Large Effects of Small Pressure Changes in the Kinetics of Low Pressure Glow Discharges

Isabel Tanarro & Víctor J. Herrero

itanarro@iem.cfmac.csic.es

Inst. de Estructura de la Materia
Consejo Superior de Investigaciones Científicas (CSIC)
Madrid, Spain

XX ESCAMPIG, 13 - 17 July 2010, Novi Sad, Serbia

Glow Discharges

- Stable over ΔP determined by the suitable conditions for e^- acceleration & multiplication in collisions with gas particles (under $P \times d$ scaling)

- Gas Pressure determines $\Rightarrow T_e$, N_e
  $\Rightarrow$ Frequency of Gas Collisions,
  $\Rightarrow$ Importance of Surface vs. Gas Processes
  $\Rightarrow$ Characteristics of the Plasma Sheath.

The composition evolves often gradually with pressure, but sometimes *ABRUPT CHANGES* are observed within a comparatively *SMALL PRESSURE INTERVAL*.

In this work, we will show that these sudden changes can provide valuable clues about the variation in the relative importance of the key mechanisms determining the plasma properties !

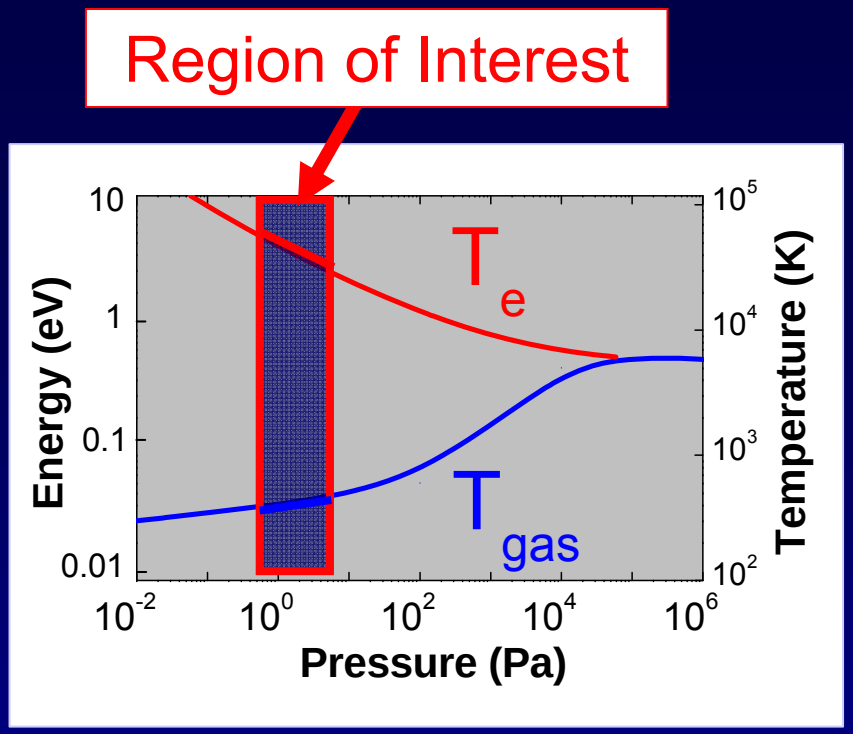
Issues of the Present Study

Generation of Plasmas in Hollow Cathode DC Discharges from Diverse Gas Precursors

Experimental Diagnostics of these Plasmas

&

Their Kinetic Modeling



Low Ionization Degree
+ Low Pressure

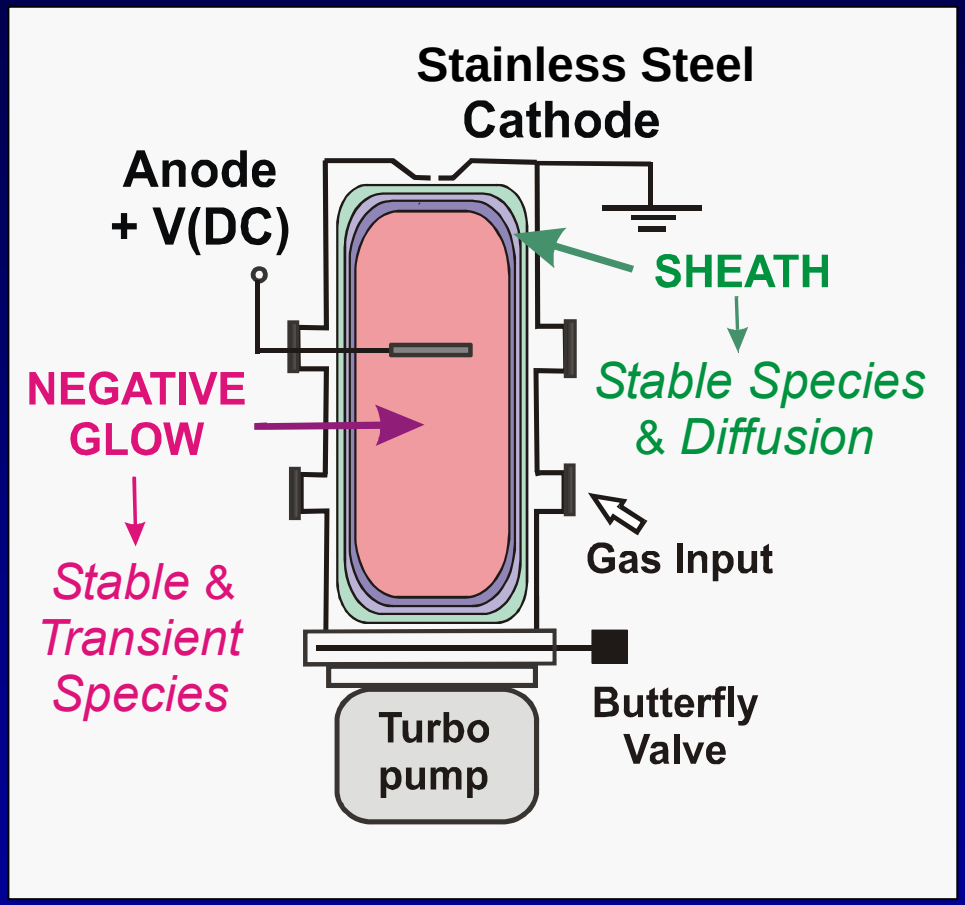
$\Rightarrow$

High Electron Temperature !
Low Gas Temperature (~ 300 K) !

Main Interest

Changes in the relevance of the different reaction paths induced by the change in plasma conditions

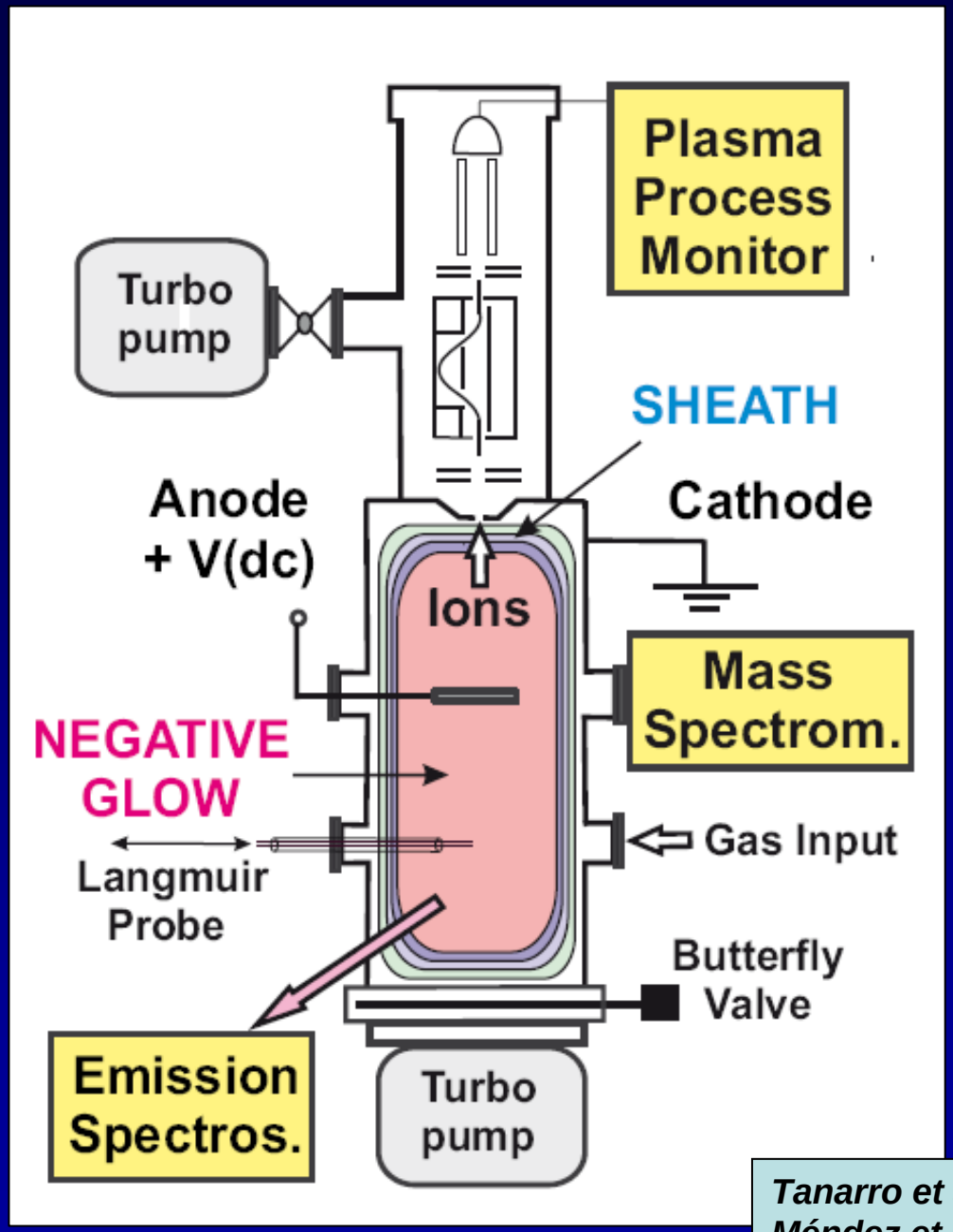
Plasma Generation in Hollow Cathode Reactors



