Plasma-surface coupled modelling of ammonia production in DC discharges

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Introduction

The search for a cleaner and more energy-efficient process for **synthesis of ammonia (NH_3)** is a global concern, to which low-temperature plasma technology has emerged as a potential solution [1].

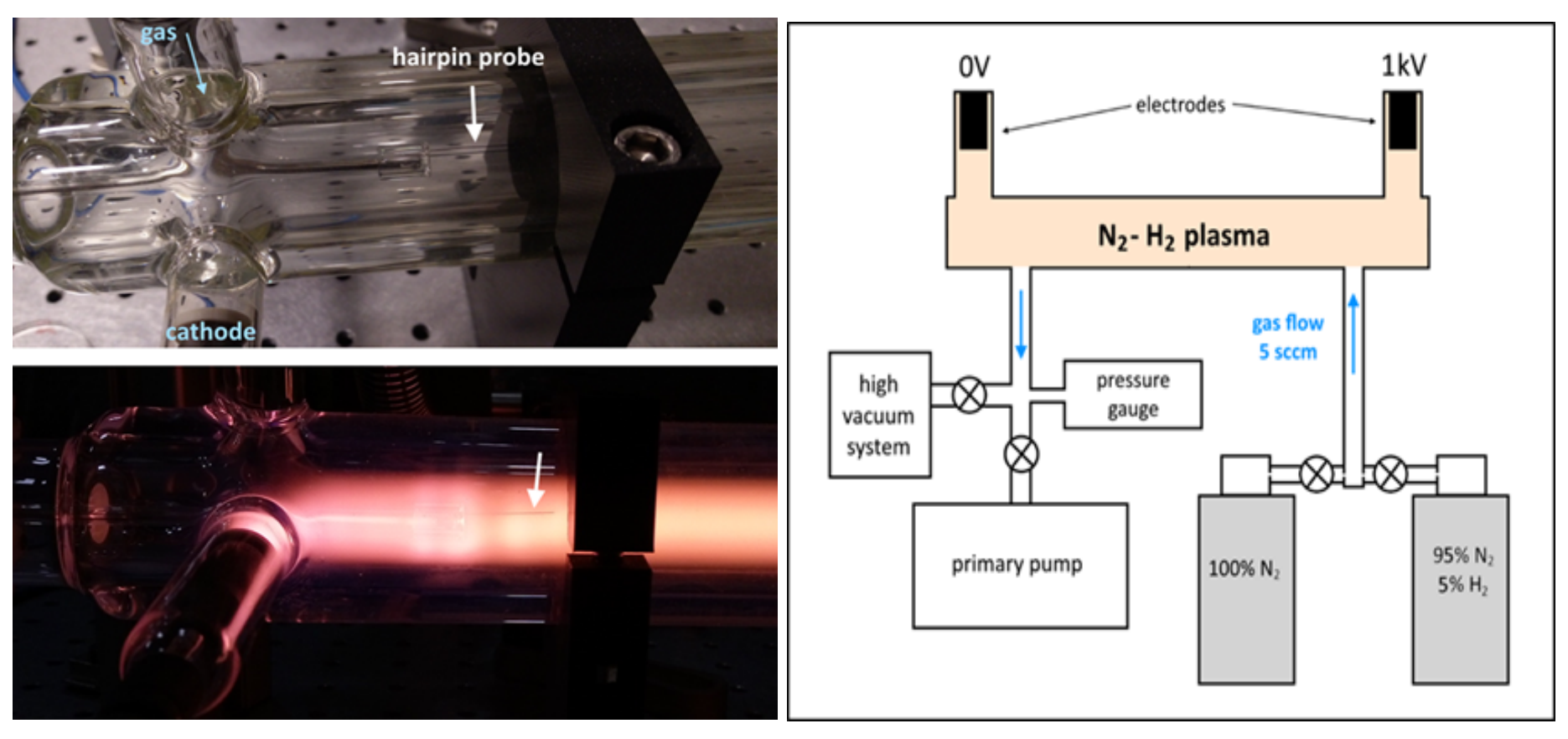
In this context, understanding the main kinetic paths leading to the plasma-assisted synthesis of NH_3 has topical interest, not only for the large-scale production of fertilizers at low cost, but also for the mitigation of ammonia generation in fusion machines.

