Modelling ammonia production in N2-H2 DC discharges

L. Marques[1], P. Pereira[2], S. Baghel[2], M. Budde[4], J. P. Booth[4], O. Guaitella[4], N. Pinhão[2], C. D. Pintassilgo[3,2], L. L. Alves[2]

[1] CF-UM-UP, Universidade do Minho, Braga, Portugal
[2] IPFN, Instituto Superior Técnico, Lisboa, Portugal
[3] Universidade do Porto, Porto, Portugal
[4] LPP, Sorbonne Université / École Polytechnique, Paris, France

OUTLINE

01

Motivation

Ammonia relevance and Plasma assisted Catalytic Ammonia synthesis.

02

N_2-H_2 Kinetic Scheme & Experiments

Species, types of mechanisms, and recent updates to the chemical scheme. Modelling framework, parameter ranges used for model validation

03

Simulation results & comparison with experiments

Plasma characteristics, species kinetics — concentrations, gain/loss channels.

04

Conclusions

Final remarks, key findings

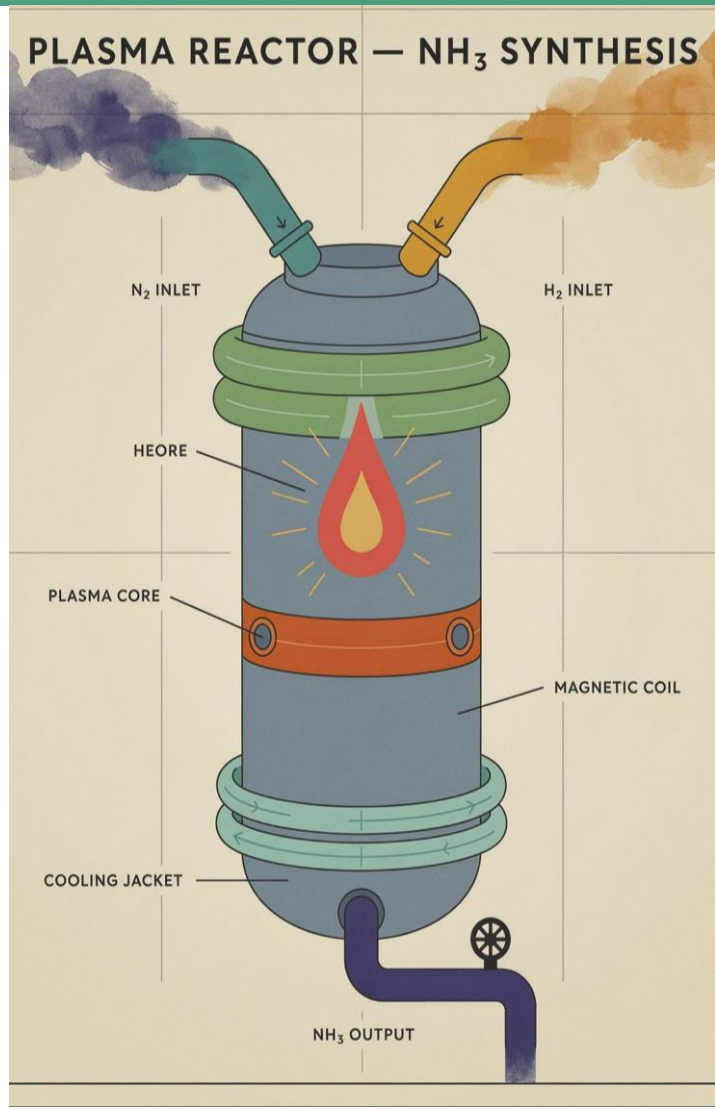
MOTIVATION

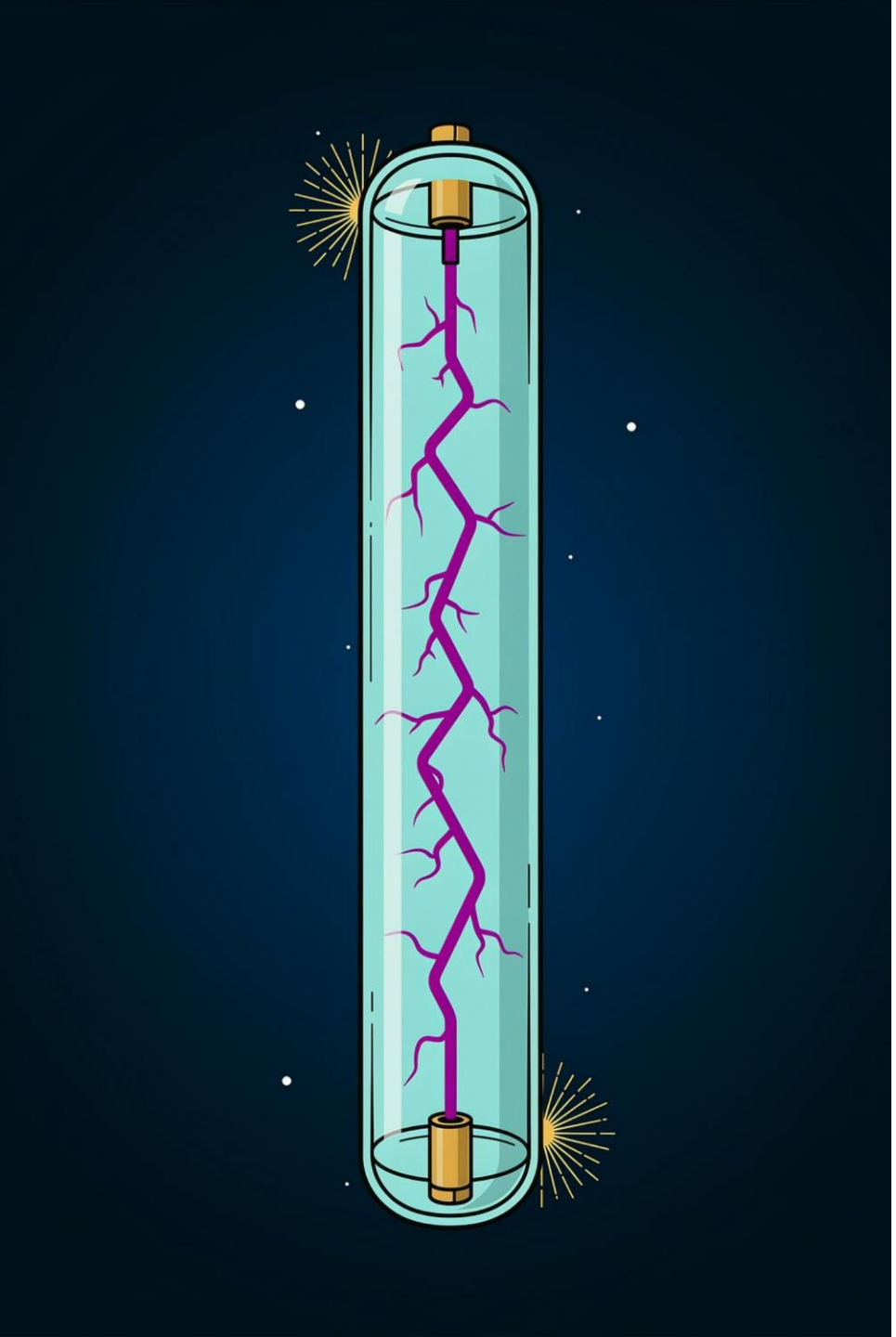
Ammonia relevance

- **Fertilizers:** Underpins food security for billions; primary end-use of global NH_3 production
- **Energy carrier:** 9× the energy density of Li-ion batteries; 1.8× that of compressed H_2; stored at −33°C (liquid) vs. −253°C for liquid H_2
- **Fusion relevance:** NH_3 synthesis in N_2-H_2 plasmas also pertinent to plasma-wall interactions in future fusion devices