Tanarro & Herrero, PSST, 18, 034007 (2009)
Herrero et al., J. Mass Spectrom., 43, 1148 (2008)

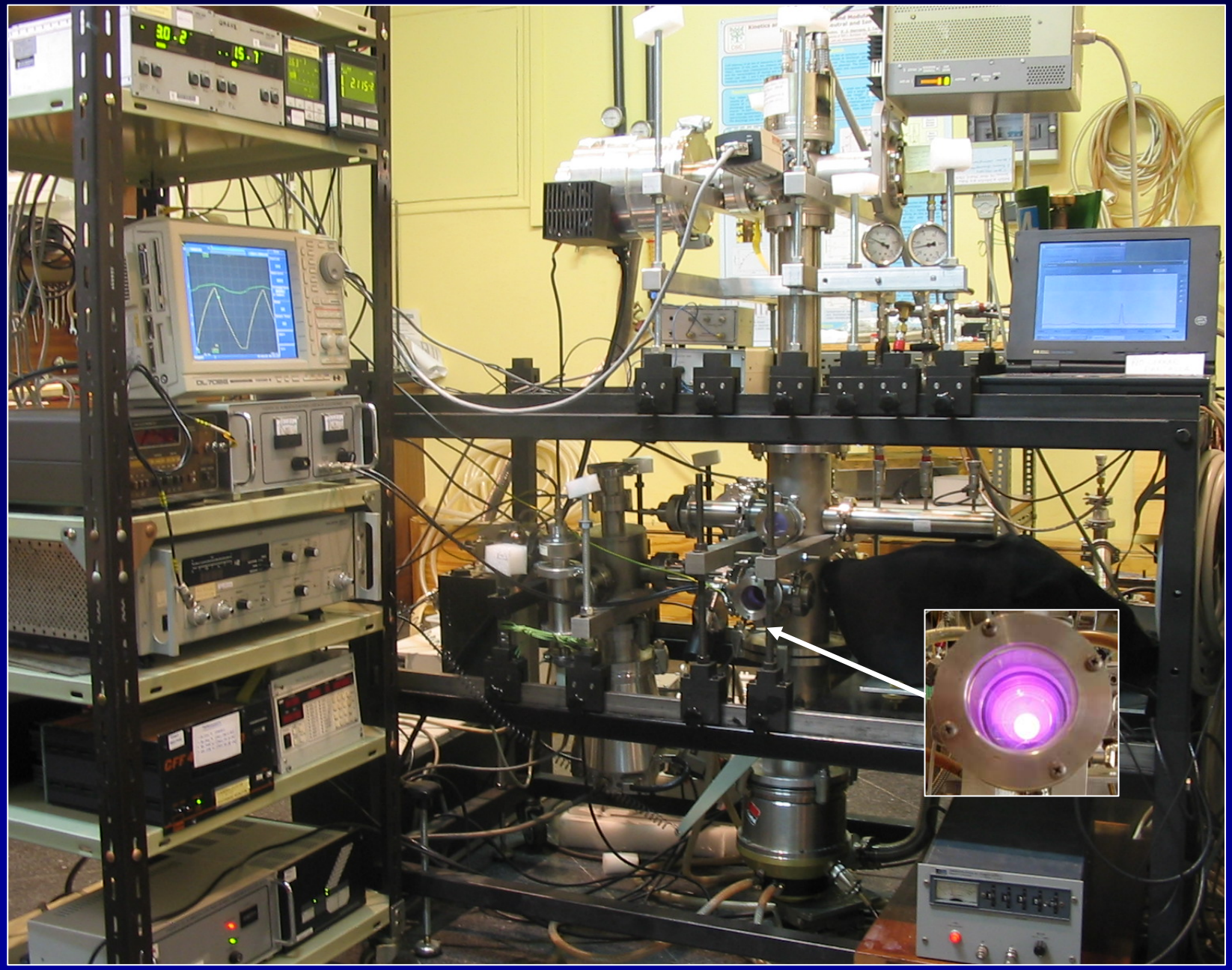
- Cathode dimensions
  10 cm Φ x 34 cm length
- Residence times ~ 0.2 – 1 s
- Constant Electric Current (DC)
  150 mA for all the experiments
- $E \approx 0$ in the Negative Glow !
  Very stable & homogeneous plasmas confined inside
- $\Delta V \sim V_{DC}$ (300 – 500 V)
  in Cathode Sheath (~ 1-2 cm)
  Ions are accelerated towards the cathode gaining energy, and neutrals diffuse to the walls

Plasma Diagnostics



- Quadrupolar Mass Spectrometry of Neutrals, e^- impact ionization (Differentially pumped)
- Quadrupolar Mass Spectrometry of Ions + Ion Energy Distributions (Differentially pumped)
- Double Langmuir Probes (N_e, T_e)
- Visible Emission Spectroscopy (Excited States, Plasma Temp.)

Tanarro et al., J.Phys.Chem.A 111, 9003 (2007)
Méndez et al, Phys.Chem.Chem.Phys., 12, 4239 (2010)



Cold Plasma Laboratory, IEM, CSIC

Kinetic Models

"As simple as possible to understand the main mechanisms"

- Zero Order Models (2 volumes: Negative Glow + Cathode Sheath)
- Time dependent Differential Equations for Neutrals and Positive Ions.
- T_e (Maxwellian) instead of a function of E/N ($E \approx 0$ in the glow)

- Main Processes Considered
  - *Ionization + Dissociation by Electron Impact in the Glow*
  - *Bimolecular Reactions with NO Potential Barrier ($k \neq f(T_{gas})$)*
  - *Diffusion through the Sheath + Surface Recombination or Neutralization*
  - *Asymmetric Charge Transfer in the Sheath (High Energetic Ions)*

- Do not include three body reactions (due to the low pressure)
- Neither reactions with potential barrier (due to the low gas temperature)

Plasma Precursor Species:

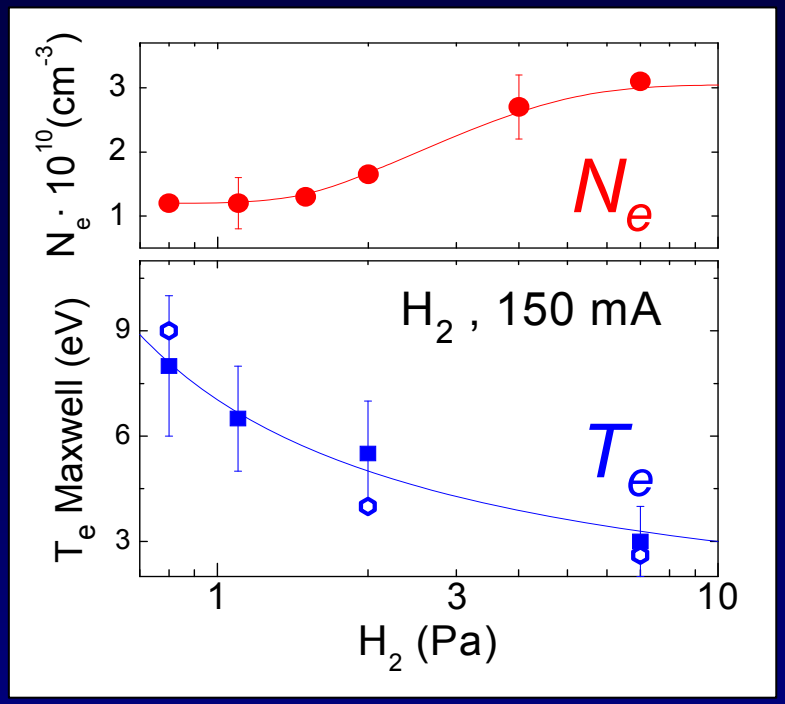
H_2

$H_2 + Ar$

$N_2 + O_2$ (air)

