

Modeling N₂-H₂ for ammonia production

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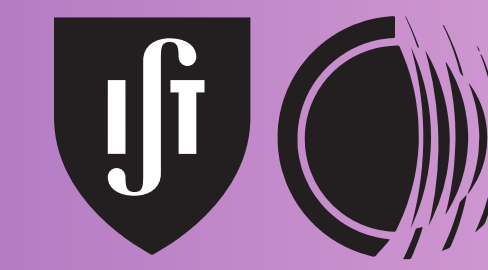


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Introduction

The search for a cleaner and more energy-efficient process for the **synthesis of ammonia (NH₃)** is a global concern, to which low-temperature plasma technology has emerged as a potential solution [1].

In this context, understanding the main kinetic paths leading to the plasma-assisted synthesis of NH₃ has topical interest, not only for the large-scale production of fertilizers at low cost, but also for the mitigation of ammonia generation in fusion machines.

It is currently believed that **plasma-surface interactions** could be the dominant mechanisms for this process [2]. In this work we address the kinetic modelling of N₂-H₂ plasmas, including the interplay between the volume and surface reactions.

We present follow-ups of our research program on nitrogen-hydrogen plasmas, based on a **very complete kinetic scheme** for this system, which was **revised and validated** using complementary modelling and diagnostics analyses.

Experiments

We model **cylindrical DC glow discharges** ($L \approx 20$ -50 cm long and $R \approx 1$ cm radius), produced in N₂-H₂ gas mixtures at various H₂ concentrations (0-100%), gas flows ($Q = 0$ -600 sccm), pressures ($p = 30$ -600 Pa) and discharge currents ($I_{dc} = 5$ -100 mA).



Measured data are taken from different works [3-6] for: the reduced electric field E/N (where E is the electric field and N is the gas density), using the potential difference between two probes immersed in the plasma; the gas temperature (deduced from OES of N₂ bands), the densities of ammonia (FTIR absorption and LIF calibrated with VUV absorption) and of H and N atoms (LIF measurements), and the fractional fluxes of the main ion species (mass spectrometry). The most recent data were obtained at the **Laboratory of Plasma Physics** (LPP) at Palaiseau.

Simulations

Simulations use the **Lisbon KInetics (LoKI) simulation tool** [7], developed under MATLAB® comprising

