tau_l > \tau_u$



Energy (eV)
13,5
13,0
12,5
12,0
11,5
4p
4s
Dye wavelength (696,5nm)
Observed wavelength (826,4nm)
s3/2
s1/2
p3/2
p1/2

Delayed responses

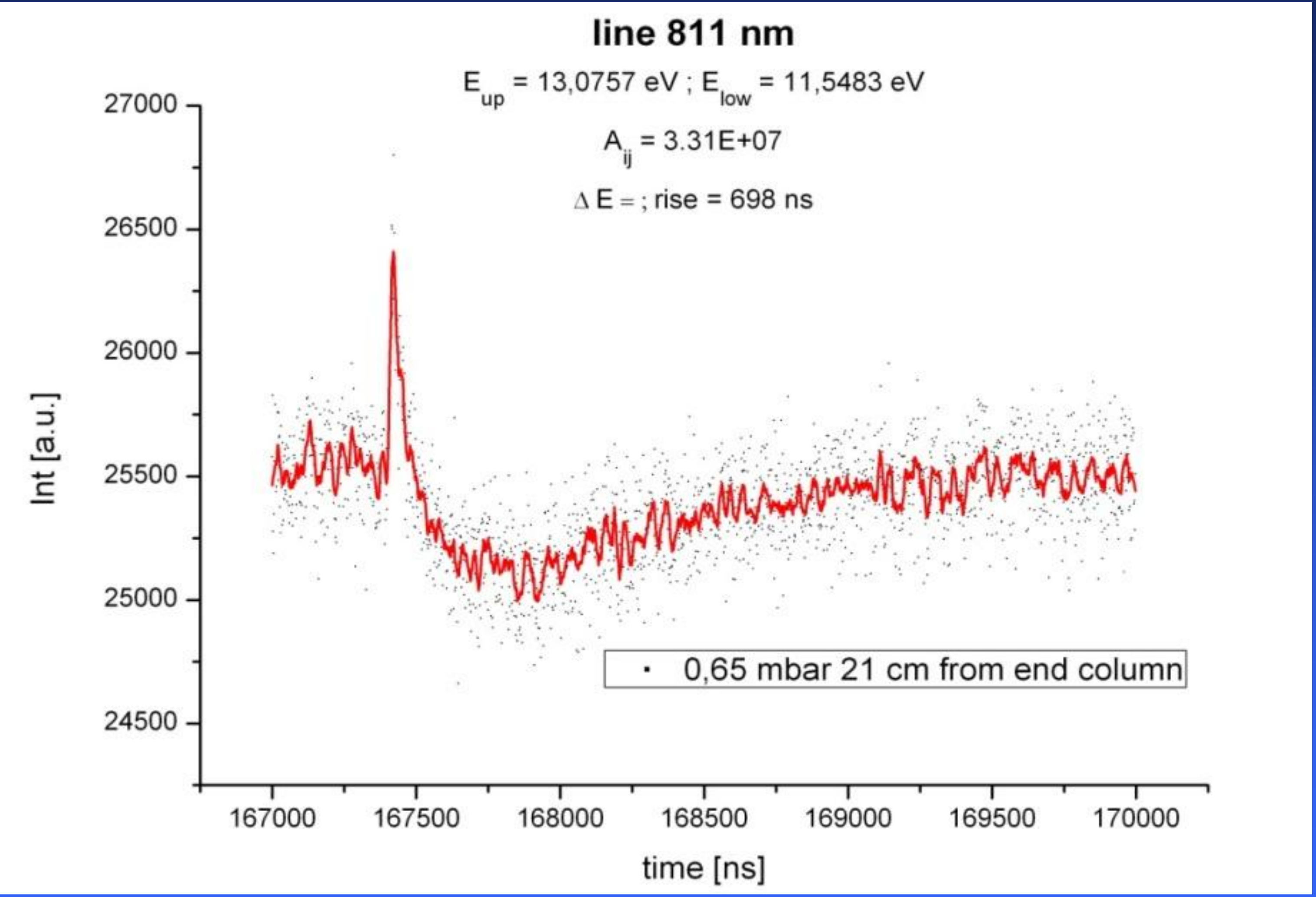




Coupled with upper level

Coupled with lower level

Mixing



Mixed influences