Plasma Catalytic Ammonia Synthesis

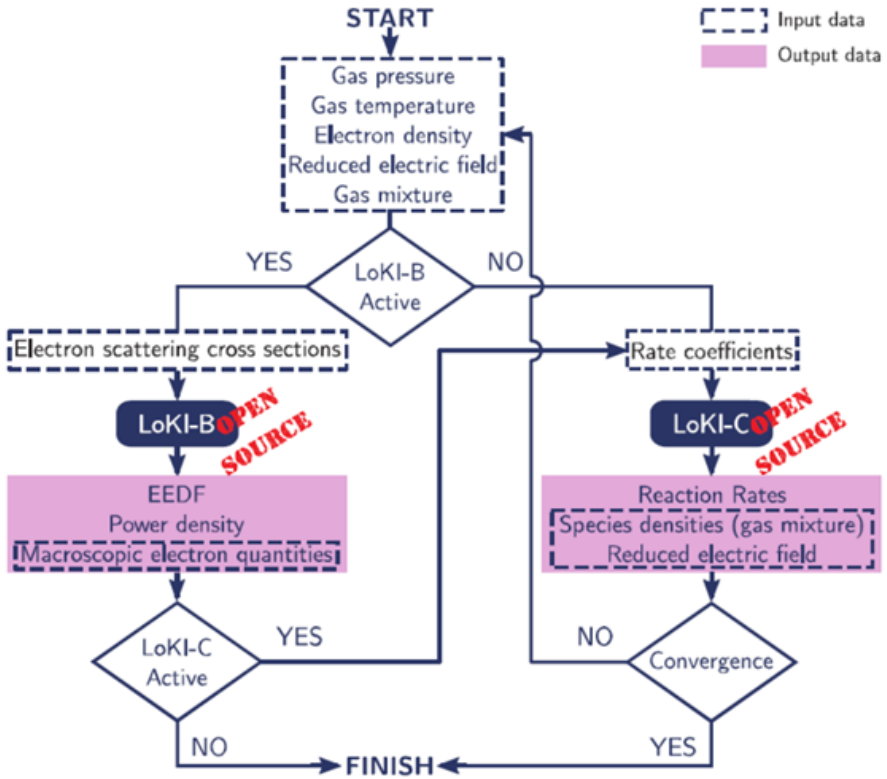
- **Mild conditions:** Near-ambient pressure; instantly switchable; directly powered by renewable electricity — ideal for distributed production
- **Modular reactors:** Compatible with intermittent solar/wind; no large-scale centralised infrastructure required
- **Open challenge:** Reaction mechanisms at plasma-surface interfaces remain poorly understood — kinetic modelling is the critical missing link





02 - N_2-H_2 Kinetic Scheme & Experiments

The LoKI Global Model



Both modules can run as standalone tools or in a fully coupled, self-consistent loop.

The **LisbOn KInetics Global Model (LoKI-GM)** is an open-source simulation tool for plasma chemistry modelling.

LoKI-B

Boltzmann solver — computes the electron energy distribution function (EEDF) and macroscopic electron parameters (e.g., power density, drift velocity)

LoKI-C

Chemical solver — solves zero-dimensional volume-averaged rate balance equations for charged and neutral species; outputs species densities and reduced electric field

N_2-H_2 kinetic scheme

Species and types of mechanisms

Species Inventory (~40 total)

Hydrogen Species

$H_2(X,v=0–14)$, H_2^+, H(1S), H(2S), H(2P), H(3–5), H^+, H^-, H_3^+

Nitrogen Species

$N_2(X,v=0–41)$, $N_2(A,B,a,a',C,w)$, N_2^+, $N(^4S,^2D,^2P)$, N^+, N_3^+, N_4^+

NH_x Species

$NH_3(X)$, NH_3^+, $NH_2(X)$, NH_2^+, NH_2^-, NH(X), NH^+, N_2H^+, NH_4^+, $N_2H(X)$, $N_2H_2(X)$, $N_2H_3(X)$, $N_2H_4(X)$

Surface Species

F(v), N(F), N(S), H(F), H(S), S(v), NH(S), $NH_2(S)$

Types of Mechanisms

- **Electron-impact:** Excitation/deexcitation, dissociation, ionization, dissociative attachment/detachment, recombination
- **Vibrational:** e-V, V-T (atomic/molecular), V-V excitation/deexcitation — critical for energy redistribution in $N_2(X,v)$ and $H_2(X,v)$ manifolds
- **Heavy-species collisions:** Neutral 2-body and 3-body; ion–atom and ion–molecule reactions
- **Radiative:** Spontaneous radiative transitions; ion-ion recombination
- **Transport & flow:** Ion and neutral transport; in/out flow boundary conditions
- **Surface reactions:** Langmuir-Hinshelwood (LH), Eley-Rideal (ER), NH_4^+ wall-recombination — governing NH_3 formation pathways on **QUARTZ** surfaces.

- Gordiets et al, *Plasma Sources Sci. Technol. 7, 379 (1998)*
- M. Jiménez-Redondo *et al., Plasma Sources Sci. Technol.* **29** 085023, 2020

Validation and working conditions

Measurement data

- **pure N_2**
  - G Cernogora *et al., J. Phys. B: At. Mol. Phys.* **14** 2977, 1981
  - I. N. Brovikova et al, *High Temperature* **39** 809, 2001

- **N_2-H_2 mixtures (including pure H_2)**
  - J. Amorim *et al., Appl. Phys. Lett.* **68** 1915, 1996
  - S. Bockel *et al., Plasma Sources Sci. Technol.* **5** 567, 1996
  - Gordiets et al, *Plasma Sources Sci. Technol. 7, 363 (1998)*
  - LPP (2026)