$H_2 + N_2$

H_2 Discharges

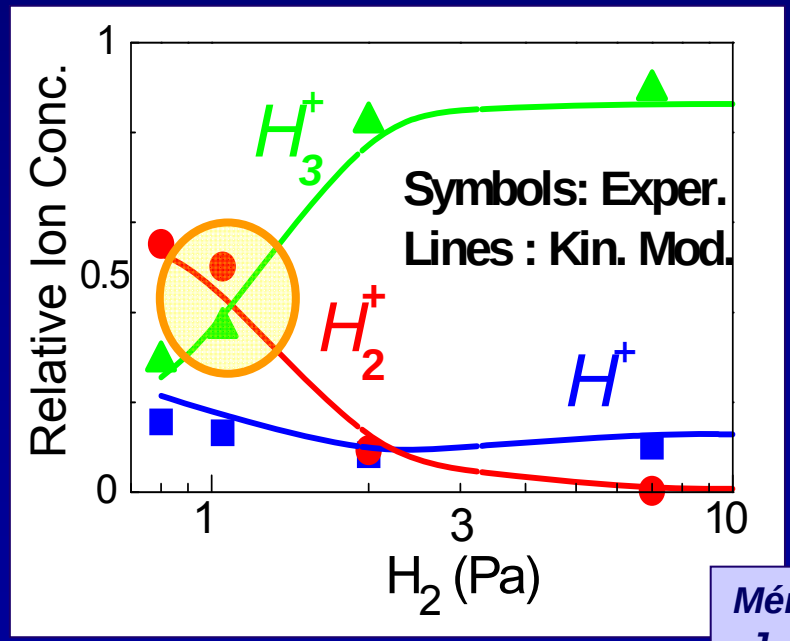


T_{vib} (H_2) ≈ 3000 K

T_{rot} (H_2) ≈ 300 K

[H] / [H_2] ≈ 0.10 – 0.15

decreases slightly with growing P



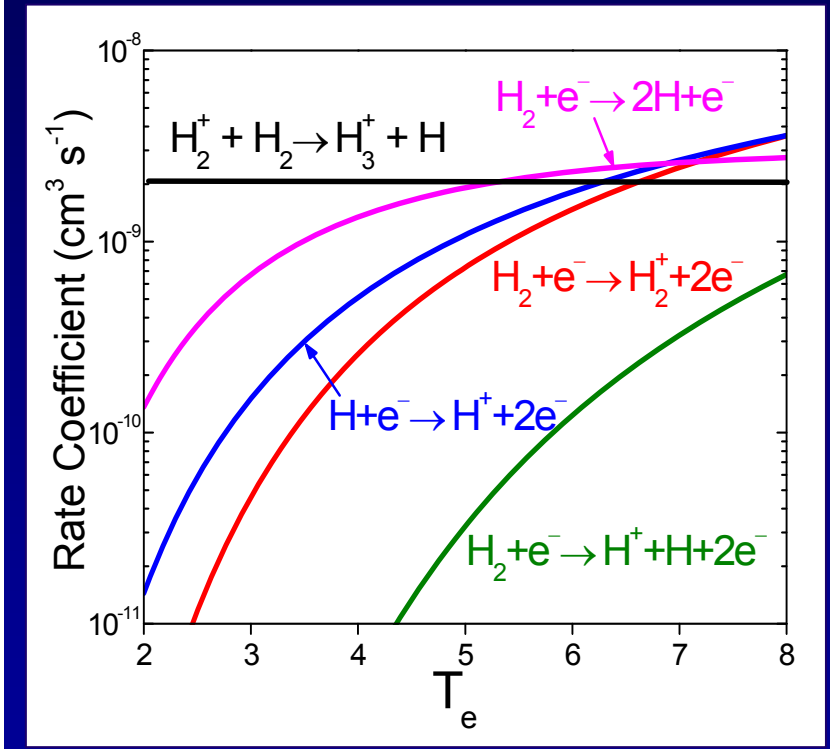
Major Ion changes from H_2^+ to H_3^+ quickly with pressure and stabilizes.

The Experimental data is well reproduced by the Model

H_3^+ : key ion in the interstellar Space

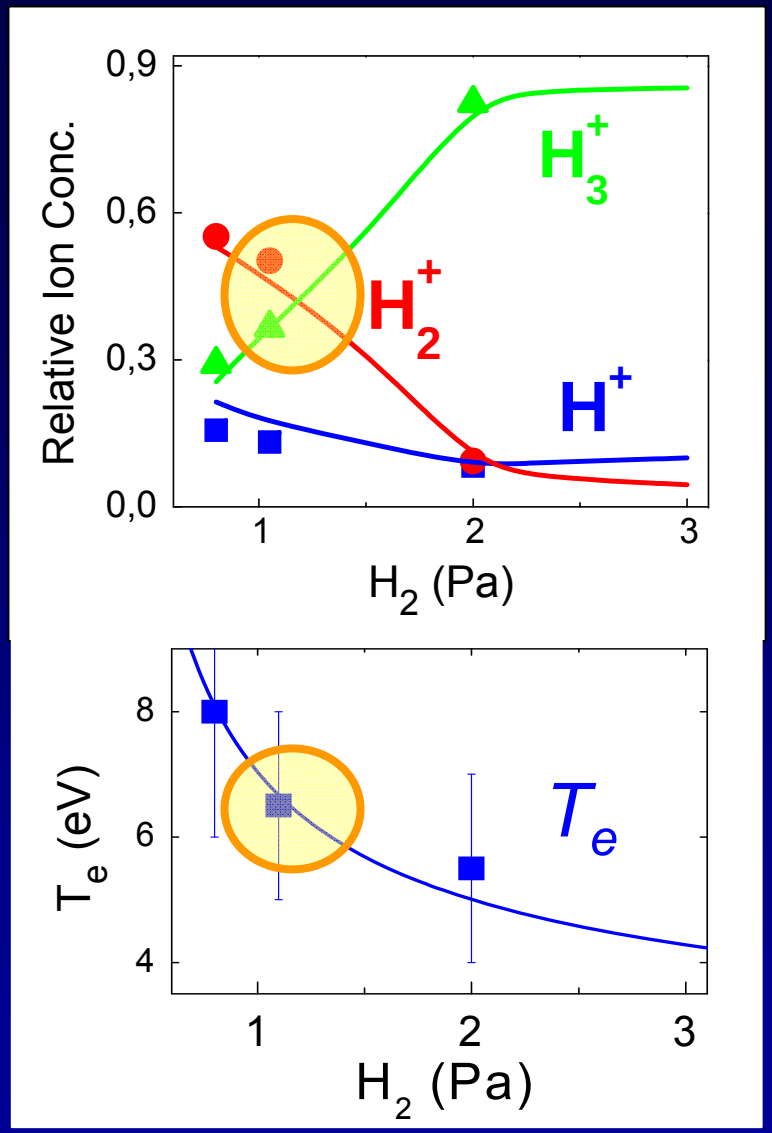
Méndez, Gordillo, Herrero, Tanarro, J. Phys. Chem. A, 110, 6060 (2006)

Main Reactions in the H_2 Kinetic Model

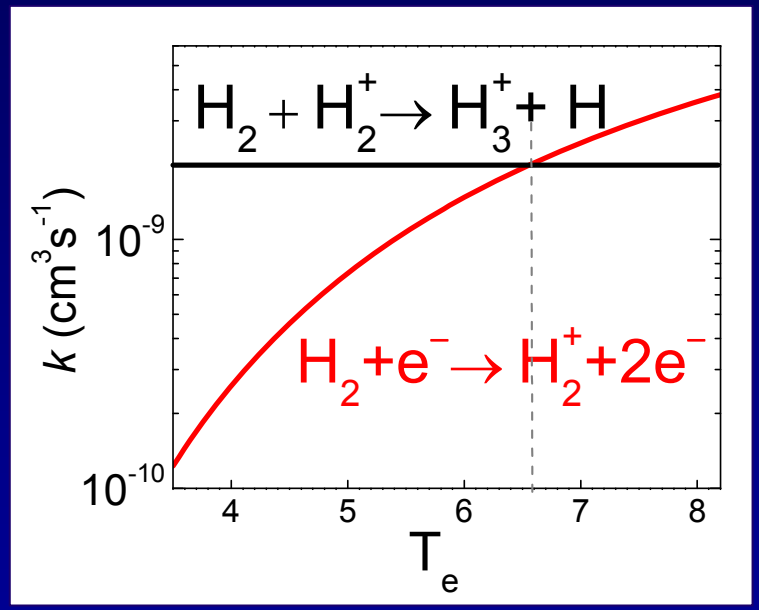


Gas Phase	*k (cm³ × s⁻¹)*
$H_2 + e \rightarrow 2\,H + e$	$1.75\times10^{-7}\times T_e^{-1.24}\times e^{-12.6/Te}$
$H_2 + e \rightarrow H^+ + H + 2e$	$3.00\times10^{-8}\times T_e^{0.44}\times e^{-37.7/Te}$
$H_2 + e \rightarrow H_2^+ + 2e$	$3.12\times10^{-8}\times T_e^{0.17}\times e^{-20.1/Te}$
$H + e \rightarrow H^+ + 2e$	$6.50\times10^{-9}\times T_e^{0.49}\times e^{-12.9/Te}$
$H_2^+ + H_2 \rightarrow H_3^+ + H$	**2.00×10^{-9}**

Heterogeneous	*γ (Recomb. Prob.)*
H + wall $\rightarrow 1/2\ H_2$	0.03
H^+ + wall $\rightarrow H$	1
H_2^+ + wall $\rightarrow H_2$	1
H_3^+ + wall $\rightarrow H_2 + H$	1