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 N_2-H_2 plasmas, including the interplay between the volume and surface reactions.

We present the first steps of our research program on nitrogen-hydrogen plasmas, based on a **very complete kinetic scheme** for this system, which has started being revised and validated using complementary modelling and diagnostics analyses.

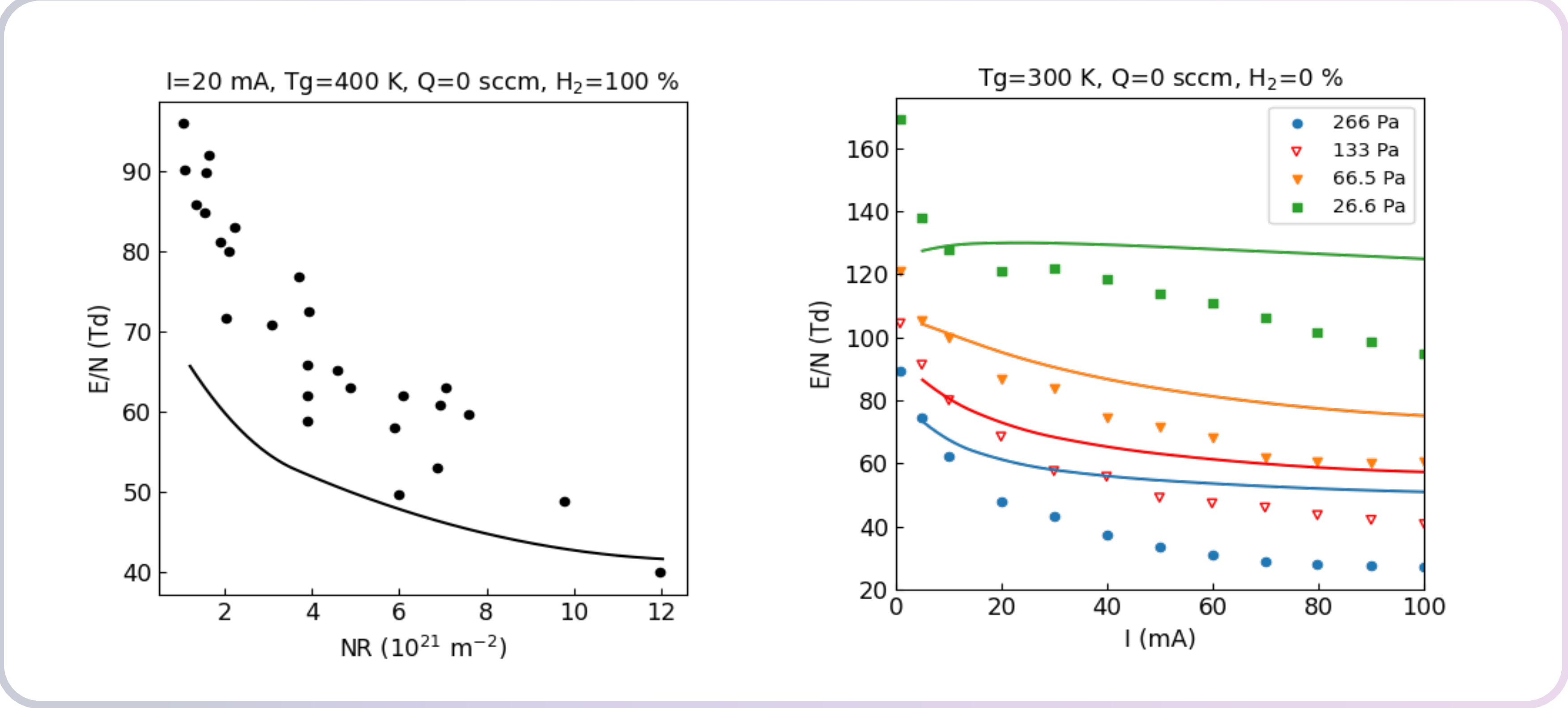
Experiments

We model **cylindrical DC glow discharges** (L~20 cm long and R~1 cm radius) with borosilicate glass walls [3,4], produced in N_2-H_2 gas mixtures at various H_2 concentrations (0-100%), gas flows (Q = 0-600 sccm), pressures (p = 30-400 Pa) and discharge currents (I_{dc} = 5-100 mA).

