Plasma-surface coupled modelling of ammonia production in DC discharges

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Introduction

The quest for an environmentally friendly and energy-efficient method for **ammonia (NH_3)** synthesis is a worldwide issue, with low-temperature plasma technology being a possible solution [1].

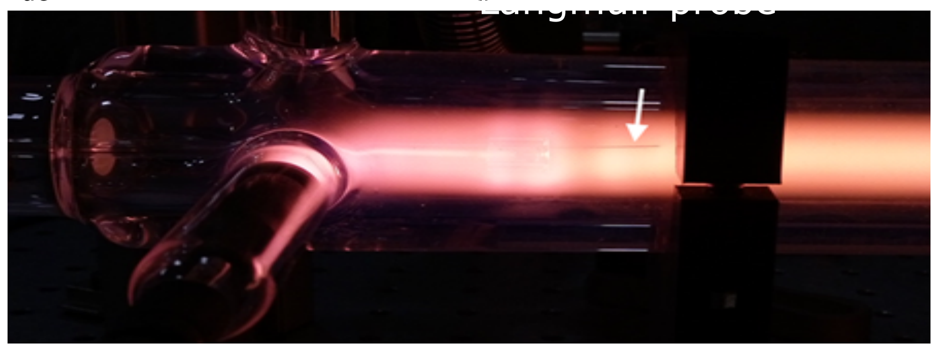
In this context, understanding the main kinetic paths leading to the plasma-assisted synthesis of NH_3 has topical interest, not only for the large-scale production of fertilizers at low cost, but also for the mitigation of ammonia generation in fusion machines.

It is currently believed that **plasma-surface interactions** could be the dominant mechanisms for this process [2]. In this work we propose a validated kinetic model for N_2-H_2 plasmas, including the interplay between volume and surface reactions.

We present the **near-final results** of our research program on nitrogen-hydrogen plasmas under different surface conditions, leveraging **complementary modelling and diagnostics analyses** to validate the kinetic model.

Experiments

The study is based on **cylindrical DC glow discharges** (10's cm long and ~1 cm inner radius), produced in N_2-H_2 gas mixtures (0-100% H_2 concentrations), at Q = 0-600 sccm gas flows, p = 10-700 Pa gas pressures, T_g = 350-600 K gas temperatures and I_{dc} = 5 - 100 mA discharge currents.



Measured data are taken from different works [3-8]. The experimental 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 gas temperature (deduced from OES of N_2 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

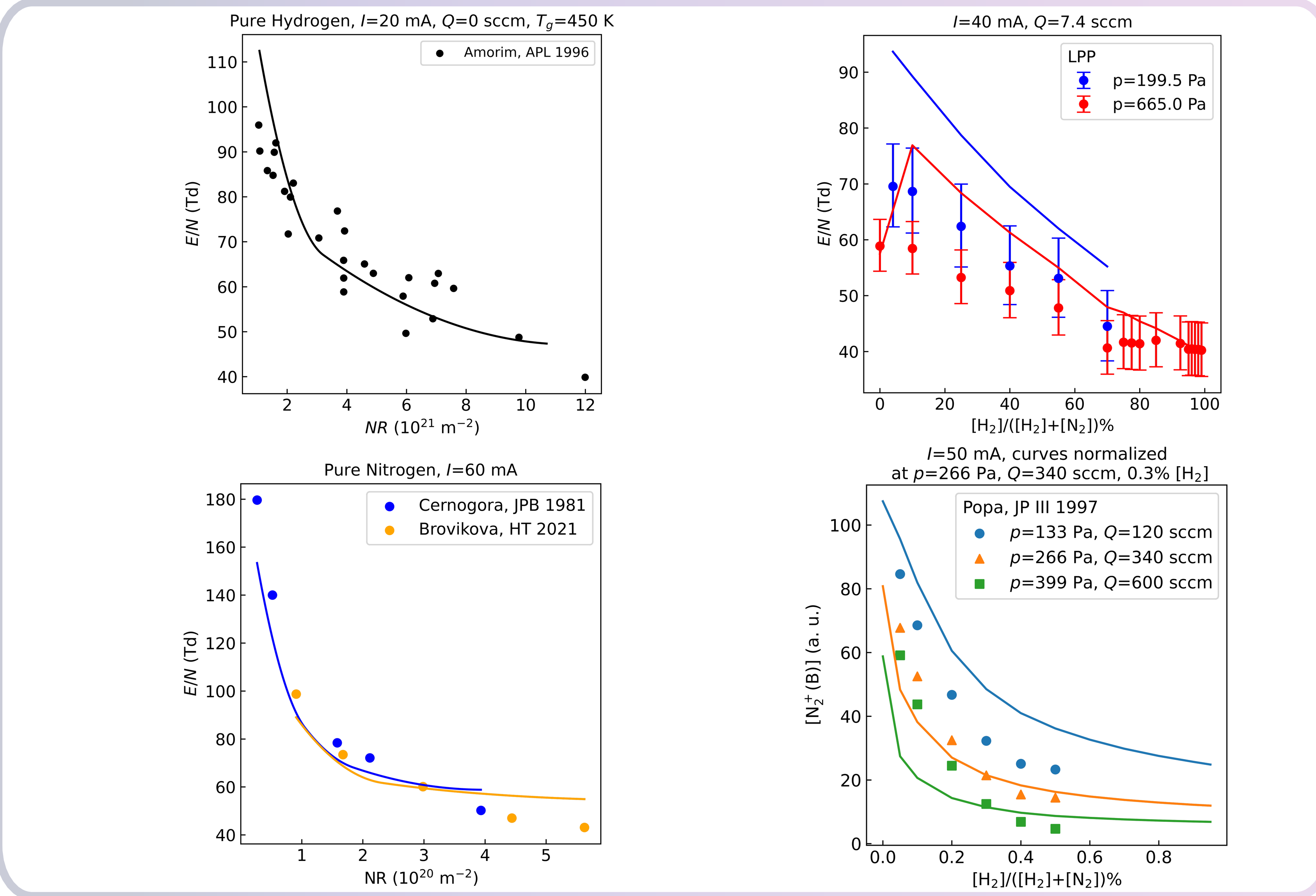
Simulations use **LisbOn KInetics Global Model (LoKI-GM)** [9], developed under MATLAB® comprising:

- **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.
- **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.

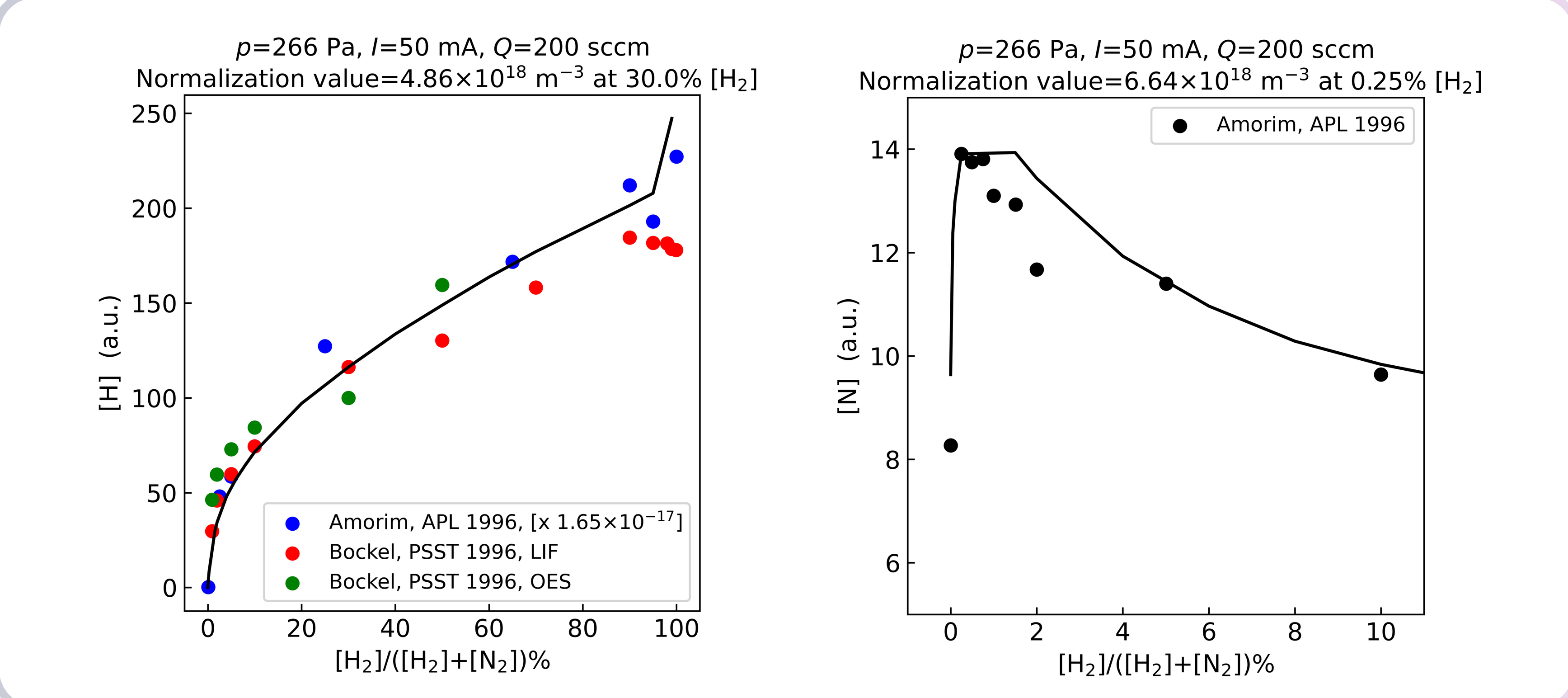
Simulations adopt an **updated version of the kinetic scheme for volume mechanisms used in [10]**, complemented by a **microkinetic mesoscopic model for plasma-surface interactions inspired in [11]**, which includes physical adsorption/desorption, chemical adsorption, surface transport, and Eley-Rideal (ER) and Langmuir–Hinshelwood (LH) recombination processes.