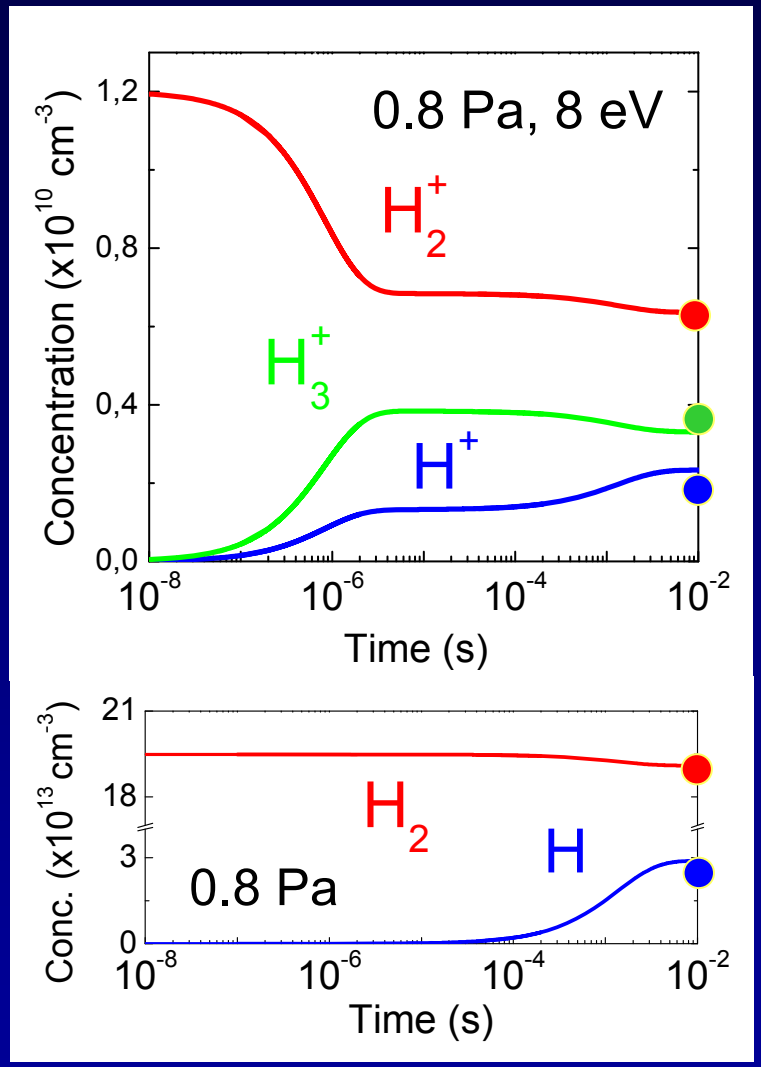


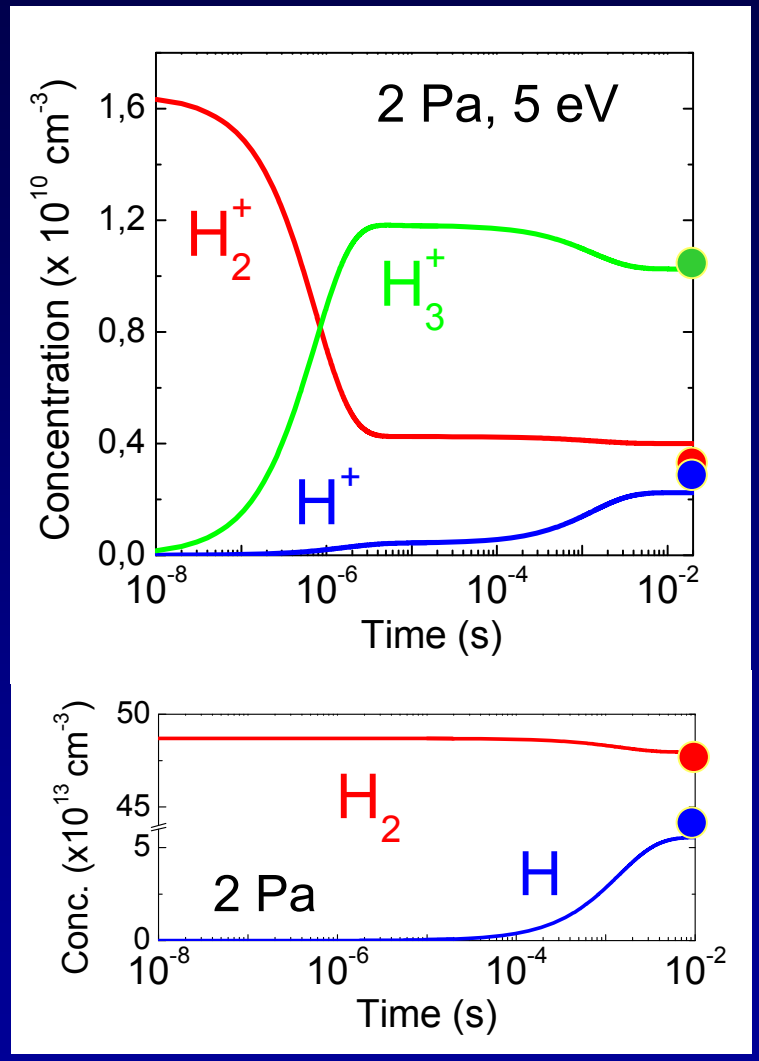
Large Changes in Ion Concentrations
& the Inversion of Major Ion
at P ≈ 1 Pa from H_2^+ to H_3^+ .
<u>WHY ?</u>



Initial concentrations of the Two Colliders
are Similar in Both Reactions:
H_2^+ is the Primary Major Ion

Evolution of Ions with Time in H_2 Model





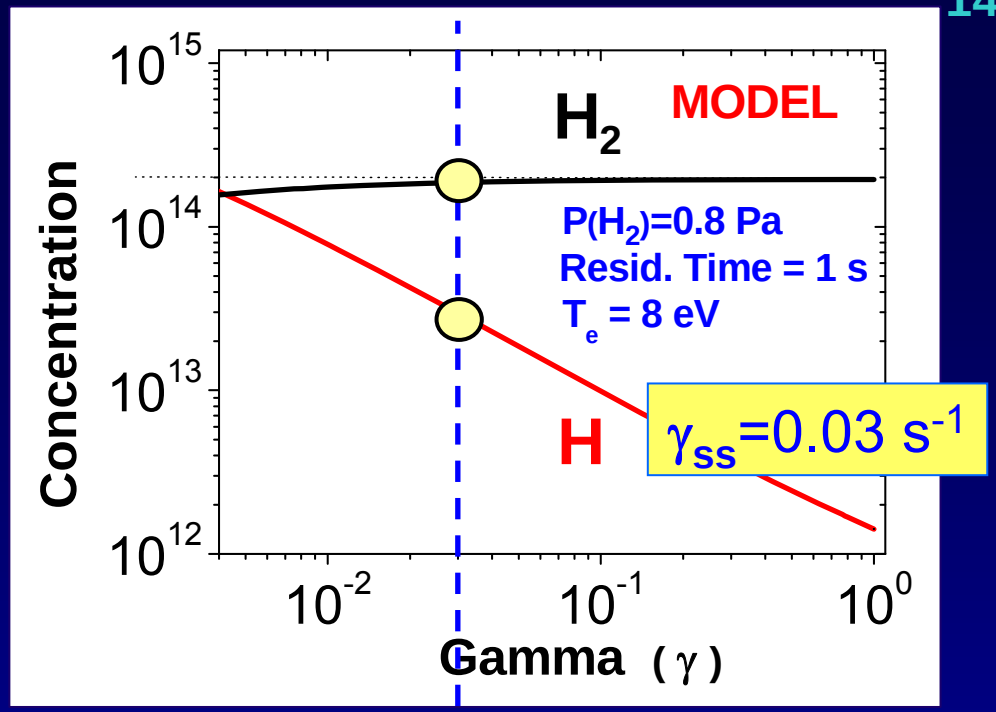
Steady State Experimental Values

Why $[H] / [H_2] \approx 0.1$?

$$H_2 + e \xrightarrow[k\,(T_e)]{} 2\,H + e$$

$$2\,H + \text{wall} \xrightarrow[\gamma_{ss}]{} H_2$$

Model Predictions ⇒



Experimental Result

Agrees with γ_{ss} of Tserepi & Miller, Appl. Phys. 75, 7231 (1994)

$$H_2^+ + H_2 \rightarrow H_3^+ + H$$

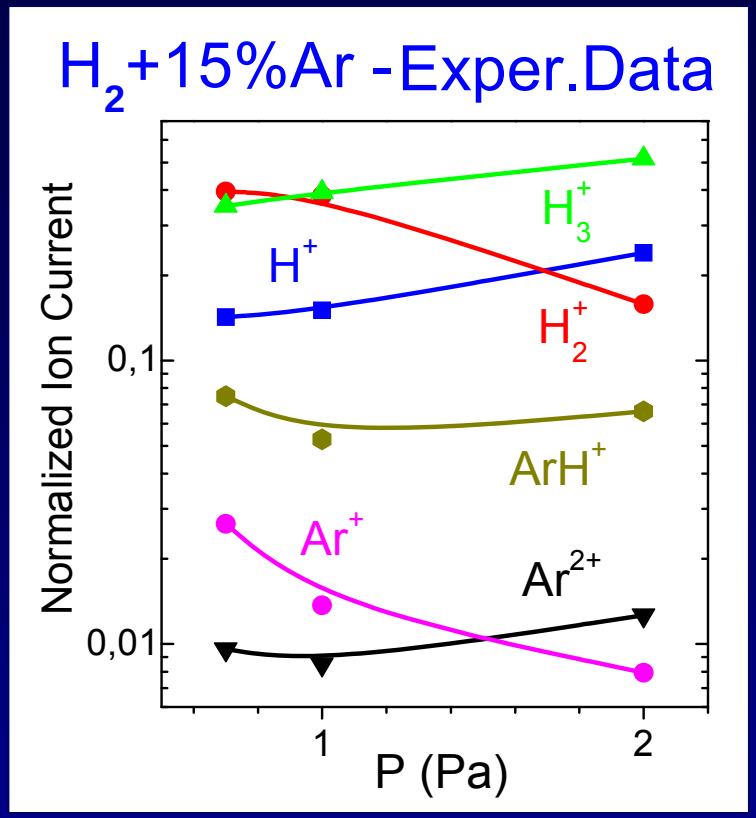
$$H^+ + \text{wall} \rightarrow H$$

$$H_3^+ + \text{wall} \rightarrow H_2 + H$$

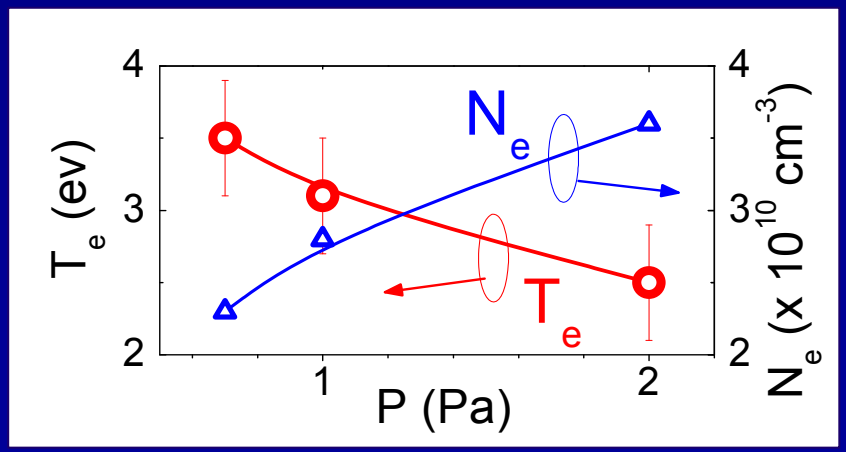
By Comparing Model With / Without Ions :

P (Pa)	2	0.8
Contribution of Ions to [H]	7%	40%

H_2 + Ar discharges



- Crossing of H_2^+ vs H_3^+ major ion, analogous to that of pure H_2 plasmas, at 1 Pa.
- Remarkable concentration of ArH^+ >> Ar^+.
- Ar^+ decreases with increasing pressure.
- Relatively high concentration of Ar^{2+}, even exceeds those of Ar^+ at 2 Pa.