Ranges of working conditions

R = 7.5x10^{-3} m – 10^{-2} m

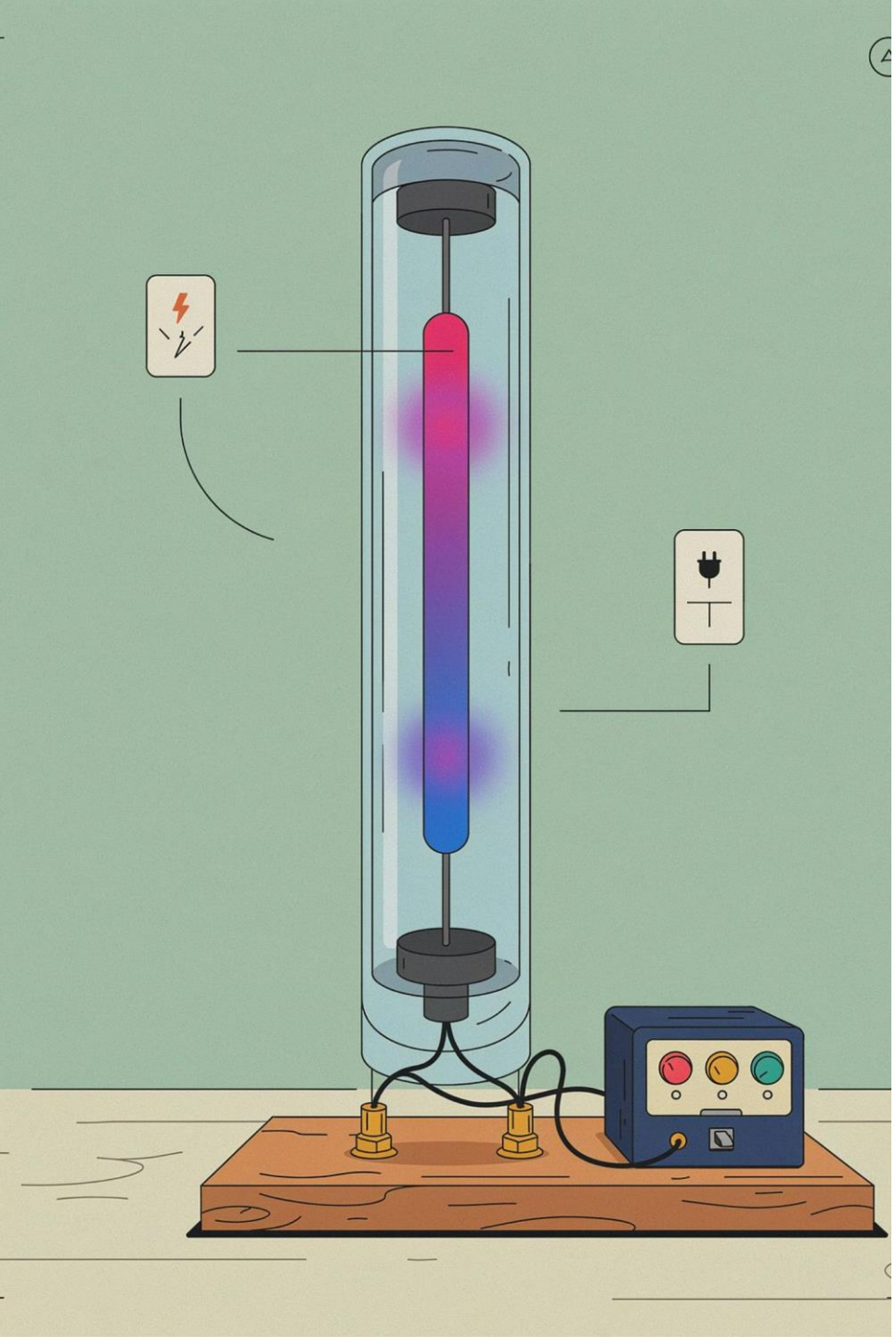
L = 15x10^{-2} m – 54x10^{-2} m

p = 10 Pa – 700 Pa

I_{dc} = 5 mA – 100 mA

Q = 0 sccm – 600 sccm

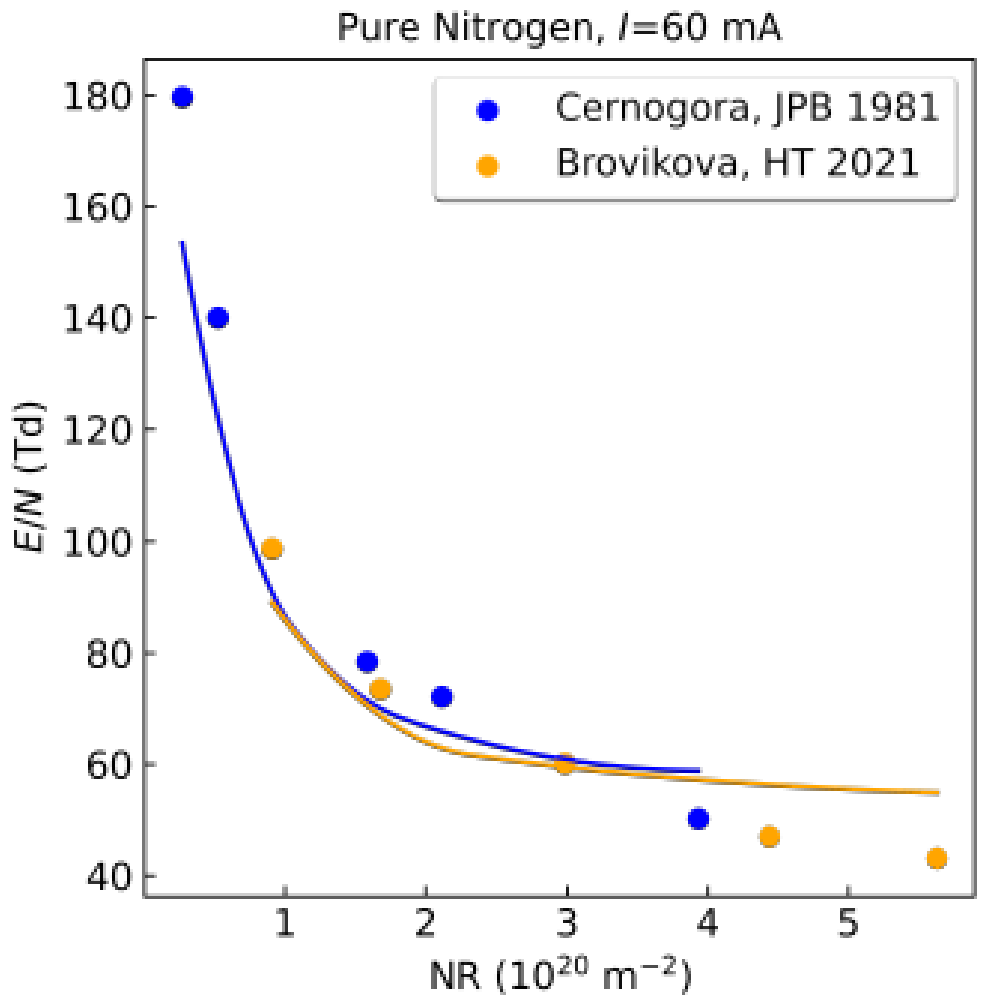
T_g=350-600K



03 – Simulation results & comparison with experiments

Discharge Characteristics

E/N vs. *NR* (pure N_2)

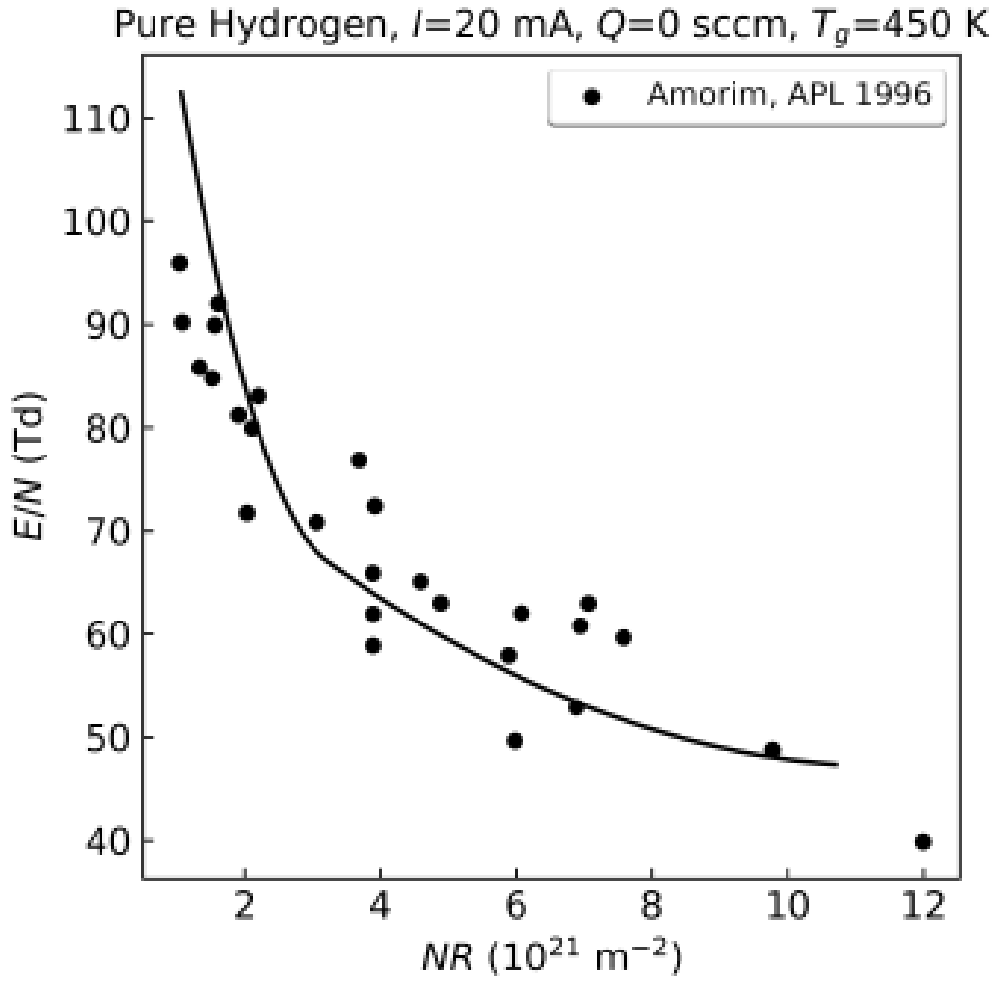


Simulations reproduce the standard discharge characteristics, exhibiting the expected universal scaling behaviour under varying working conditions (pressure, geometry).