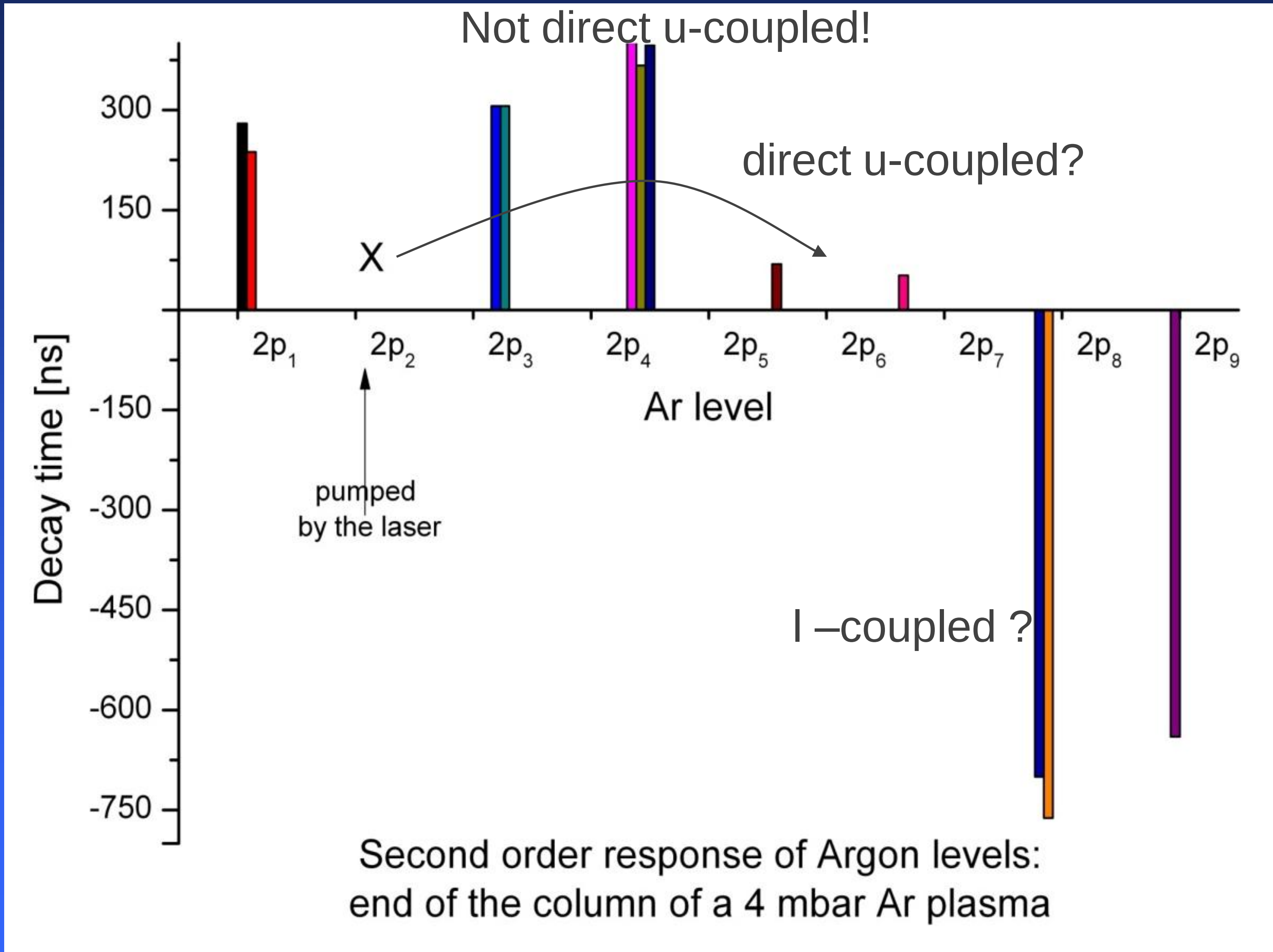
TU/e

Bump/Dip exploration

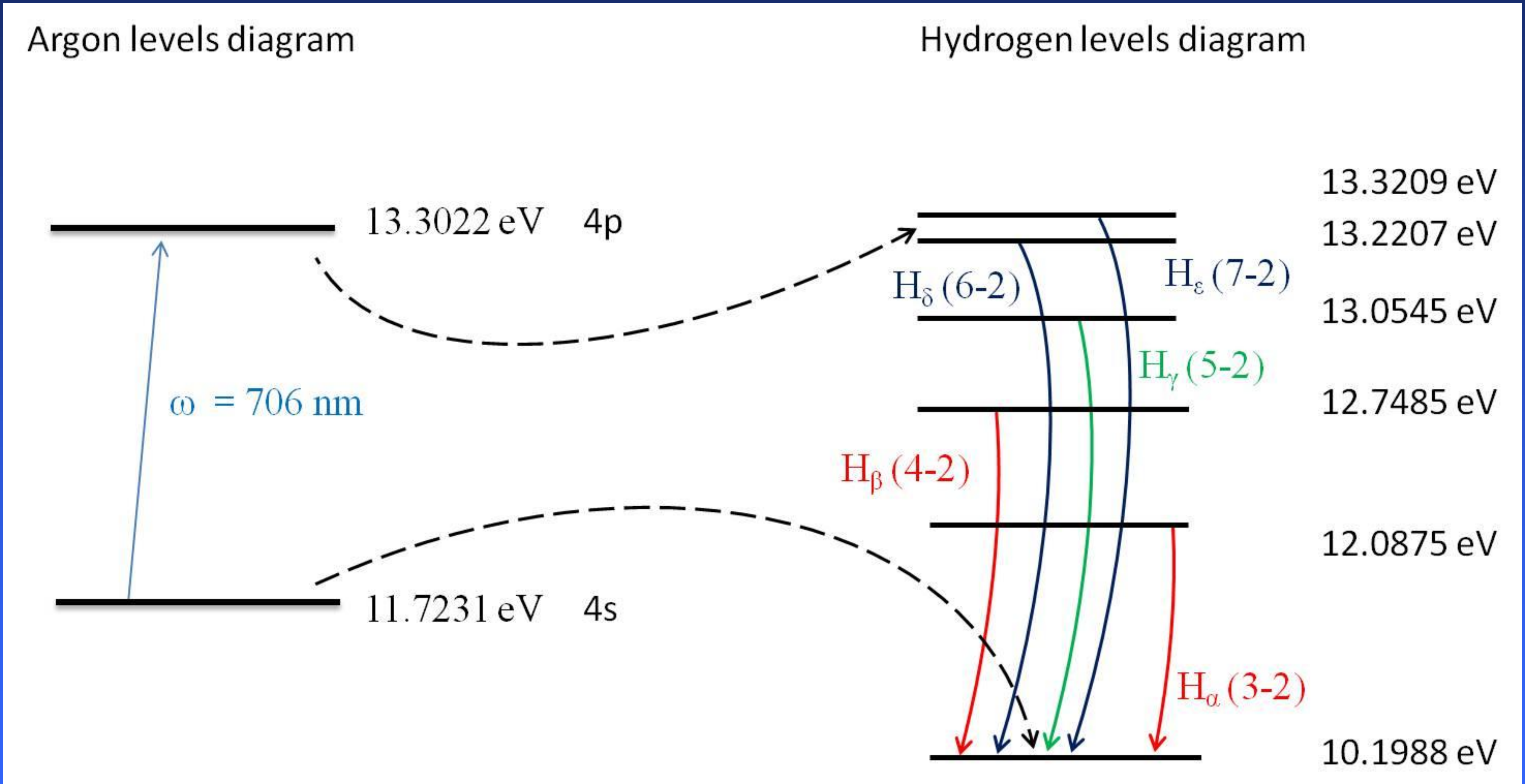
Sources: level s	upper level	u
	lower level	l