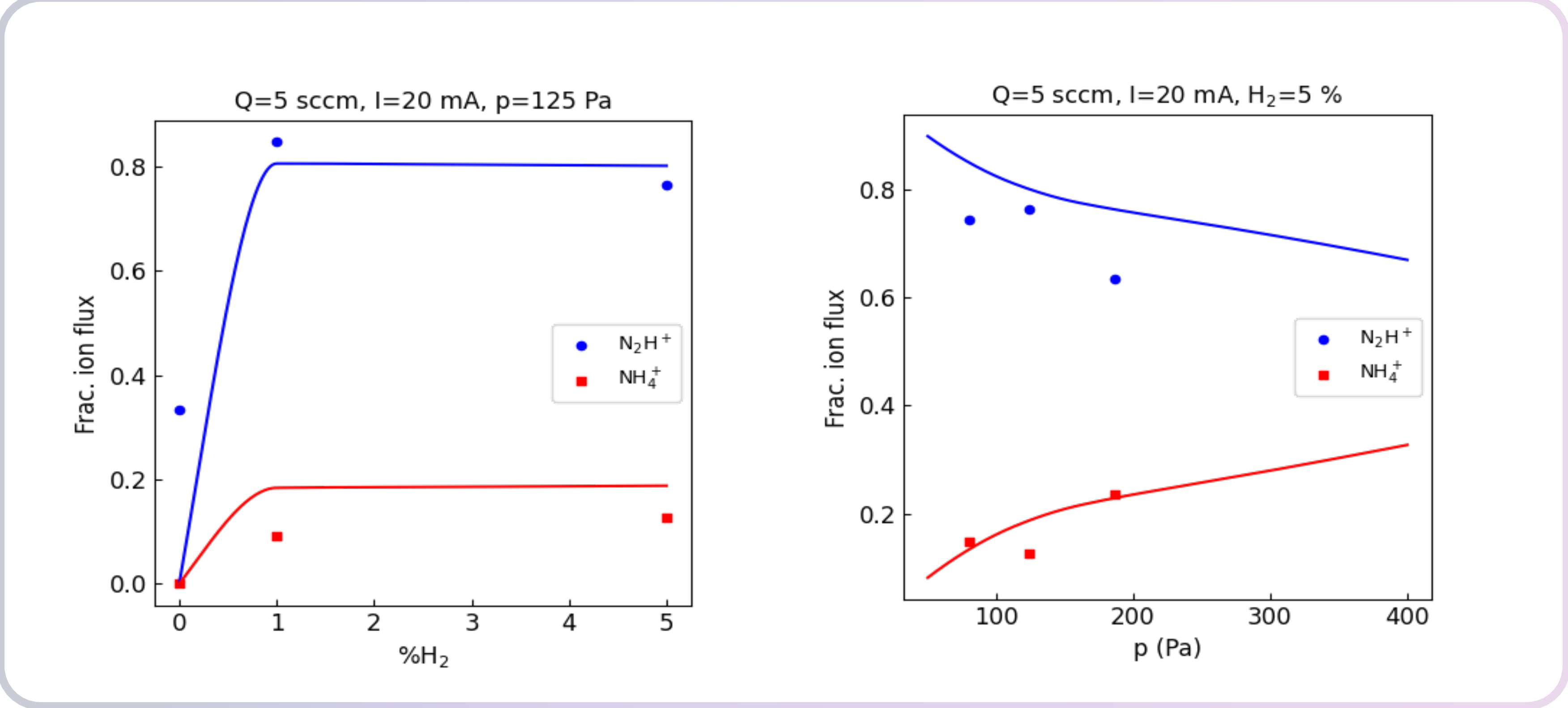


The figure shows the **experimental setup with the Laboratory of Plasma Physics** (LPP) in Paris. Typical measurements include: the **reduced electric field *E/N*** (where E is the electric field and N is the gas density), using the potential difference between two tungsten Langmuir probes immersed in the plasma; the **densities of ammonia** (FTIR absorption), and of **H and N atoms** (LIF measurements), and the **fractional fluxes of the main ion species**, using mass spectrometry.