The universal behaviour disappears when gas temperature *T*g is excluded from the representation — confirming the importance of thermal effects in the model.

Discharge Characteristics

E/N vs. *NR* (pure H_2)

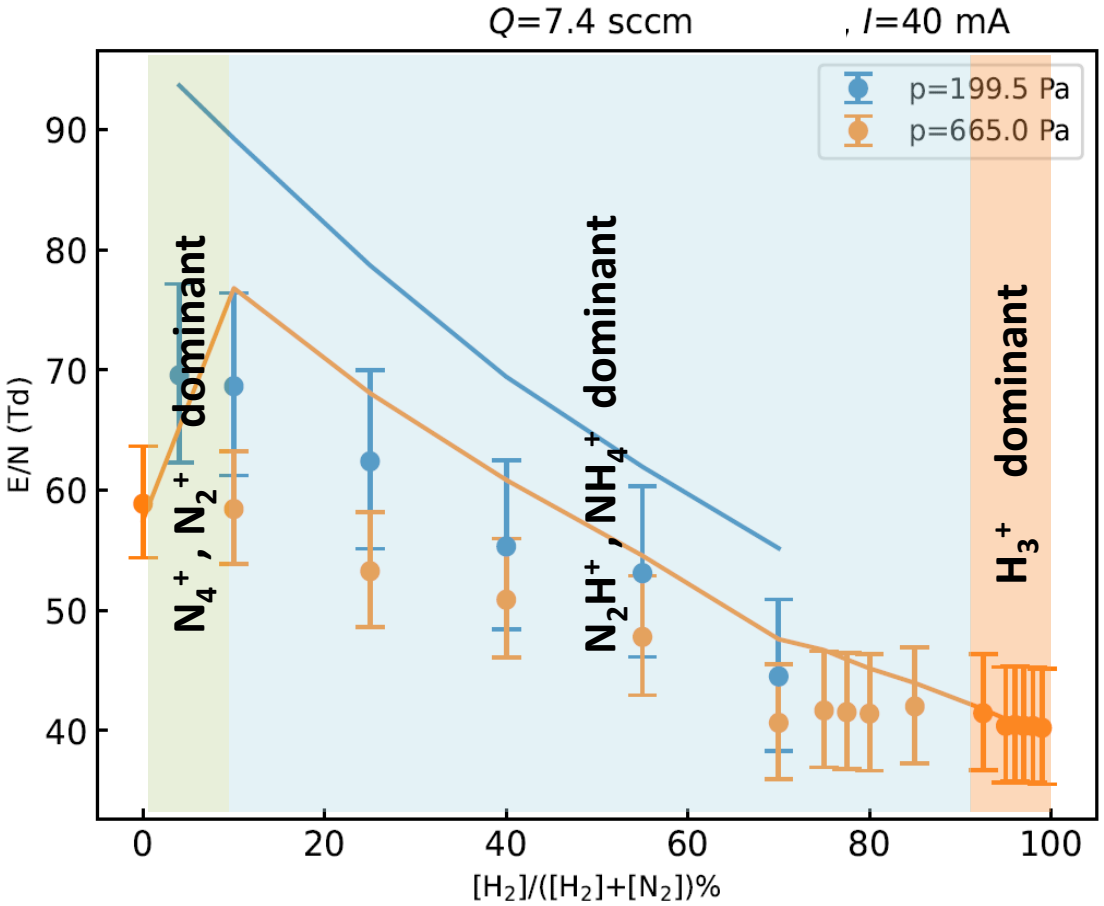


Measurements from Amorim (1994)
Simulations used temperatures estimated from Gordiets.

Excellent agreement between simulation and measurements, mainly due to the charged particle transport model adopted, using the approximation of purely diffusive transport for multiple positive and negative ions

Discharge Characteristics

LPP – E/N vs. %H2 (N2 -H2)



The *E/N* raise at low %H2 is due to the increased energy budget required to produce the dominant N_4^+ ions, in quasi-pure nitrogen plasmas.

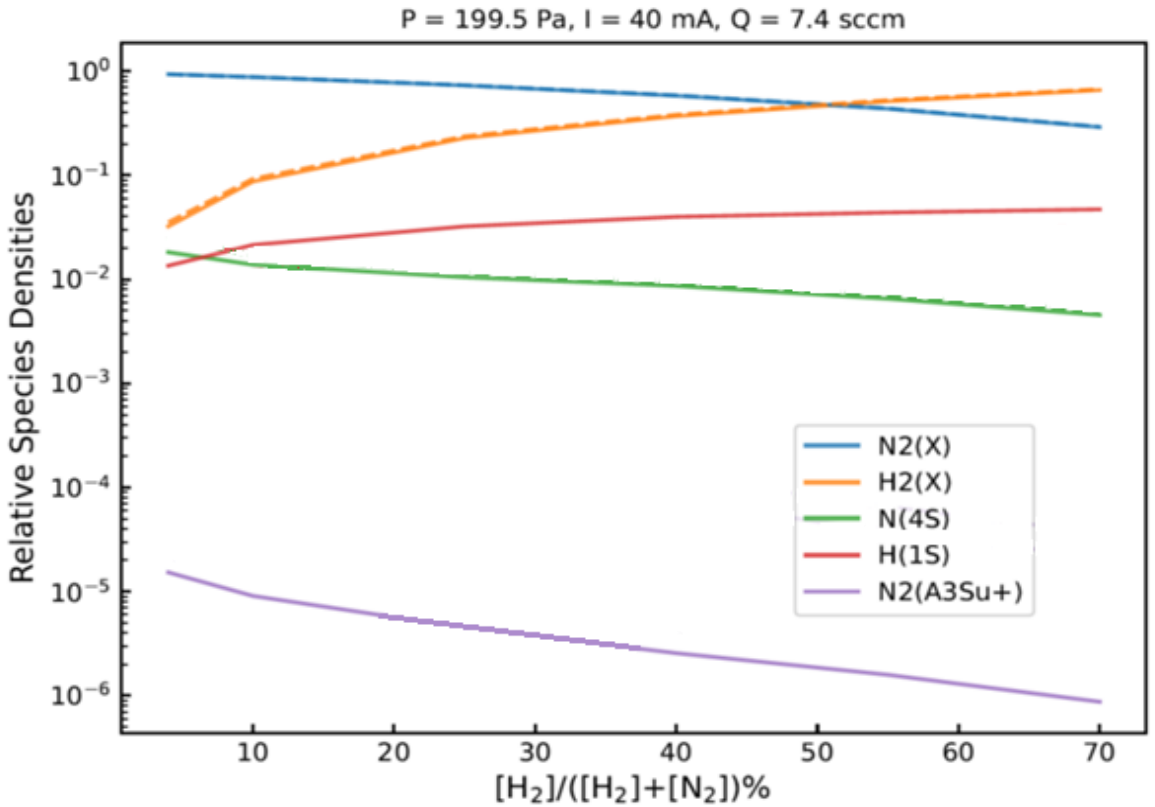
Decrease of E/N with H2 due to lower energy budget to produce dominant ions.