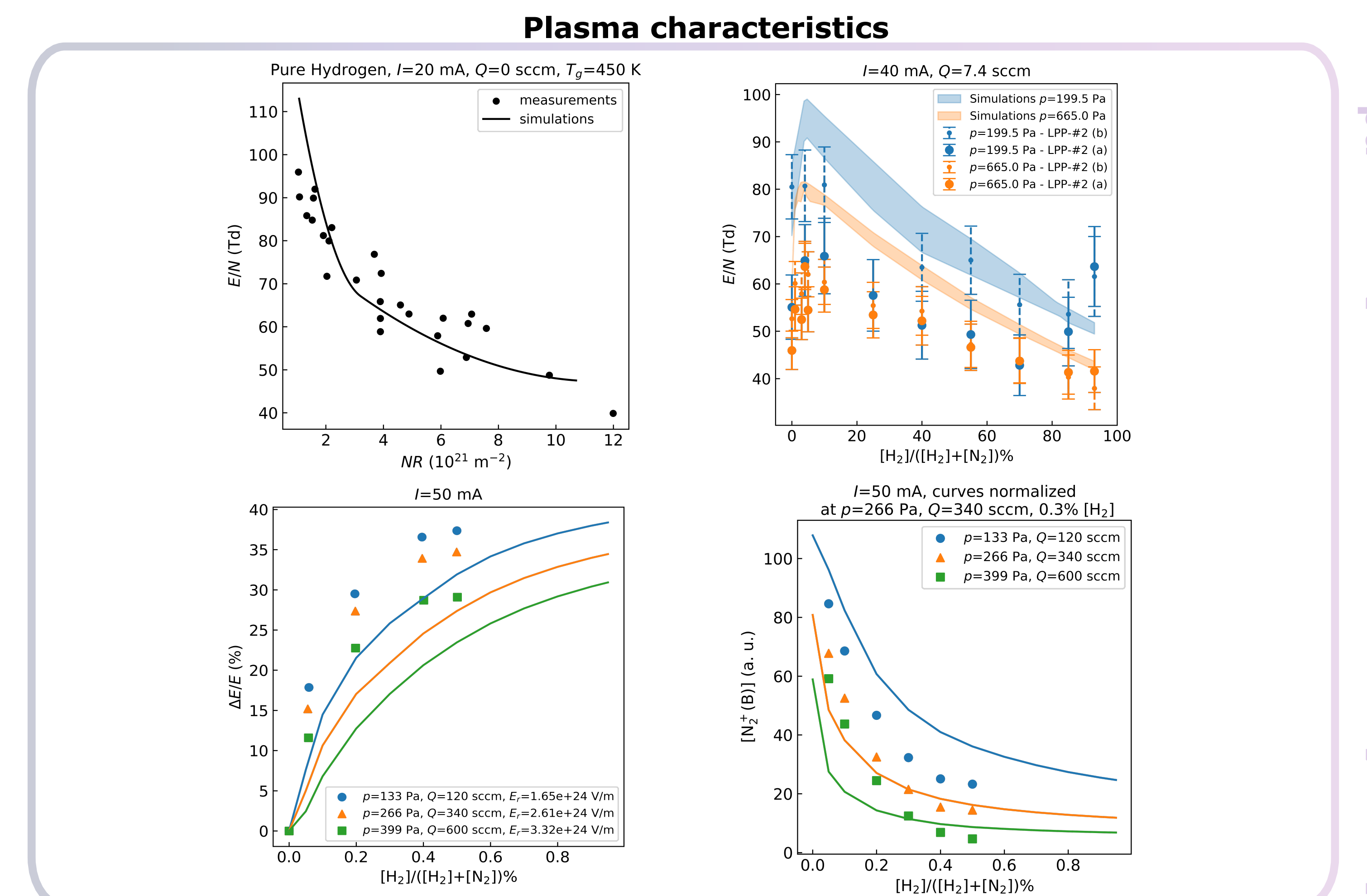
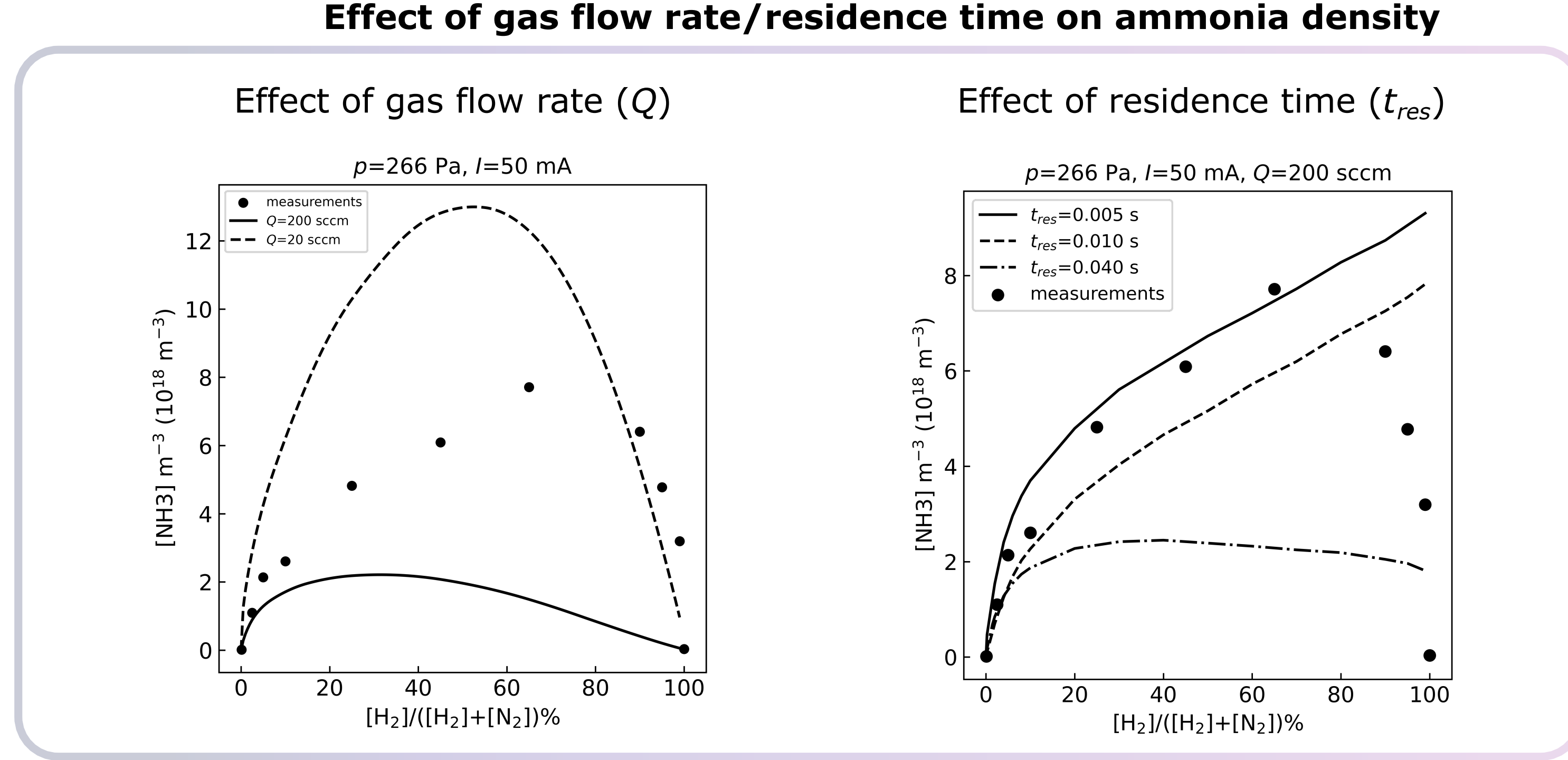
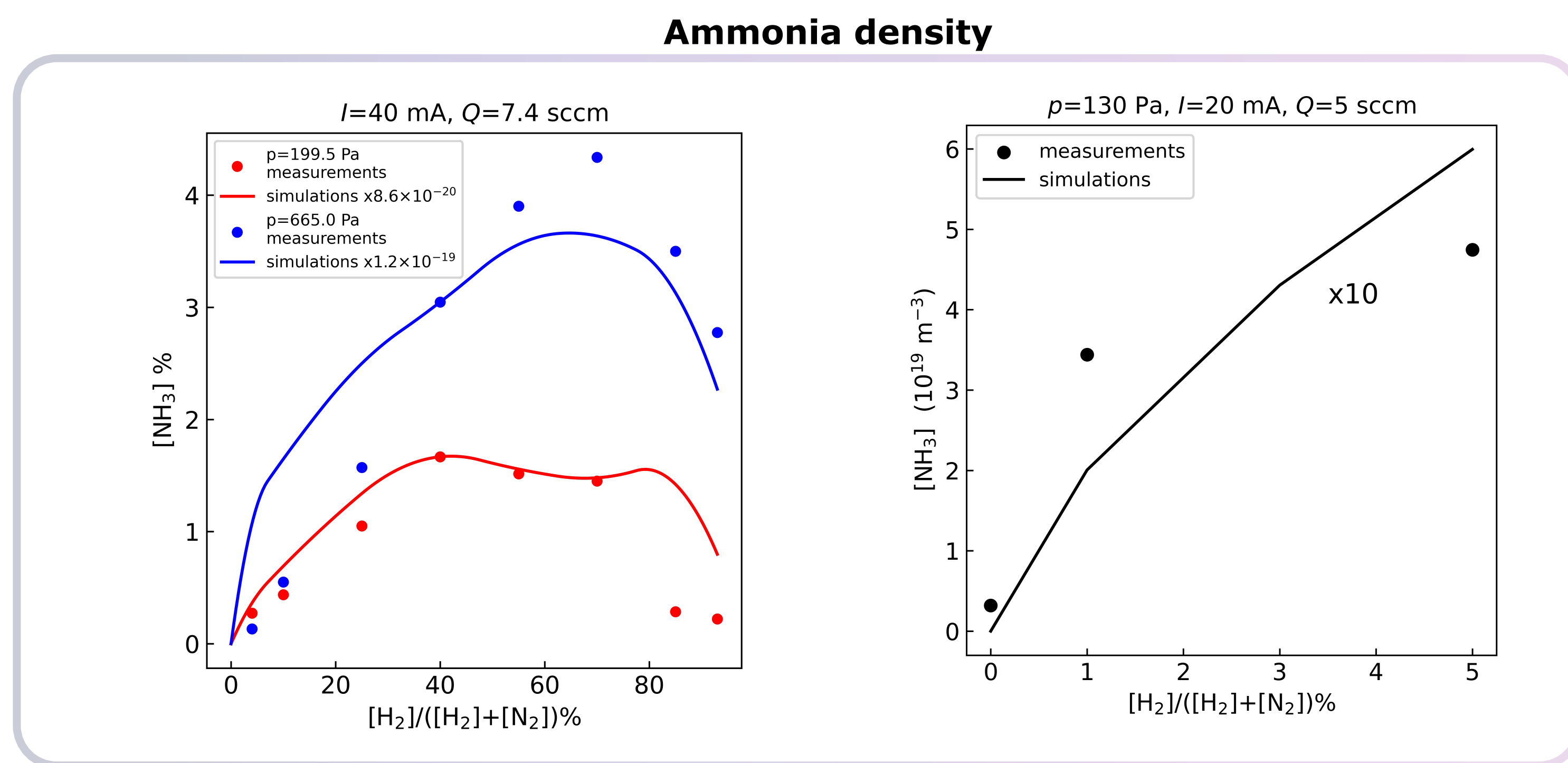
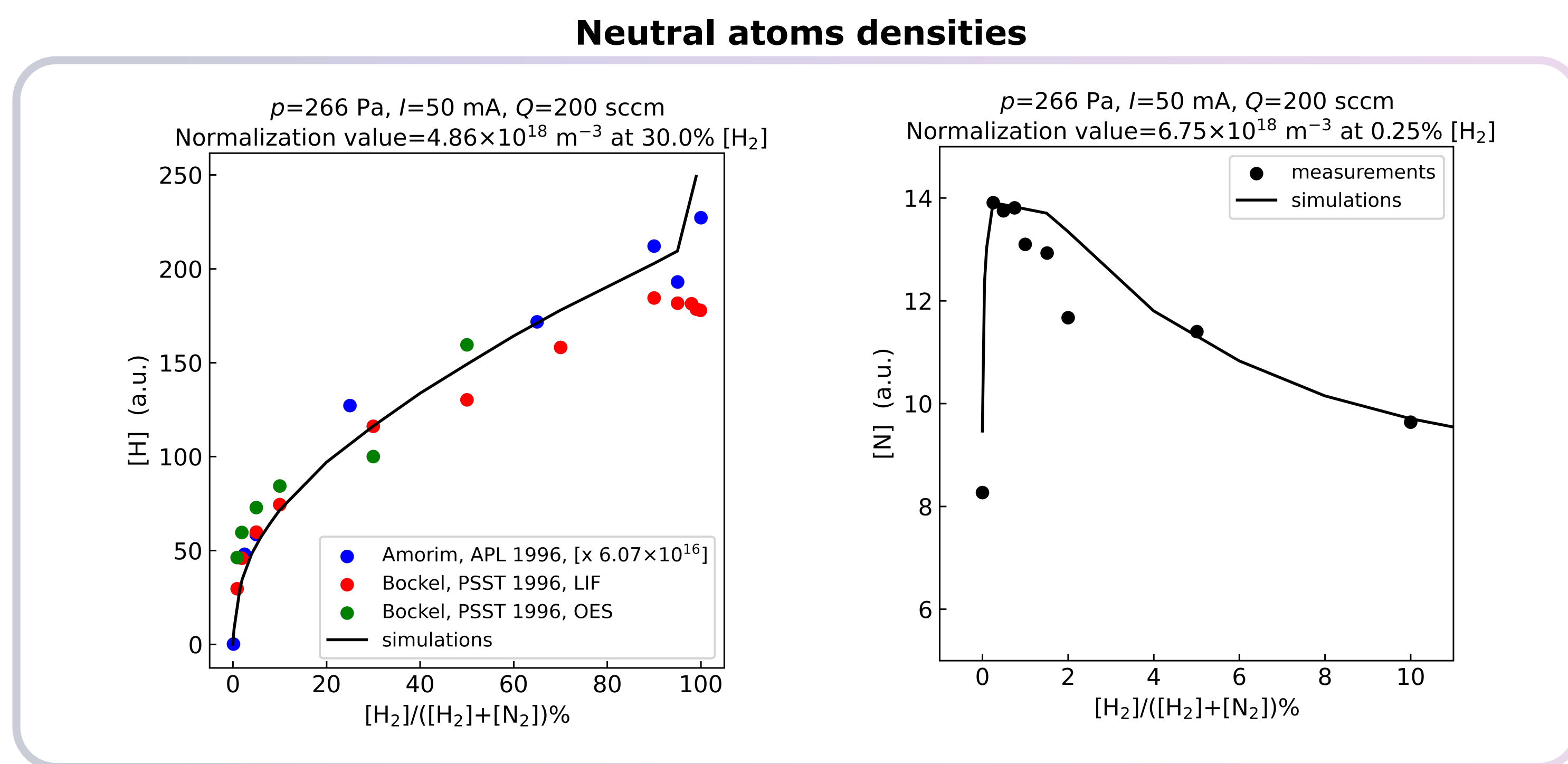
- **LoKI-B** that solves a space-independent form of the two-term **electron Boltzmann equation** (EBE) for non-magnetised non-equilibrium low-temperature plasmas excited by DC/HF, or time-dependent (non-oscillatory), electric fields, using electron-scattering cross sections that can be downloaded from the LXCat open-access website [8].