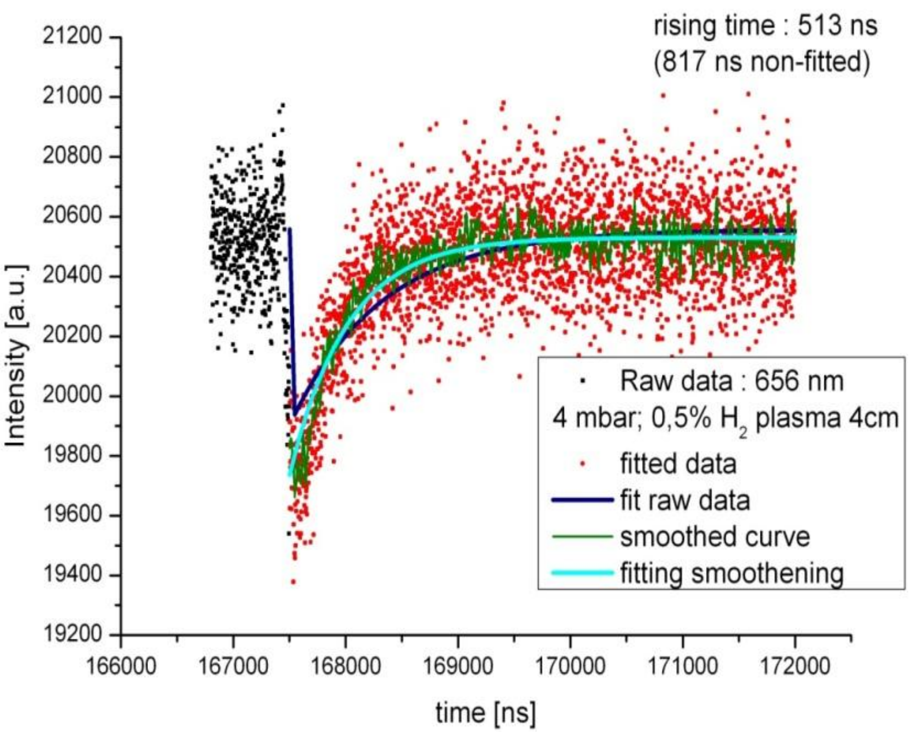
Response level r	**temporal** structure	D(s) and D(r)
	amplitude coupling	D (s, r)