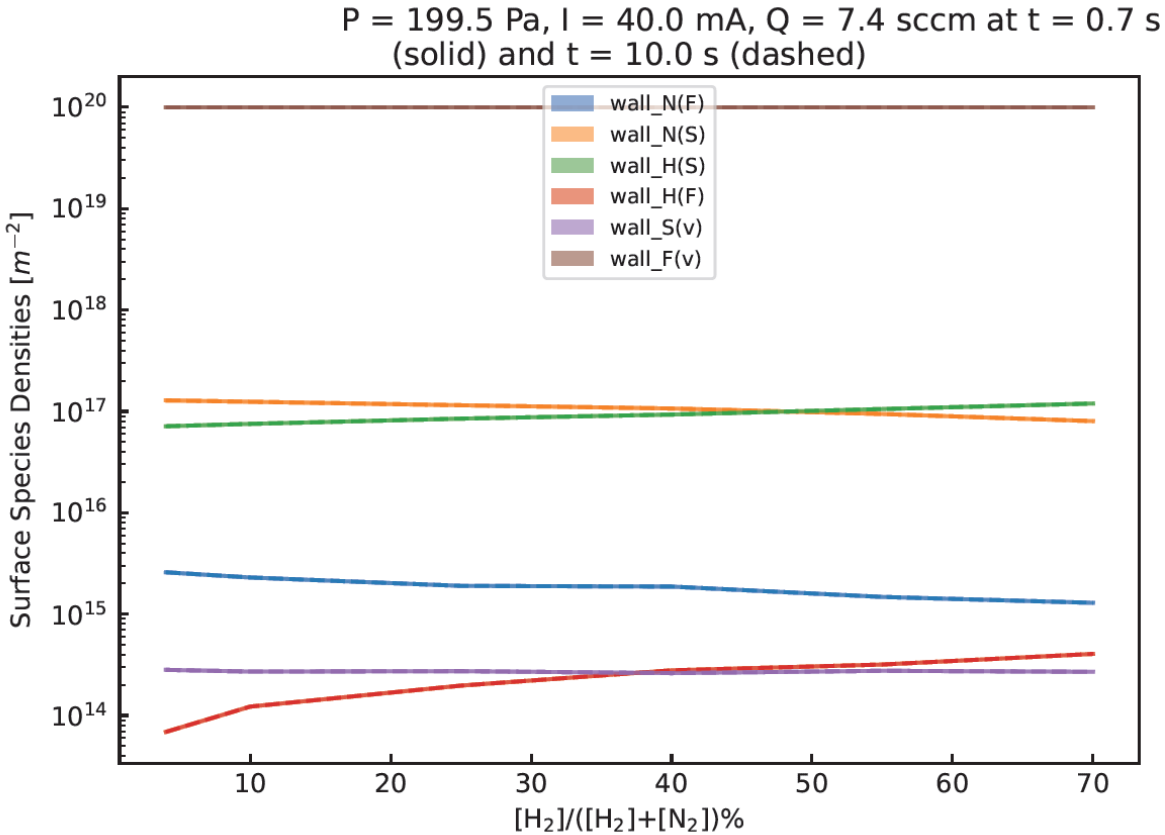
As expected, *E/N* is larger for the lower pressures

Good qualitative agreement between simulations and measurements
(in general, simulations overestimate measurements)

Volume and Surface species

Species densities vs. %H_2 (Simulation Results)



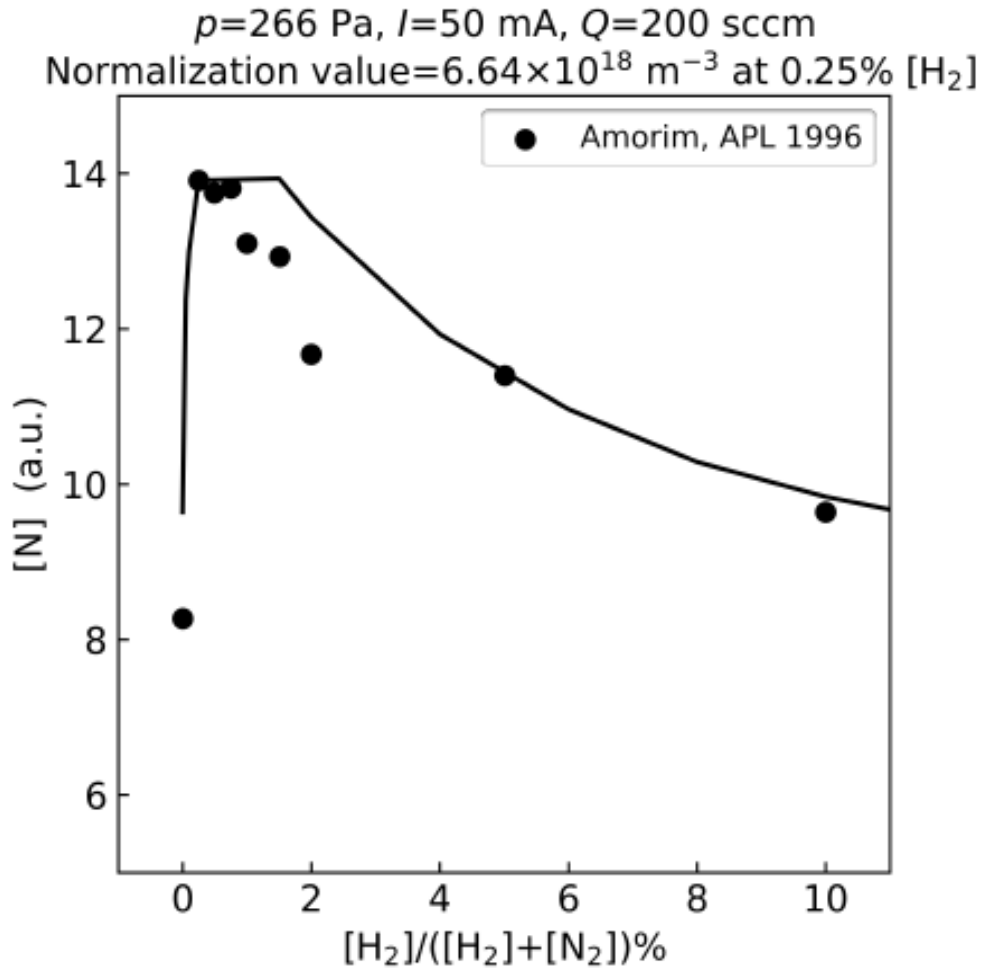


[H] > [N] across almost all conditions, except at very low %H_2 where N dominates.

[N(S)] > [H(S)] across almost all conditions, except at high %H_2 where H(S) dominates.