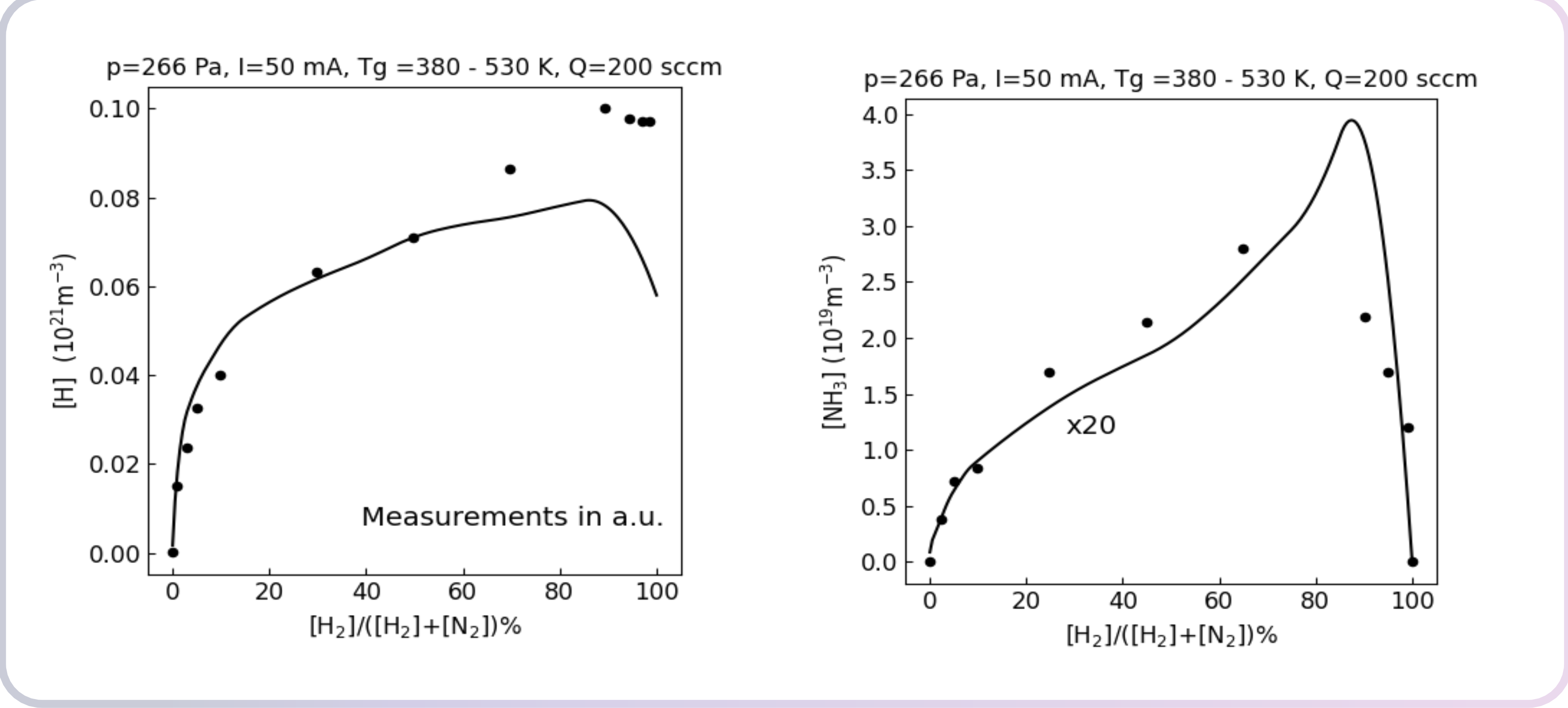
Plasma Characteristics



Fractional Ion Fluxes



Density of Neutral Species



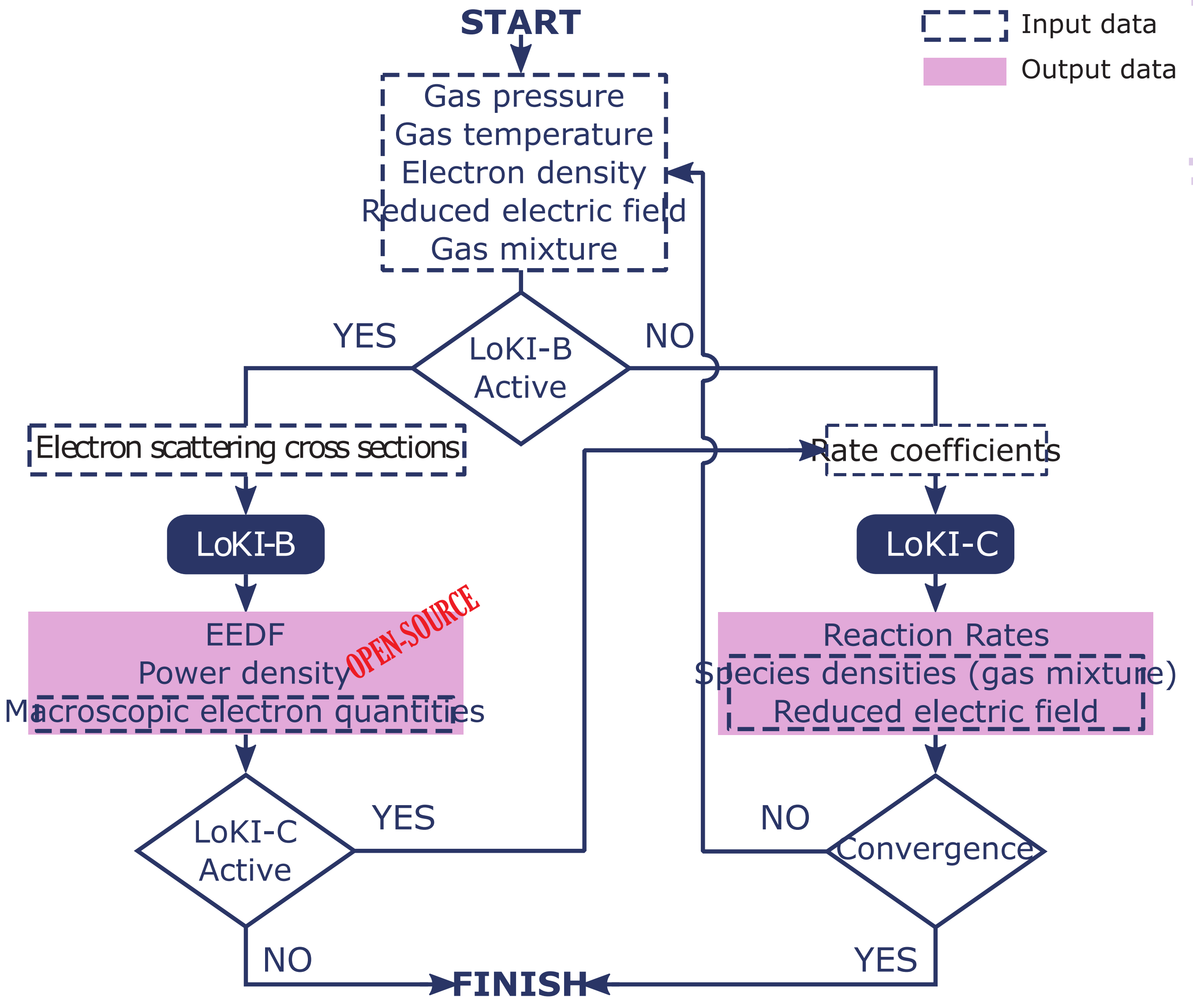
Simulations

Simulations use the **LisbOn KInetics (LoKI) simulation tool** [5,7], developed under MATLAB® comprising

- **LoKI-B** [5,6] 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** [7] 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-B and LoKI-C are **coupled via a series of convergence cycles**, ensuring a self-consistent solution for the electron energy distribution function, the species densities, and the reduced electric field, for given pressure, mixture composition and discharge current.