BUT measured T_e ≈1/2 those for pure H_2 ! Very Important in the Model

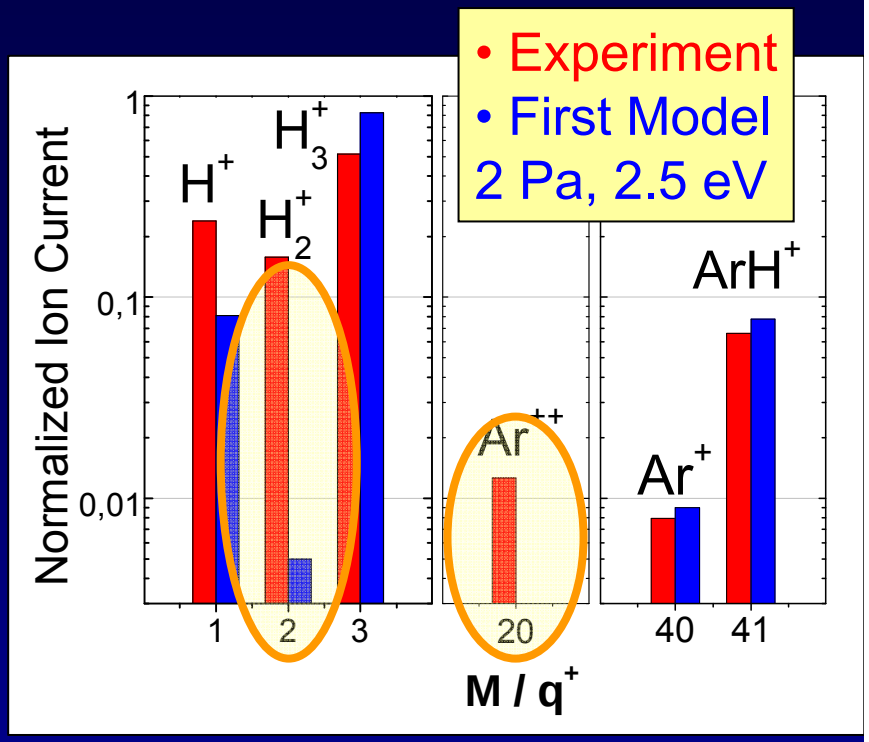
Simulation at 2 Pa…

Essential Reactions in H_2 + Ar Kinetic Model

Those of H_2, and ⇒ …

Gas Phase	*k ($cm^3 \times s^{-1}$)*
$Ar + e \rightarrow Ar^+ + e$	$2.53\times10^{-8}\times T_e^{0.5}\times e^{-16/Te}$
$Ar + e \rightarrow Ar^{++} + 3e$	$2.58\times10^{-9}\times T_e^{0.5}\times e^{-47/Te}$
$Ar^+ + H_2 \rightarrow H_2^+ + Ar$	1.78×10^{-11}
$Ar^+ + H_2 \rightarrow ArH^+ + H$	8.72×10^{-10}
$ArH^+ + H_2 \rightarrow H_3^+ + Ar$	6.30×10^{-10}

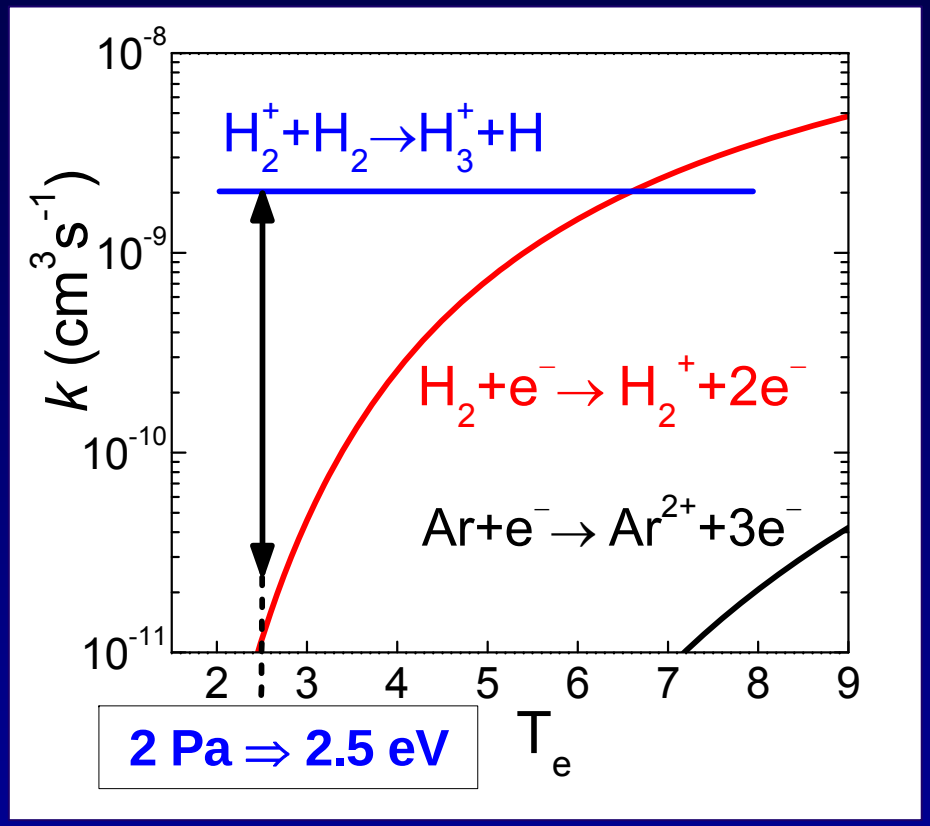
Heterogeneous	*γ (Recomb. Prob.)*
$Ar^+ + wall \rightarrow Ar$	1
$ArH^+ + wall \rightarrow Ar+H$	1
$Ar^{++} + wall \rightarrow Ar$	1

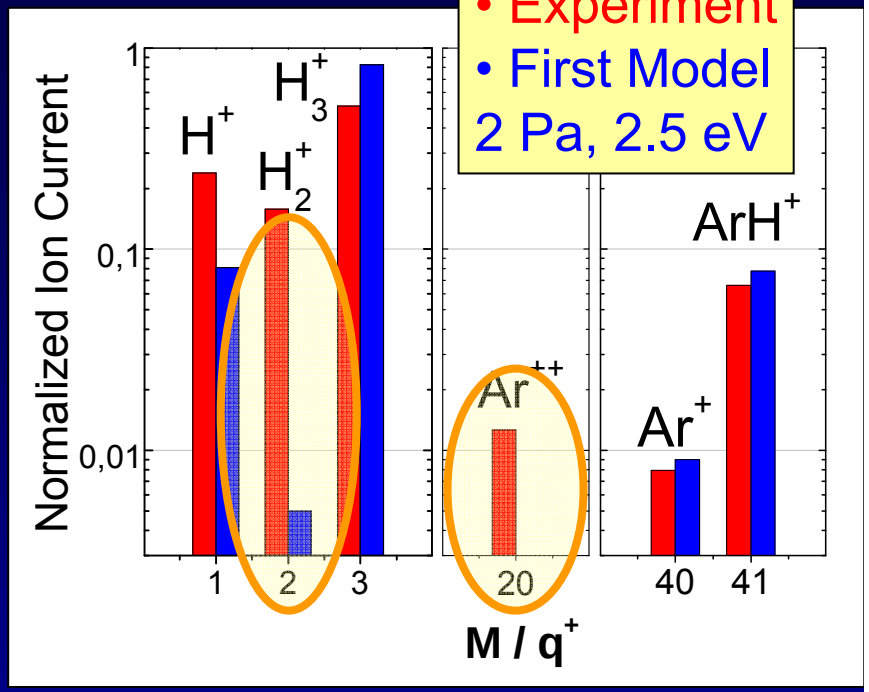


Large Discrepancies
Experiment vs. Model in
H_2^+ & Ar^{++}

Méndez, Tanarro, Herrero,
Phys. Chem. Chem. Phys. 46, 4239 (2010)

It is just because the measured T_e is Too Low

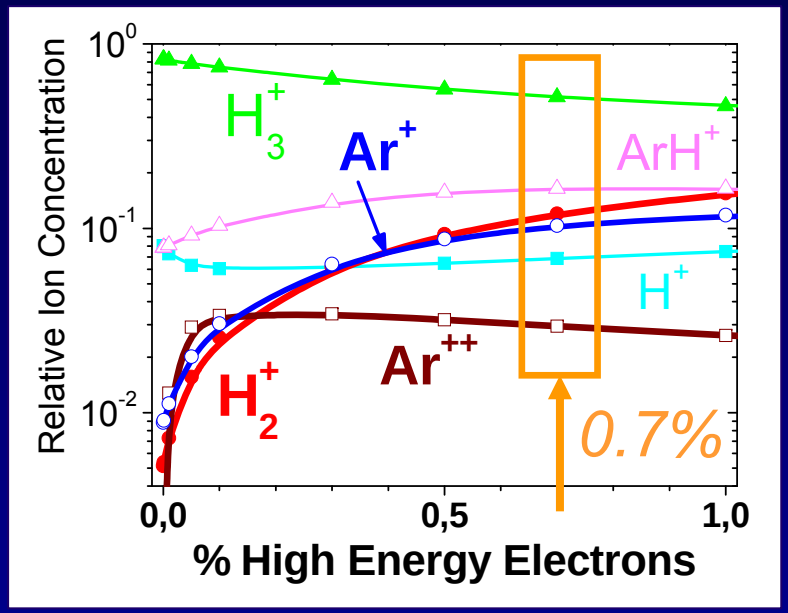




To solve the discrepancy Experiment - Model, we assume:

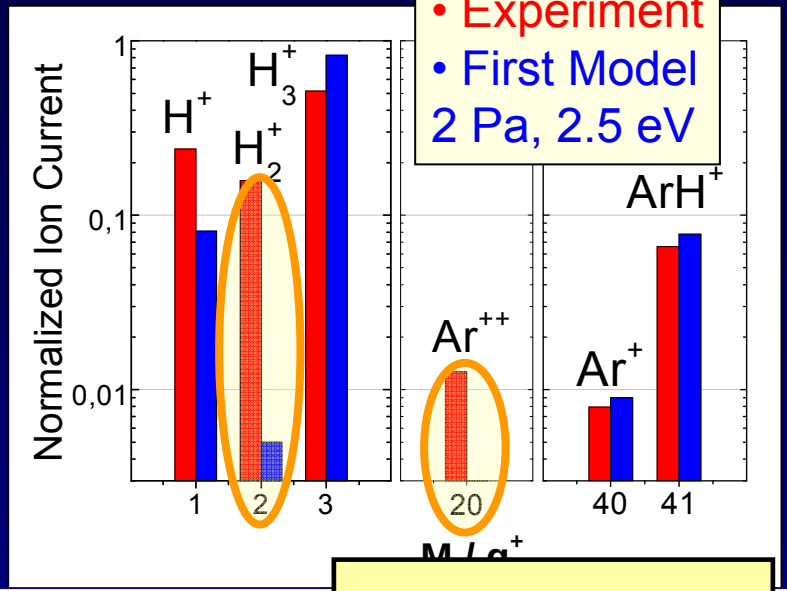
a) Small % of Electrons (> 47 eV)

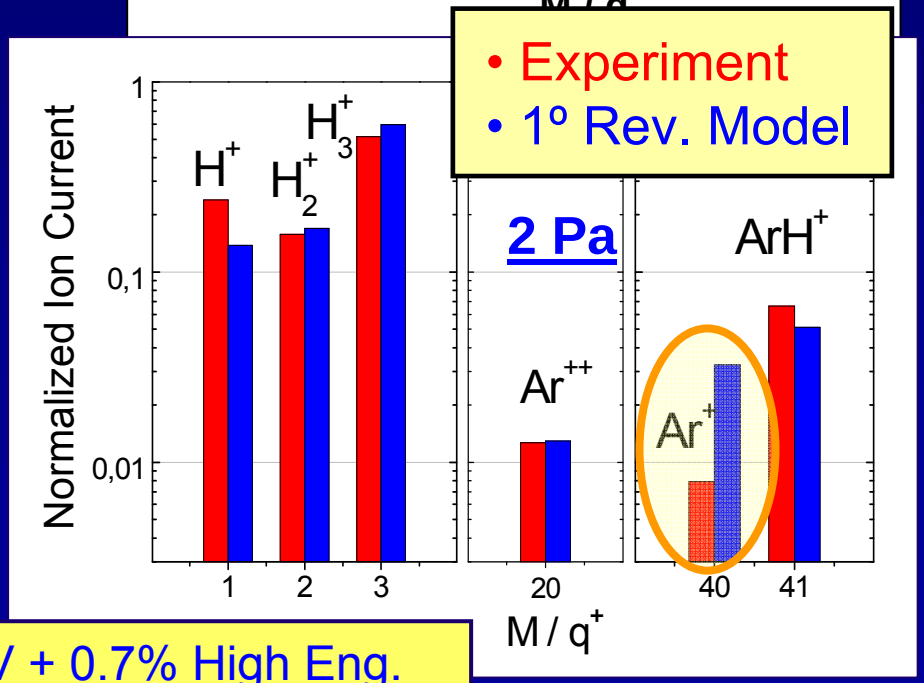
Not detectable with the Langmuir Probe.



- *$[Ar^{++}]$ & $[H_2^+]$ grow markedly*
- *$[H_3^+]$, $[H^+]$, $[ArH^+]$ change slightly*

- *But $[Ar^+]$ increases too much !*



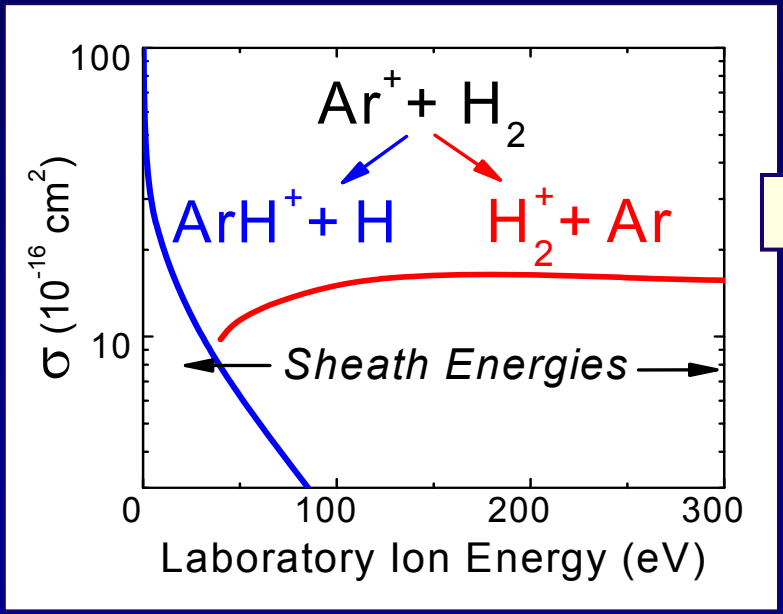


T_e = 2.5 eV + 0.7% High Eng.

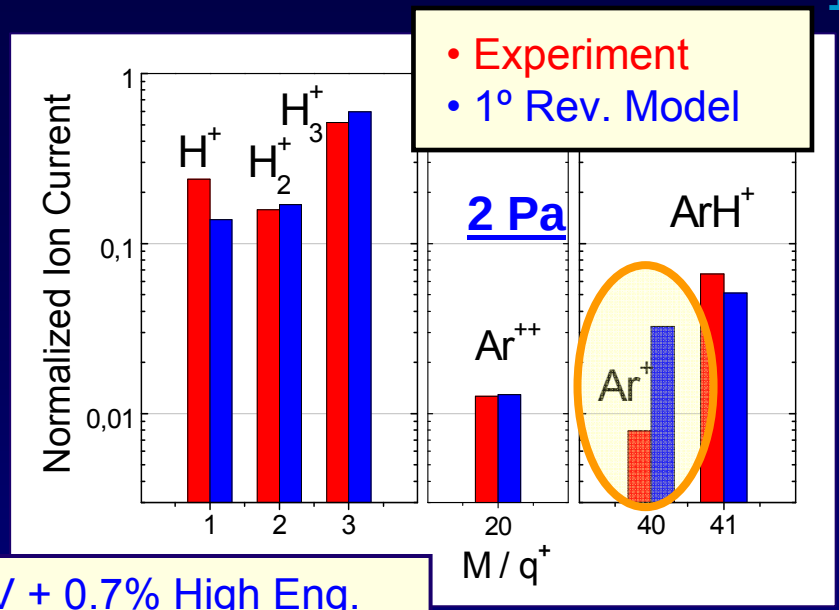
To solve this 2nd discrepancy,

we also propose:

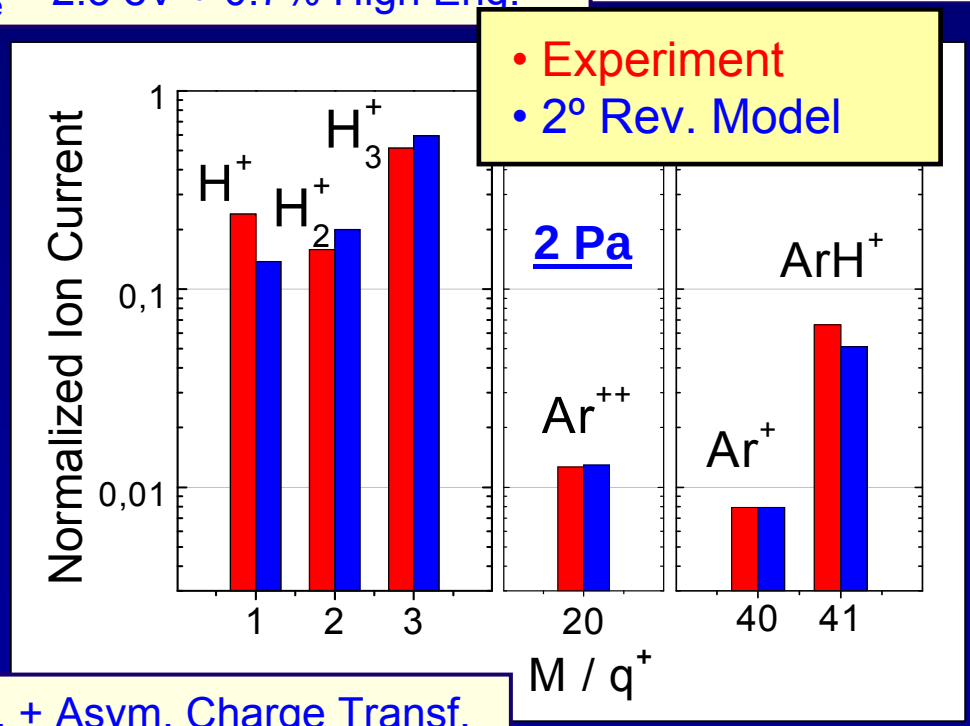
b) Asymmetric Charge Transfer of High Energetic Ions in the Sheath



Sheath ~ 2 cm width ⇒
75% decrease in Ar^+ at 2 Pa



T_e = 2.5 eV + 0.7% High Eng.