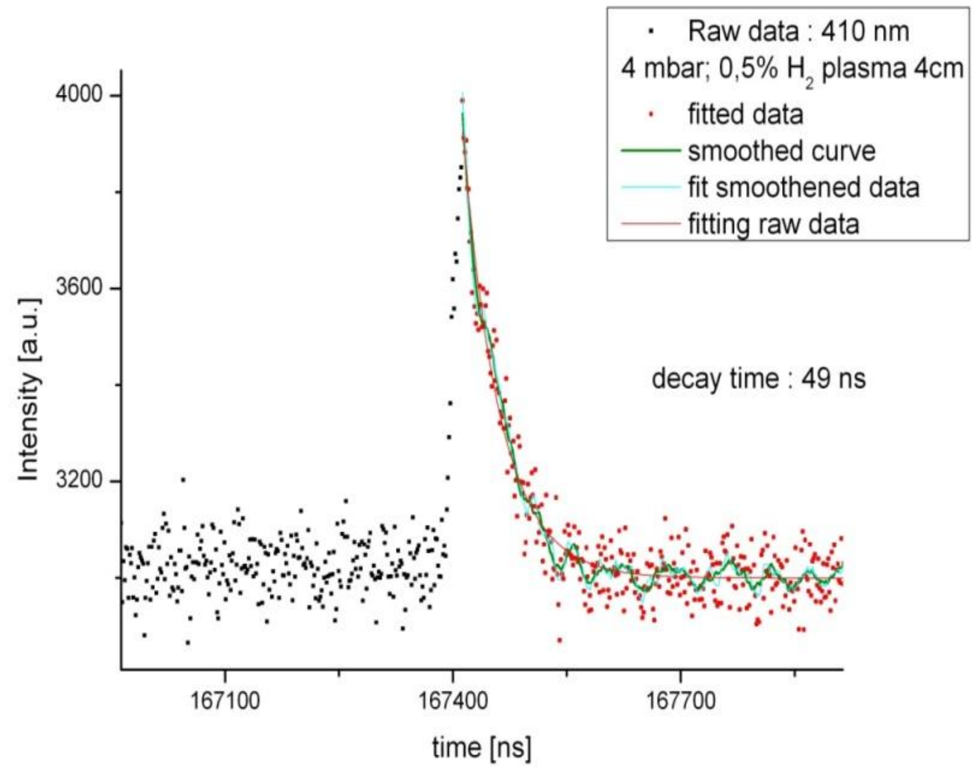
Temporal features



Romance in excitation space Ar x H

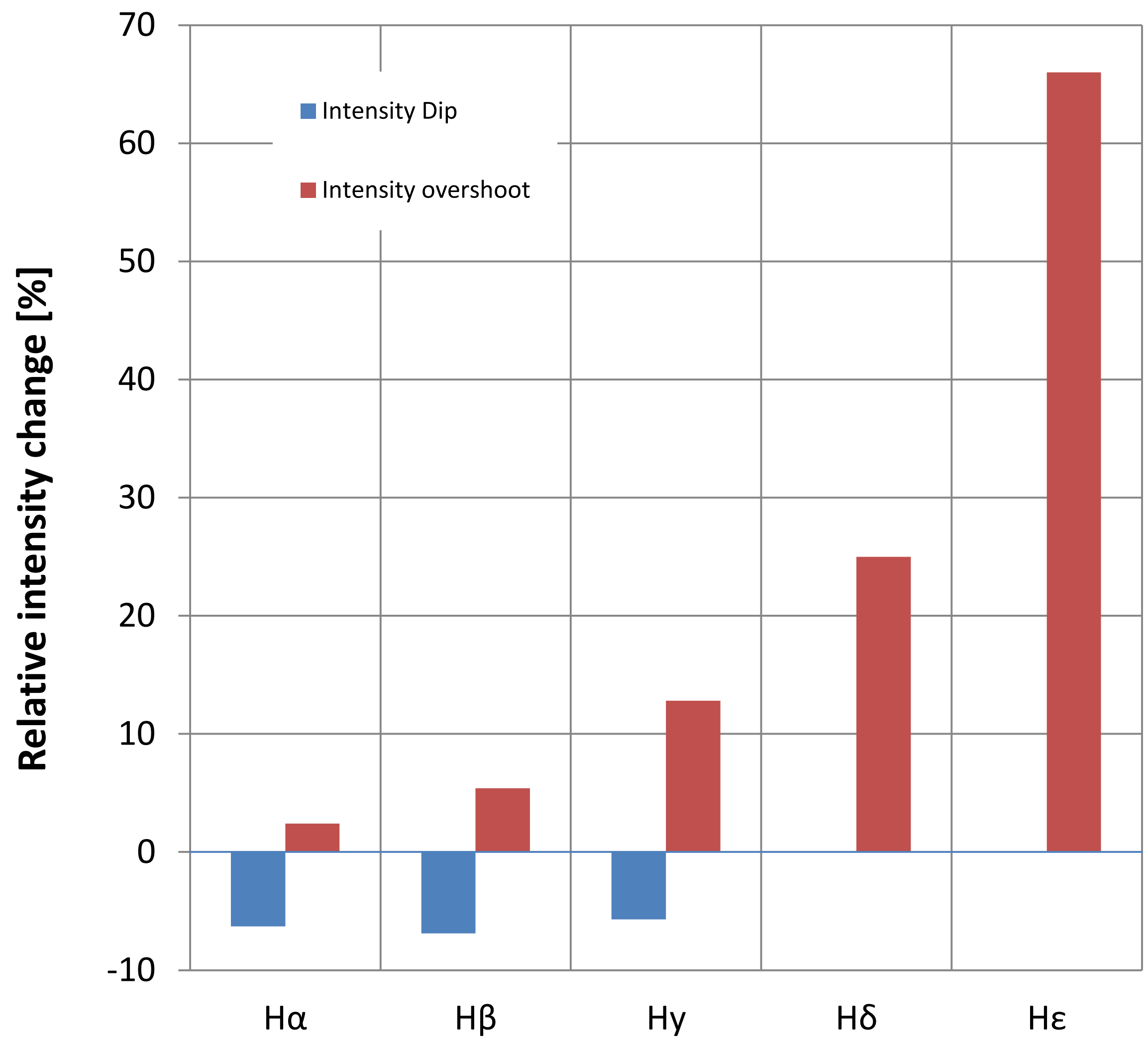






H_α (656 nm) p =3

H_δ (410 nm) p=6


Relative intensity change [%]
70
60
50
40
30
20
10
0
-10
Intensity Dip
Intensity overshoot
Hα
Hβ
Hγ
Hδ
Hε

Concluding

Combining high rep rate laser system
well known Surfatron

gives an enormous data flow

Rates of e-induced destruction

Rates of a-induced destruction

Population of meta-stables even beyond the plasma ?

Coupling **in** Ar

Coupling **with** Ar

Overall Conclusion

Combining Power Manipulation with t-LIF

Gives insight in

transport phenomena of the plasma as a whole

the role of individual processes.

These are only the first steps in understanding
The complex phenomena of plasma applications

Acknowledgement

Thanks

for the attention

the honor

the fun