Neutral species densities

[N] vs. %H_2



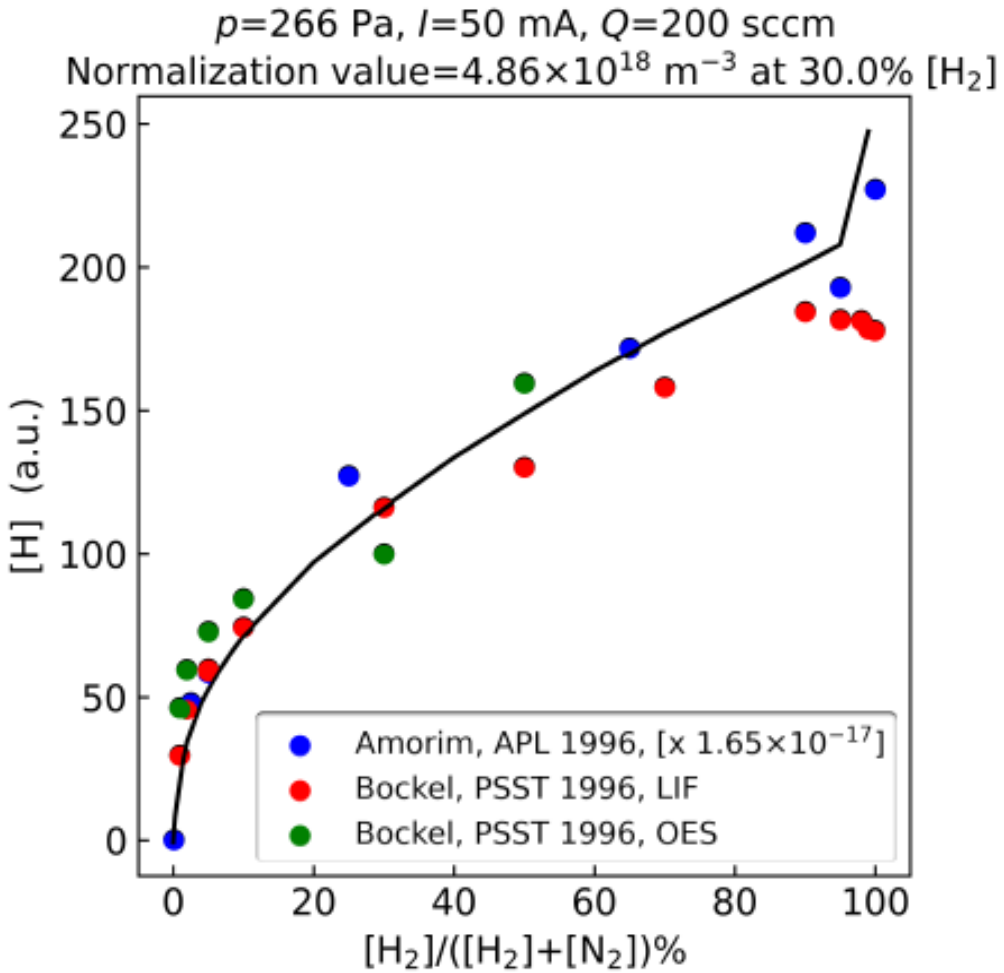
- **Measurements using LIF**
  Simulations used temperatures estimated from Gordiets.
- **The steep increase and the subsequent decrease in [N] strongly depends on the quenching reaction**
  $N_2(A) + H(^1S) \rightarrow N_2(X, v^*) + H(^1S)$
- **The slope of the smooth decrease of [N] with H2% is influenced by neutral-transport model and parameters**

Good qualitative agreement between simulations and measurements.

The evolution trend of [N] is affected by the surface activation and desorption energies of N and H

Neutral species densities

[H] vs. $\%H_2$

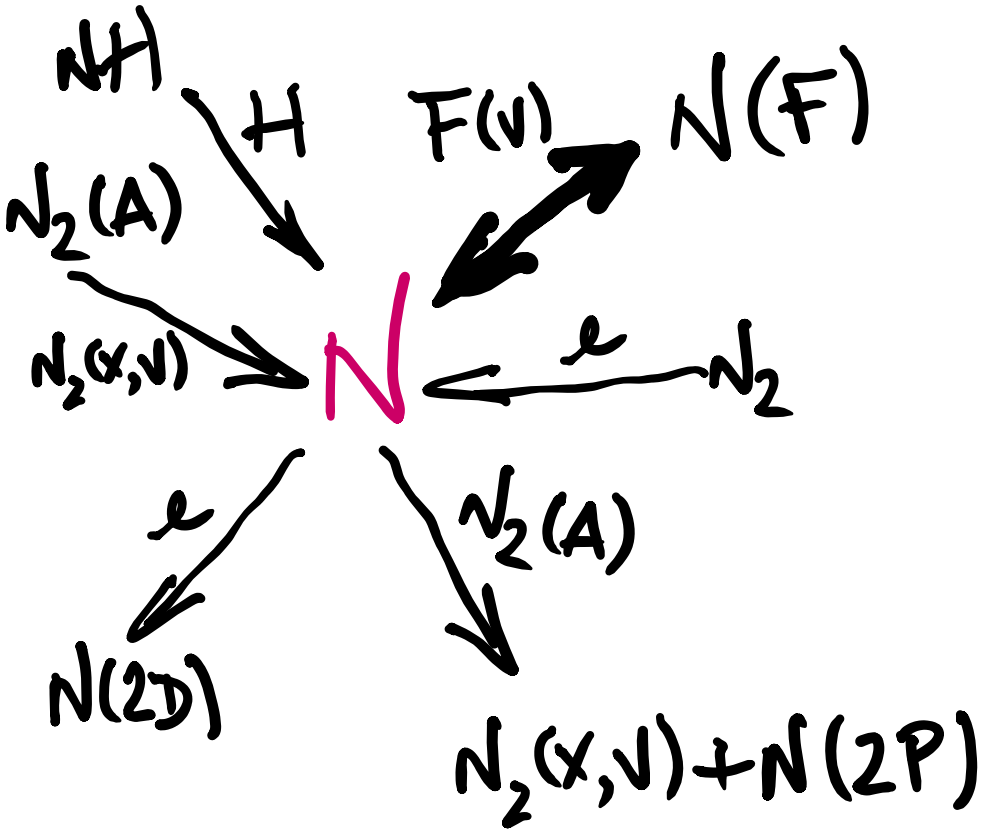


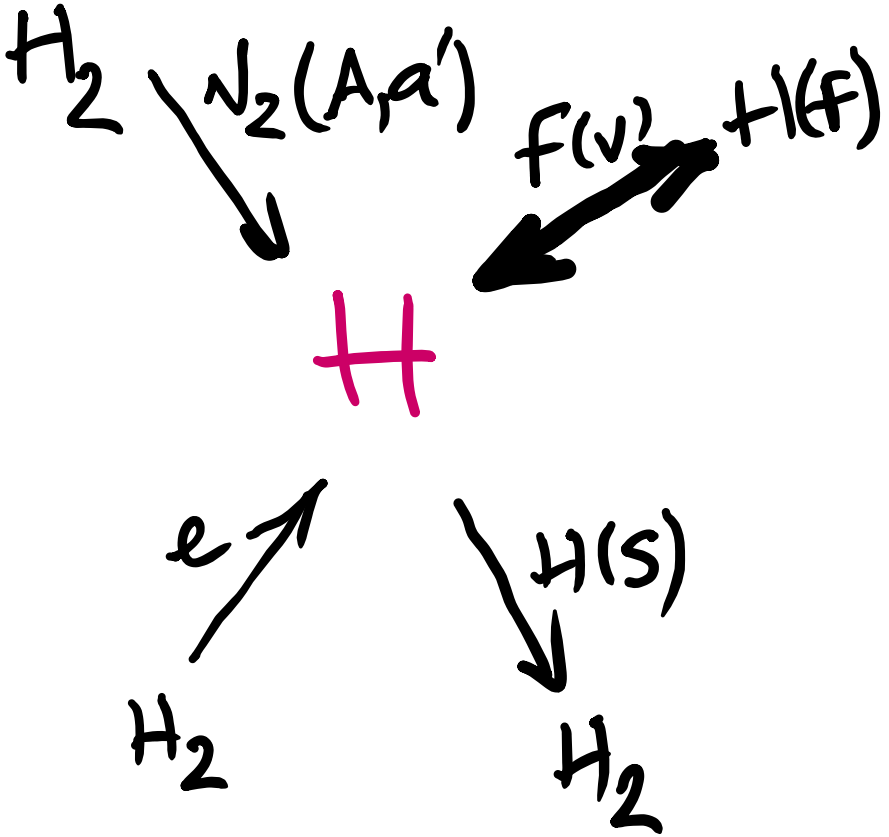
- **Measurements using LIF calibrated with VUV absorption Simulations used temperatures estimated from Gordiets.**
- **Measured absolute values (Amorim) are 10x below simulations.**

Excellent qualitative agreement between simulation and measurements

The evolution trend of [H] is affected by the surface activation and desorption energies of N and H