T_e = 2.5 eV + 0.7% High Eng. + Asym. Charge Transf.

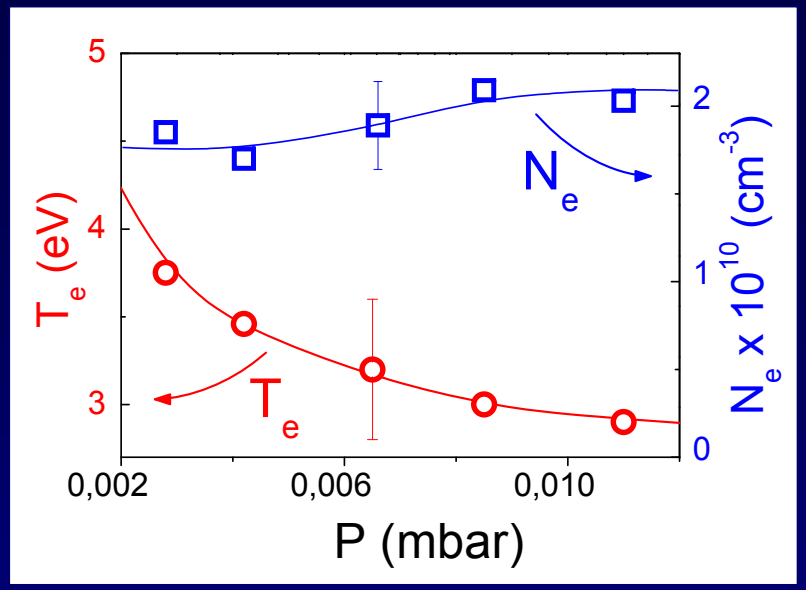
Air Discharges

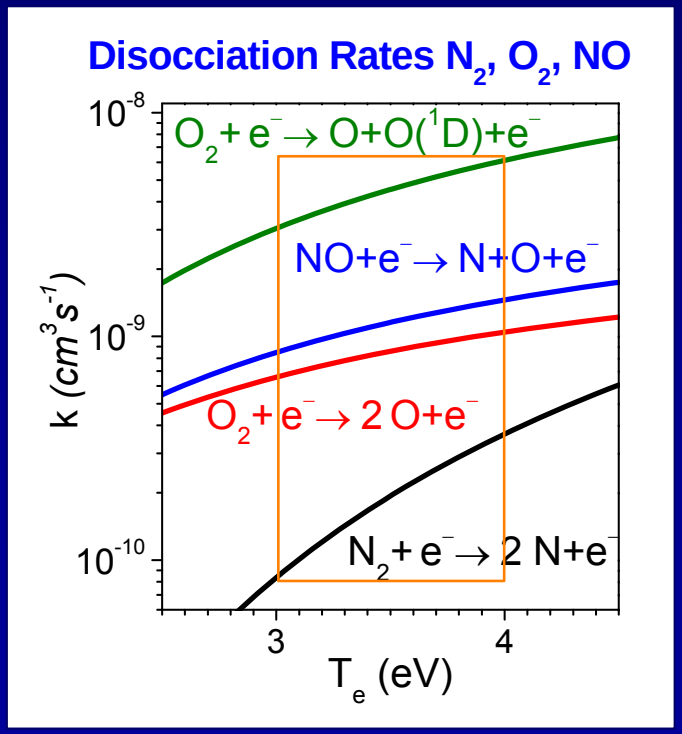
T_e grows from ~ 3 eV to 4 eV with decreasing pressure

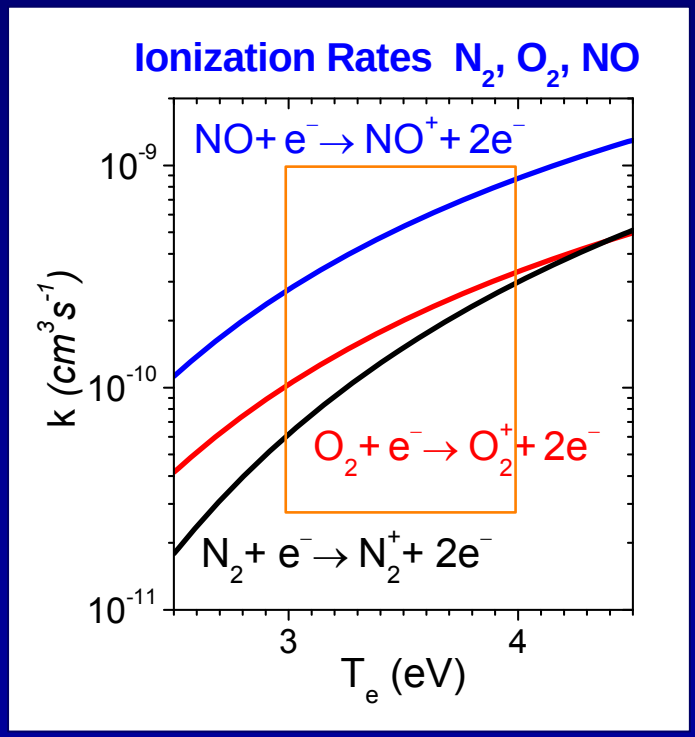
$N_e \approx 2 \times 10^{-10}\ cm^{-3} \Rightarrow$

as pressure decreases a factor 10

ionization grows from ~ 10^{-5} to 10^{-4}

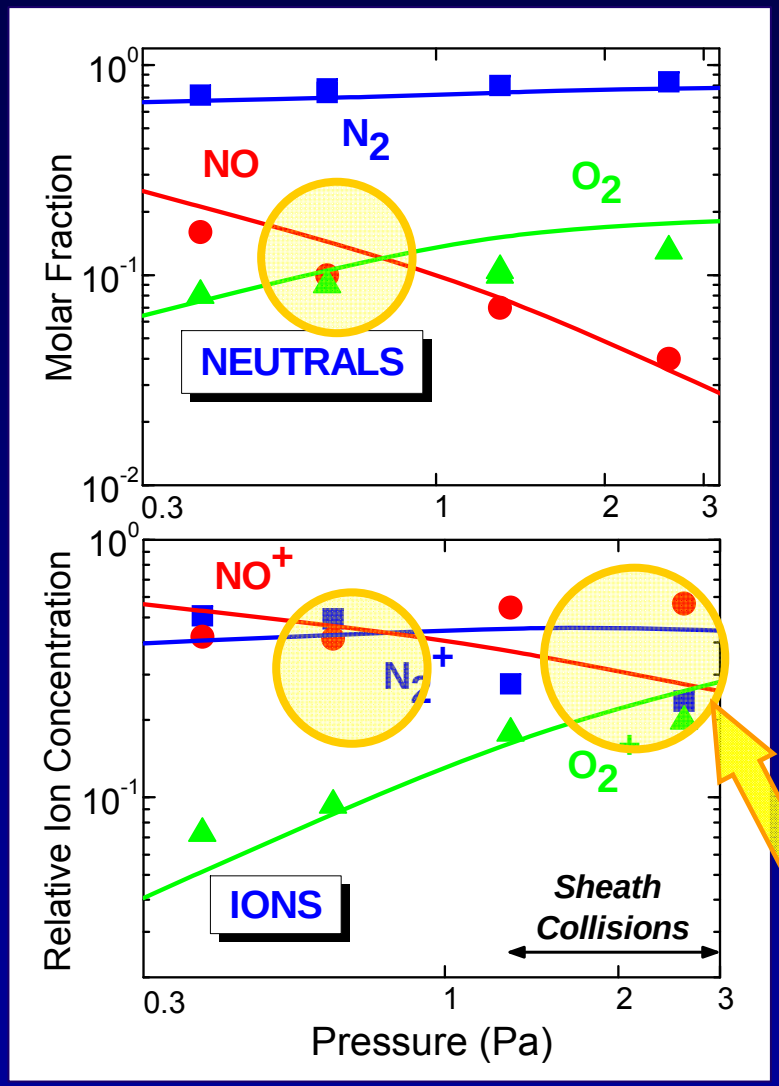






Air discharges

Symbols ⇒ Experiment
Lines ⇒ Kinetic Model



NO produced mainly in wall reactions, with recombination coefficients tested in other reactor geometries and pressureranges.