START
Input data
Output data
Gas pressure
Gas temperature
Electron density
Reduced electric field
Gas mixture
YES
LoKI-B Active
NO
Electron scattering cross sections
Rate coefficients
LoKI-B
LoKI-C
EEDF
Power density
OPEN-SOURCE
Macroscopic electron quantities
Reaction Rates
Species densities (gas mixture)
Reduced electric field
LoKI-C Active
YES
NO
Convergence
NO
YES
FINISH

The **kinetic scheme for nitrogen-hydrogen plasmas** [9], considers the main heavy species $N_2(X, v=0\text{-}44)$, $H_2(X, v=0\text{-}14)$, NH_3, $N(^4S)$, $H(^1S)$, in addition to: 13 electronic excited states (6 for N_2, 2 for N and 5 for H); positive ions N^+, N_2^+, N_3^+, N_4^+, H^+, H_2^+, H_3^+, N_2H^+, NH^+, NH_2^+, NH_3^+ and NH_4^+; negative ions H^- and NH_2^-; surface species H(S,F), N(S,F), NH(S), NH_2(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.*** [4], considering physical adsorption/desorption, chemical adsorption, surface transport, and Eley-Rideal and Langmuir–Hinshelwood recombination processes. The surface density was assumed $[S]+[F] = 10^{20}$ m^{-2}.

Results and discussion

The adjacent figures present examples of comparisons between simulations and measurements, obtained for the working conditions mentioned above.

The **"Plasma Characteristics" panel** shows measurements and calculations of ***E/N* in pure H_2** (as a function of NR) and **pure N_2** (as a function of I_{dc}). Model predictions underestimate the values of E/N for pure H_2, whereas showing good agreement for pure N_2 at low discharge currents. An improvement in the results may require revising the kinetic description of the dominant ions species: N_4^+ and N_2^+ in pure nitrogen; H_3^+ in pure hydrogen; N_2H^+ and NH_4^+ in the N_2-H_2 mixture (see **"Fractional Ion Fluxes" panel**). In particular, decreasing the production rate coefficient of H_3^+, and increasing the production rate of N_2(A) and N_2(a') may increase / decrease the value of E/N for pure H_2 / N_2 cases.

Note that the model correctly predicts the **fractional ion fluxes of N_2H^+ and NH_4^+**, as a function of H_2 concentration (0-5%) and pressure (75-400 Pa), as shown in the **"Fractional Ion Fluxes" panel**.

The **"Density of Neutral Species" panel** presents results for the **H-atom (left) and the NH_3 (right) densities**, as a function of the H_2 concentration.
The LIF **measurements of [H]** were given in arbitrary units, so they have been normalized to the calculated values at 50% H_2 for comparison purposes. In this case, simulations show good qualitative agreement with the experiment.
The **absolute measurements of [NH_3]** employed photofragment translational spectroscopy associated with LIF of $H(^1S)$, calibrated by VUV absorption spectroscopy on the Lyman-α (121nm) line [10]. In this case, model predictions undestimate the measurements by 20x, but once the simulated curve is multiplied by this factor it agrees very well with the experiment.

The mesoscopic surface kinetic model efficiently describes the ammonia production by plasma-surface interaction. The physical adsorption of N,H atoms on physical vacant sites F(v) is crucial to engage the surface pathway leading to the most important ammonia production channels: Eley-Rideal and Langmuir–Hinshelwood recombination. A revision of the model mesoscopic parameters may significantly improve the results.

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] B. Gordiets *et al.*, *Plasma Sources Sci. Technol.* **7** 379–88, 1998.
[5] A. Tejero-del-Caz *et al. Plasma Sources Sci. Technol.* **28** 043001, 2019.
[6] IST-Lisbon. LoKI repository on GitHub. https://github.com/IST-Lisbon/LoKI
[7] V. Guerra *et al. Plasma Sources Sci. Technol.*, **28** 073001, 2019.
[8] LXCat, www.lxcat.net
[9] M. Jiménez-Redondo *et al. Plasma Sources Sci. Technol.* **29** 085023, 2020.
[10] J. Amorim, G. Baravian and G. Sultan *Appl. Phys. Lett.* **68** 1915, 1996.

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