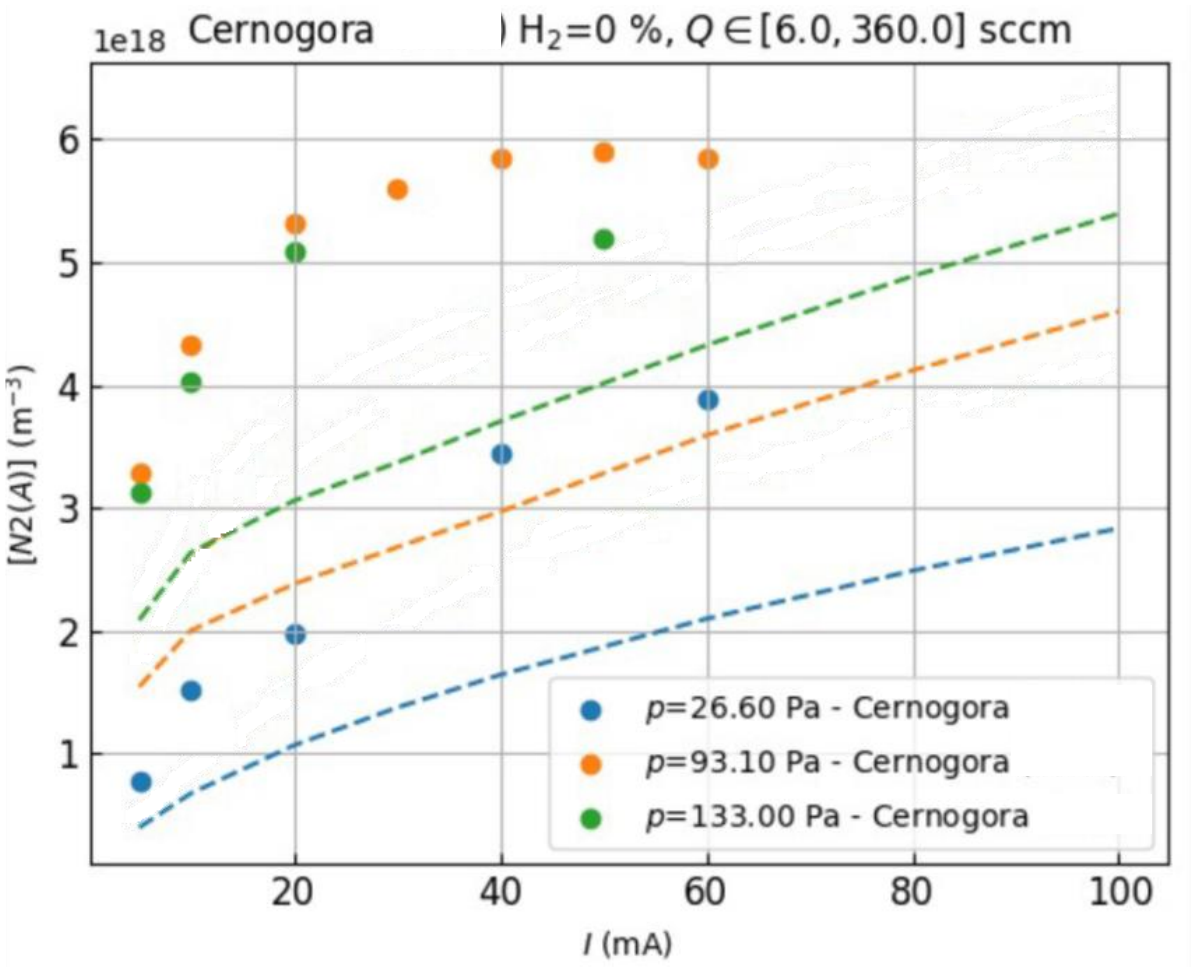
Schematic kinetic paths: N and H





Neutral species densities

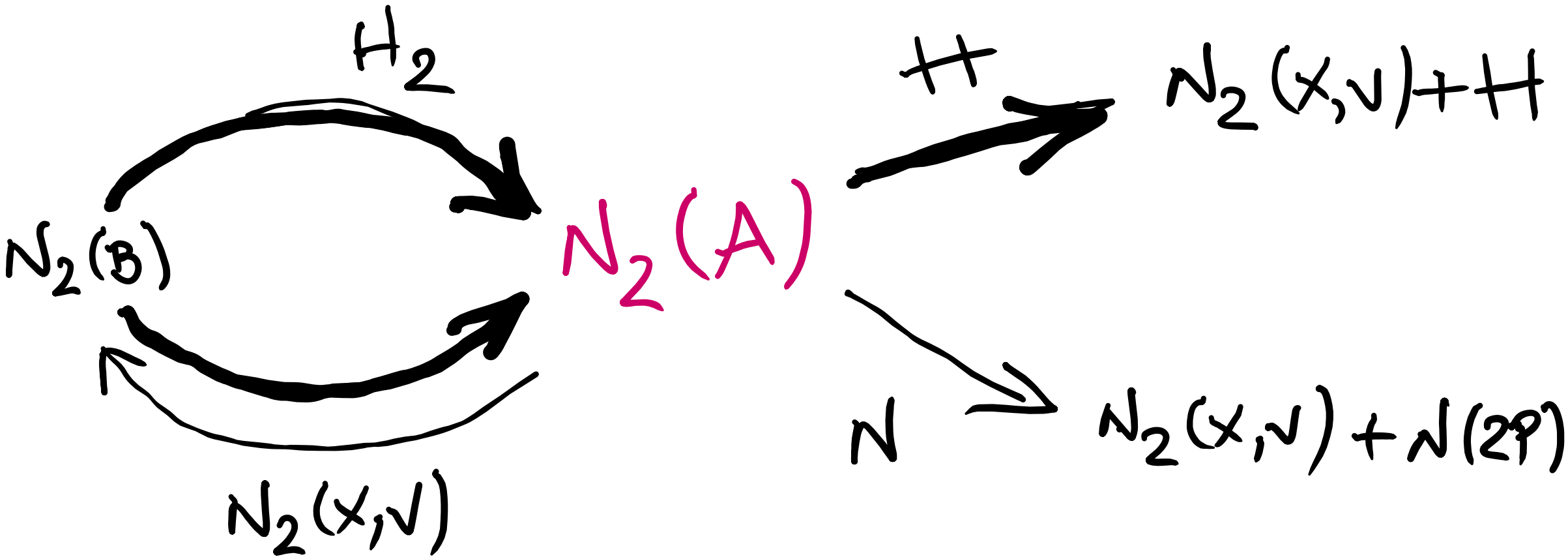
$[N_2(A)]$ vs. I_{dc} (pure N_2)



Measurements using OAS (Cernogora)