Change of tendencies as pressure decreases

Lowest Pressures:

a) ⇒ NO >> O_2

Larger dissociation of precursors by growth in T_e & Ionization Degree

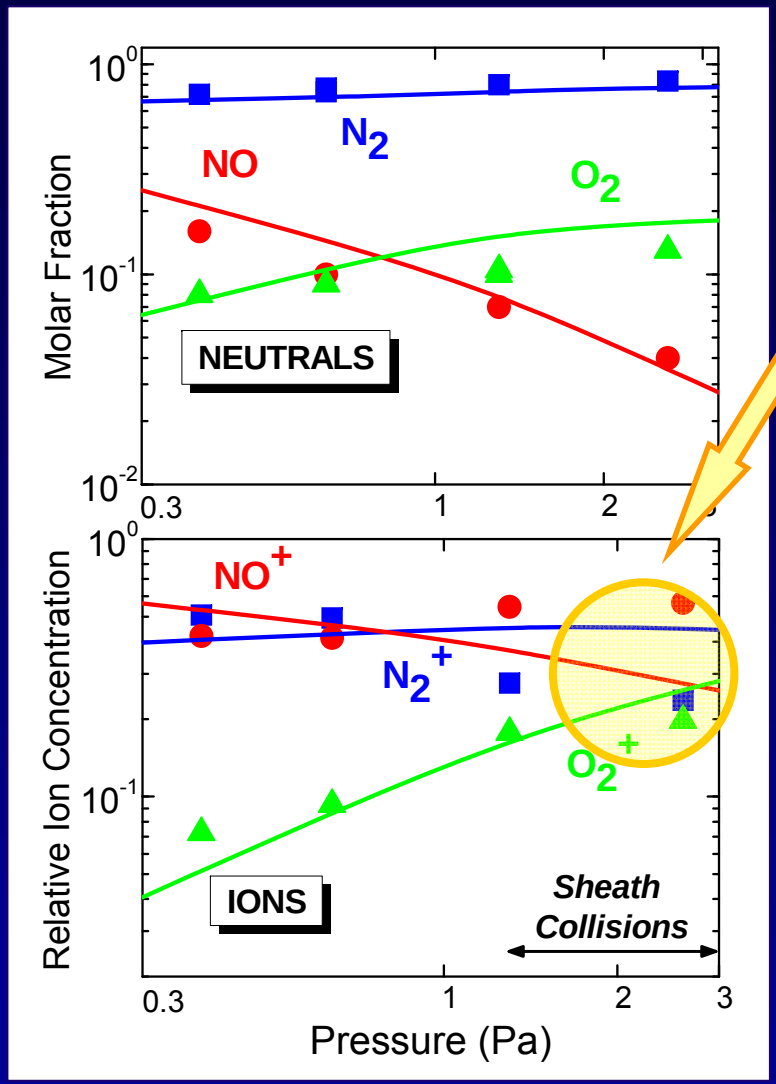
b) ⇒ Ionic composition dominated by N_2^+ and NO^+.

Encouraging Agreement Experiment vs. Model…

Except for Ions at the Higher Pressures

Sheath process ?

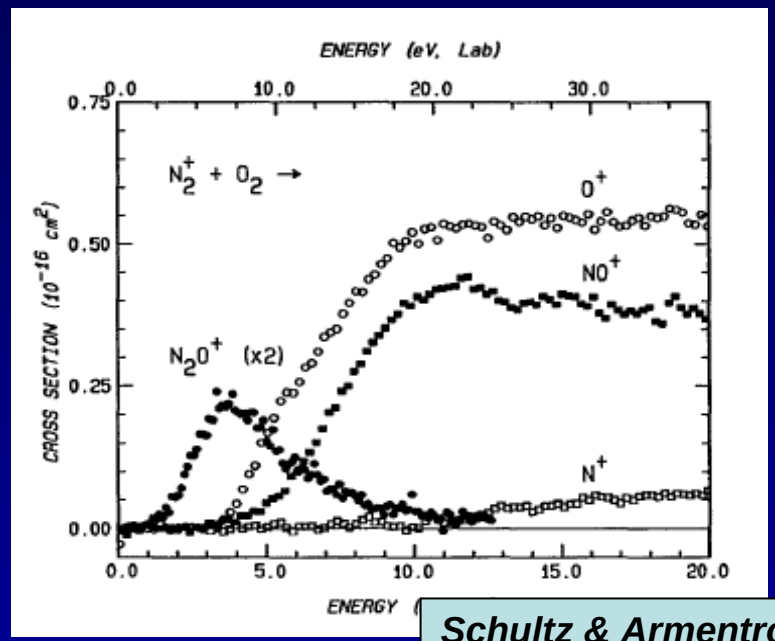
Castillo, Herrero, Tanarro et al, J. Phys. Chem. A 109, 6255 (2005)



Might it be

$N_2^+ + O_2 \rightarrow NO^+ + NO$??

Literature: Cross Sections up to 20 eV.

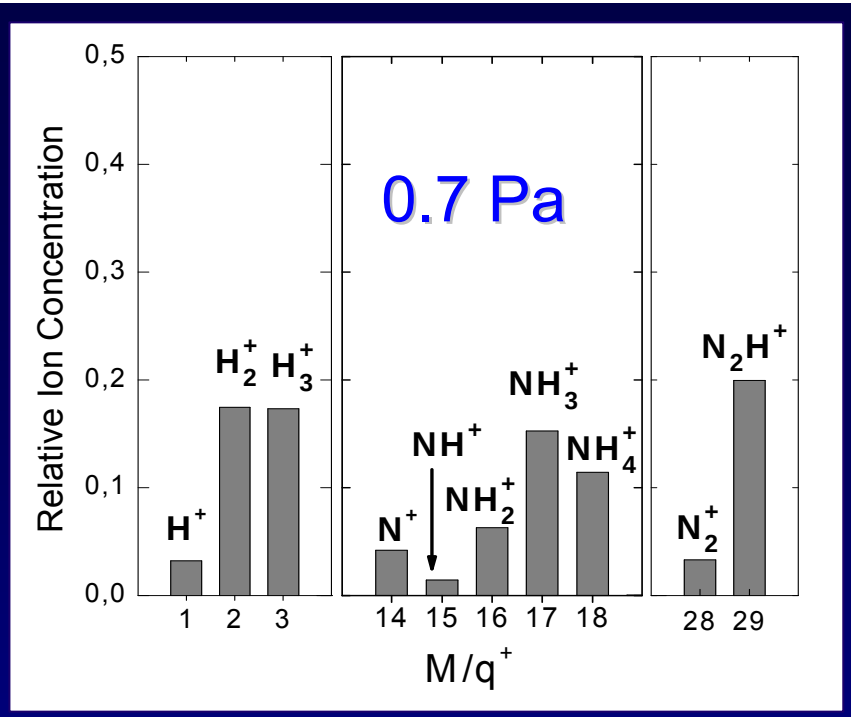


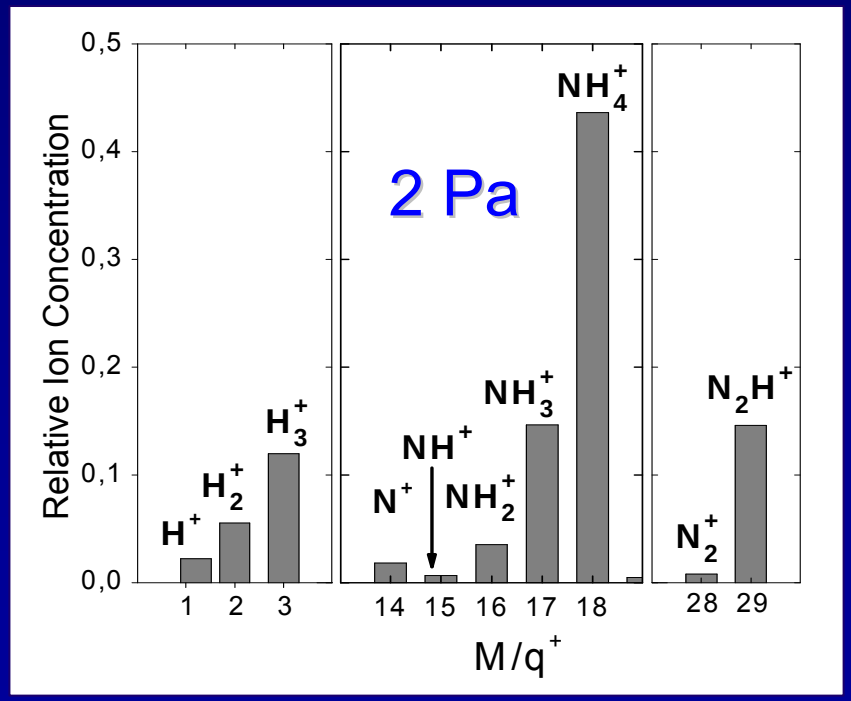
Schultz & Armentrout, J. P. C. 95, 121 (1991)

But they should be ~ 20 times larger in E_{ion} ~100 - 400 eV to explain the observed $[NO^+]$, $[N_2^+]$.

<u>Need for data at higher energies !</u>

Preliminary Results: H_2 + 7% N_2





Very large variations of Ion Concentrations with small pressure increase.

$N_xH_y^+$ very important in Astrophysics

Main Ion Reactions	k (cm^{-3} s^{-1})
$N_2 + H_2^+ \rightarrow N_2H^+ + H$	2.00×10^{-9}
$N_2 + H_3^+ \rightarrow N_2H^+ + H_2$	1.86×10^{-9}
$H_2 + N_2^+ \rightarrow N_2H^+ + H$	2.00×10^{-9}
$NH_3 + H_2^+ \rightarrow NH_3^+ + H_2$	5.70×10^{-9}
$NH_3 + H_3^+ \rightarrow NH_4^+ + H_2$	4.40×10^{-9}
$NH_3 + N_2H^+ \rightarrow NH_4^+ + N_2$	2.30×10^{-9}

and Surface Reactions $\Rightarrow NH_3$

Model being developed

SUMMARY & CONCLUSIONS

- Glow discharges are studied in the low pressure range (~ 0.5 – 5 Pa).
- Large changes are found in their T_e & Neutral & Ion composition that may be very important in plasma applications and in explaining some phenomena in natural plasmas.
- The kinetic models developed allow to assign the main processes responsible of such behaviors:

  - *Relevance of gas phase non barrier reactions.*
  - *Relevance of charge transfer reactions in the sheath.*
  - *Relevance of surface reactions.*

- In general, the models fit quite well the experimental results.

The Team at Present

Prof. Víctor J. Herrero
Co-author

Dr. Esther Carrasco
PhD Contract

Isabel Méndez
Writing Thesis

Miguel Jiménez
Student

Myself

The Excellent Technicians of our Department

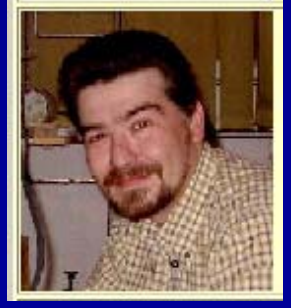
Mª José Malagón

José M. Castillo

David Pérez

Javier Rodríguez

Miguel A. Moreno



Thank you very much

for your attention