- **LoKI-C** that solves the system of **zero-dimensional (volume average) rate balance equations** for the most relevant heavy species (charged and neutral) in the plasma, receiving as input data the kinetic schemes for the gas/plasma system under study, and using several modules to describe the mechanisms (collisional, radiative and transport) controlling the creation / destruction of species.

LoKI gives a self-consistent solution for the electron energy distribution function, the densities of volume and surface species, the reduced electric field and the outflow, for given gas pressure and temperature, mixture composition and discharge current.

The **kinetic scheme for nitrogen-hydrogen plasmas** [9], considers the main heavy species N₂(X, v=0-44), H₂(X, v=0-14), NH₃, N(⁴S), H(¹S), in addition to: 13 electronic excited states (6 for N₂, 2 for N and 5 for H); positive ions N⁺, N₂⁺, N₃⁺, N₄⁺, H⁺, H₂⁺, H₃⁺, N₂H⁺, NH⁺, NH₂⁺, NH₃⁺ and NH₄⁺; negative ions H⁻ and NH₂⁻; surface species H(S,F), N(S,F), NH(S), NH₂(S), (physically (F) or chemically (S) adsorbed on the wall); and other molecules and radicals.

The **surface kinetics is inspired by the mesoscopic model of Gordiets et al.** [10], considering physical adsorption/desorption, chemical adsorption, surface transport, and Eley-Rideal and Langmuir-Hinshelwood recombination processes. The surface density was assumed $[S]+[F] = 10^{20} \text{ m}^{-2}$.



Results and discussion

The adjacent figures present examples of comparisons between simulations and measurements.

The **"Plasma characteristics"** panel shows results of E/N and $\Delta E/E$ as a function of either NR or the concentration of H₂, at different pressures [4,6]. For comparison, we also show results of the **N₂^(B) density** for various H₂ concentrations [6]. Model predictions tend to overestimate the values of E/N for pure N₂ (used to calculate the reference electric field E_r in the lower-left figure), whereas showing good agreement for pure H₂. The gas temperature T_g has a relevant impact on the results, as demonstrated by the experimental error bars (resulting from different (a)/(b) measurement campaigns of T_g) and the simulation bands (obtained using an uncertainty of 50 K in the input gas temperature).

The N and H atoms kinetics can also influence model predictions, by changing the N₂(A) density. The **"Neutral atoms densities"** panel presents results of simulations and LIF measurements for the **relative densities of atomic H (left) and atomic N (right)**, as a function of the H₂ concentration [4,5]. In this case, simulations show good qualitative agreement with the experiment.

Simulations of **"Ammonia density"** at various H₂ concentrations show good qualitative agreement with experimental measurements [3,4], although they appear to underestimate the absolute values. At high flow rates, this discrepancy may be due to the short residence time in the discharge, as illustrated in the **"Effect of gas flow rate / residence time"** panel. Here, we compare **[NH₃] values** obtained under different conditions: **steady-state simulations at Q=200, 20 sccm (left)**, and simulations at **200 sccm for residence times $t_{res}=5$ -40 ms (right)**.

Model predictions confirm that gas flow can be a significant **loss channel for NH₃** (~40%), rivaling losses from electrons, N₂(A) and N₂H⁺ collisions (~20% each). The mesoscopic surface kinetic model effectively captures **ammonia production** via plasma-surface interaction, where the physical adsorption of N,H atoms on physical vacant sites F(v) enables key pathways - Langmuir-Hinshelwood and Eley-Rideal - in addition to wall recombination of NH₄⁺.

References

- [1] M. L. Carreon, *J. Phys. D: Appl. Phys.* **52** 0483001, 2019
- [2] A. Bogaerts et al., *J. Phys. D: Appl. Phys.* **53** 443001, 2020
- [3] A. Chatain et al., *Plasma Sources Sci. Technol.* **32** 035002, 2023
- [4] J. Amorim et al. *Appl. Phys. Lett.* **68** 1915, 1996
- [5] S. Bockel et al. *Plasma Sources Sci. Technol.* **5** 567, 1996
- [6] S.D. Popa et al. *J. Phys. III France* **7** 1331, 1997
- [7] LoKI, <https://nprime.tecnico.ulisboa.pt/loki/>
- [8] LXCat, www.lxcat.net
- [9] M. Jiménez-Redondo et al. *Plasma Sources Sci. Technol.* **29** 085023, 2020
- [10] B. Gordiets et al., *Plasma Sources Sci. Technol.* **7** 379-88, 1998

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