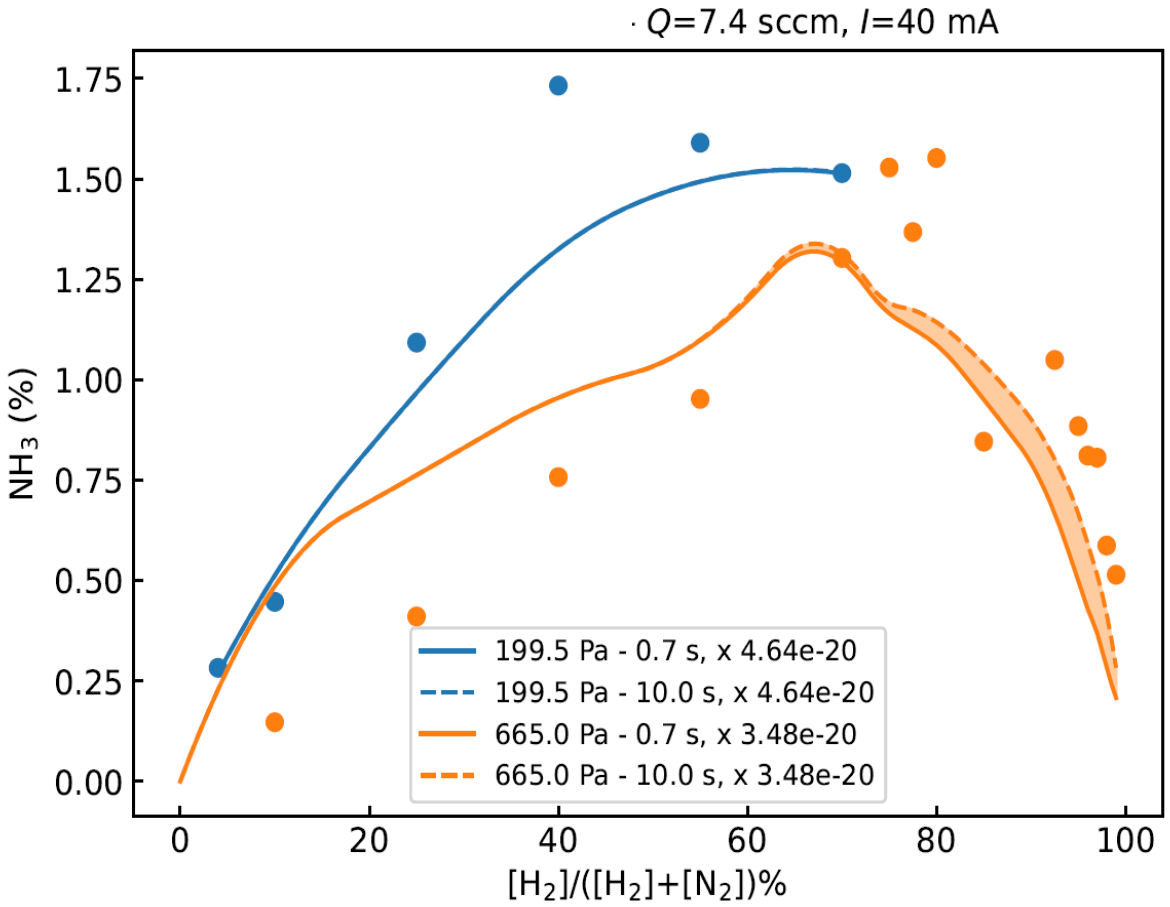
Good qualitative agreement between simulations and measurements, with simulations underestimating measurements.

Schematic kinetic paths: $N_2(A)$



Neutral species densities

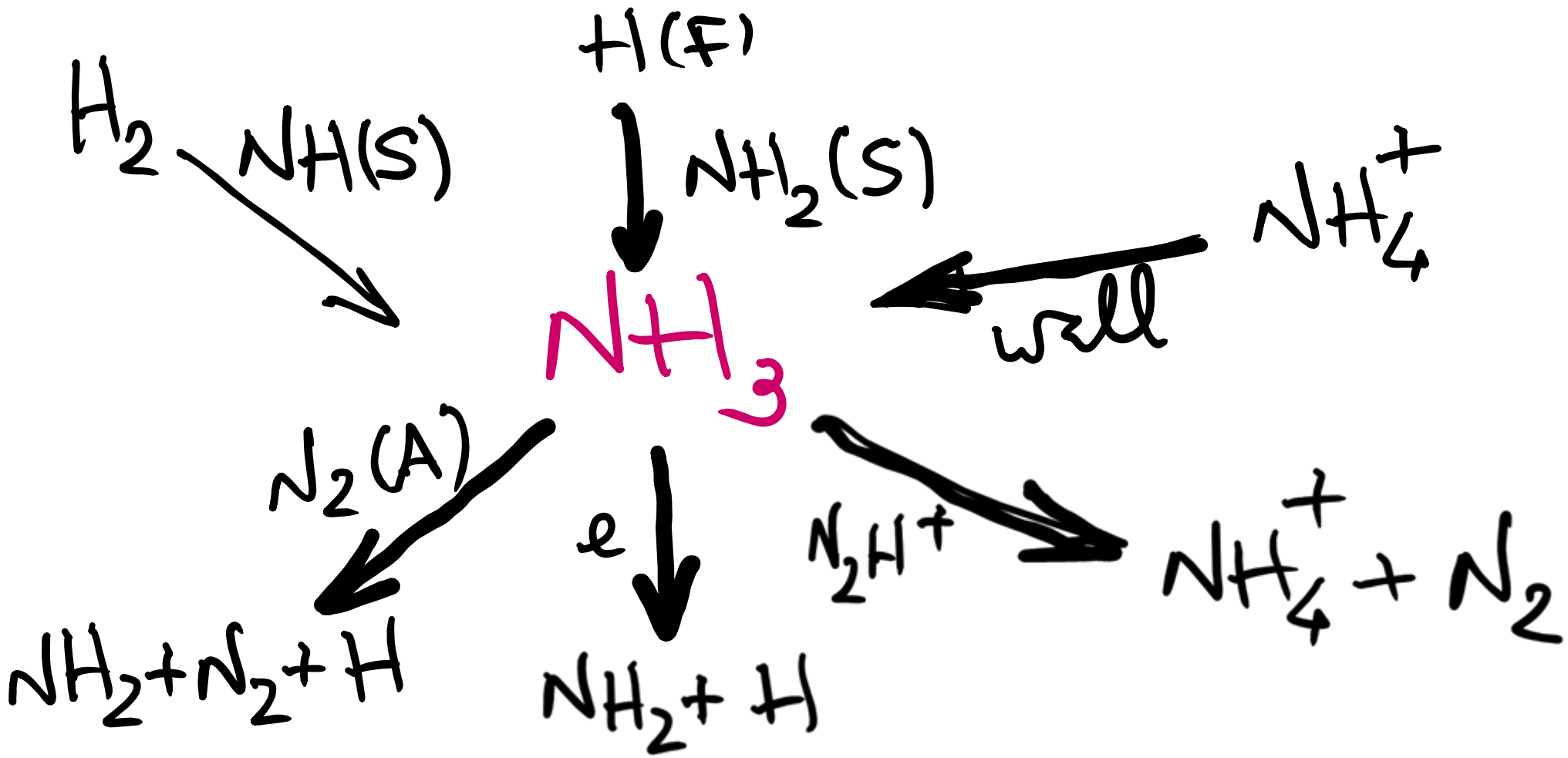
$[NH_3]$ vs. $\%H_2$



- **Measurements using FTIR on the LPP setup.** Simulations used experimental gas temperatures**.**
- **Simulation bands between residence times $t_{min}/2$ = 0.7s and $2t_{max}$ = 10s (under present working conditions)**

- **Simulations (normalized at 70% H2) in good qualitative agreement with measurements**
- **The absolute $[NH_3]$ is larger at high pressure**

Schematic kinetic paths: NH_3



Conclusions

Final remarks

- **General good agreement between simulations and measurements**
- **The model can predict a maximum of [NH_3] around 70% H_2, consistent with FTIR measurements**
- **Some kinetic pathways were revealed / confirmed**
  - There is a crossed-influence of $N(^4S)$ and $N_2(A)$ kinetics
  - Evolution trends of [$N(^4S)$] and [$H(^1S)$] vs. %H_2 depend on
    - the surface parameters adopted for these species.
    - the quenching reaction $N_2(A) + H(^1S) \rightarrow N_2(X, v^*) + H(^1S)$, affecting mainly $N(^4S)$
    - neutral-transport model and parameters
  - the main gain/loss channels of NH_3 are, in order
    - production : Langmuir-Hinshelwood, NH_4^+ wall-recombination and Eley-Rideal
    - destruction: e-impact, collisions with $N_2(A)$ and N_2H^+

Acknowledgements

UID/50010/2025 (https://doi.org/10.54499/UID/50010/2025)

UID/PRR/50010/2025 (https://doi.org/10.54499/UID/PRR/50010/2025)

UID/PRR2/50010/2025 (https://doi.org/10.54499/UID/PRR2/50010/2025)

LA/P/0061/2020 (https://doi.org/10.54499/LA/P/0061/2020)

UID/04650/2025 (https://doi.org/10.54499/UID/04650/2025) and

Ψ.COM Plasma Surface Interaction (Data and Tools) COupled Modelling (https://doi.org/10.54499/2022.04128.PTDC).