The kinetic scheme considers the main heavy species N_2(X, v=0-44), H_2(X, v=0-14), NH_3, N(^{4}S), H(^{1}S), 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 density was assumed [S]+[F] = 10^{20} m^{-2}.

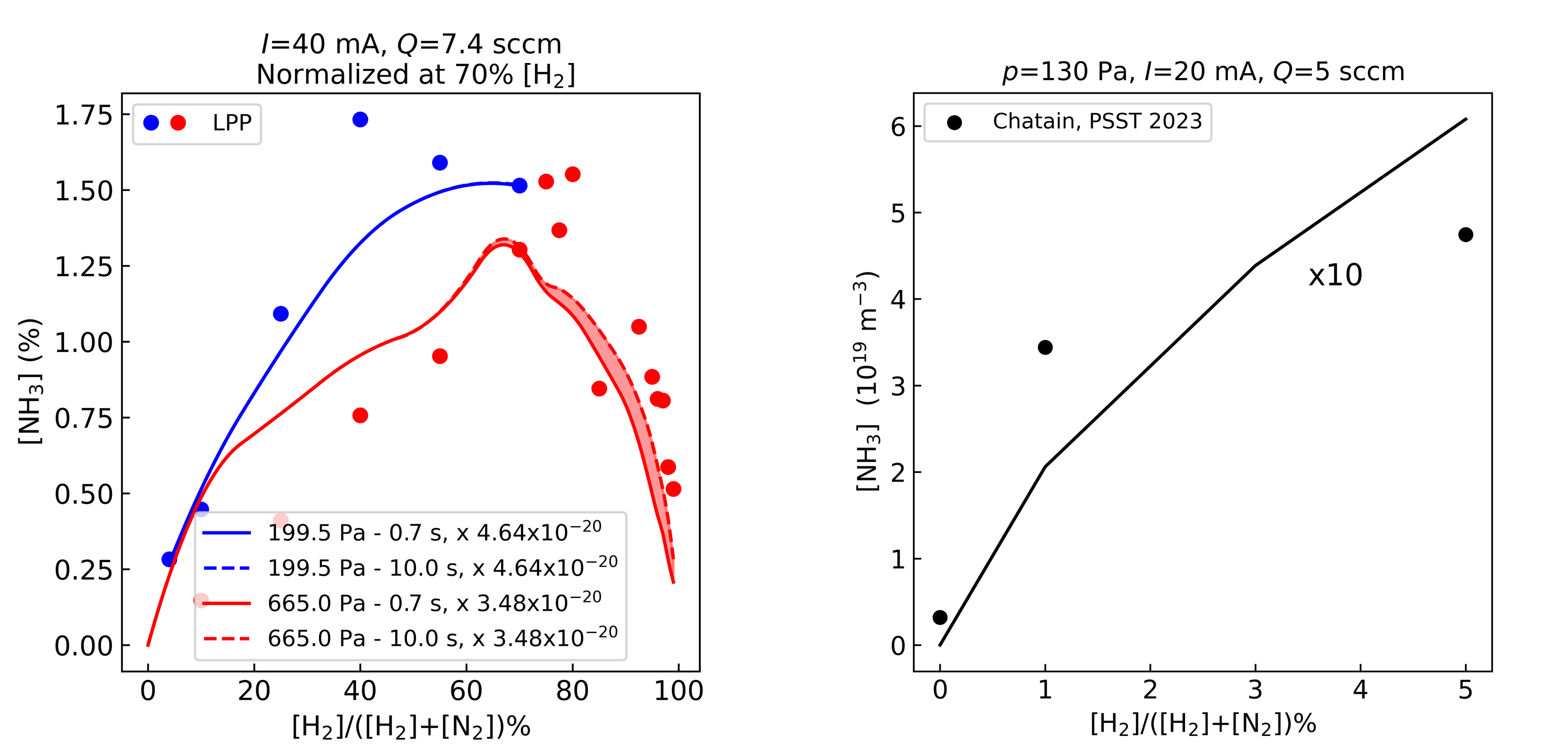
Plasma characteristics



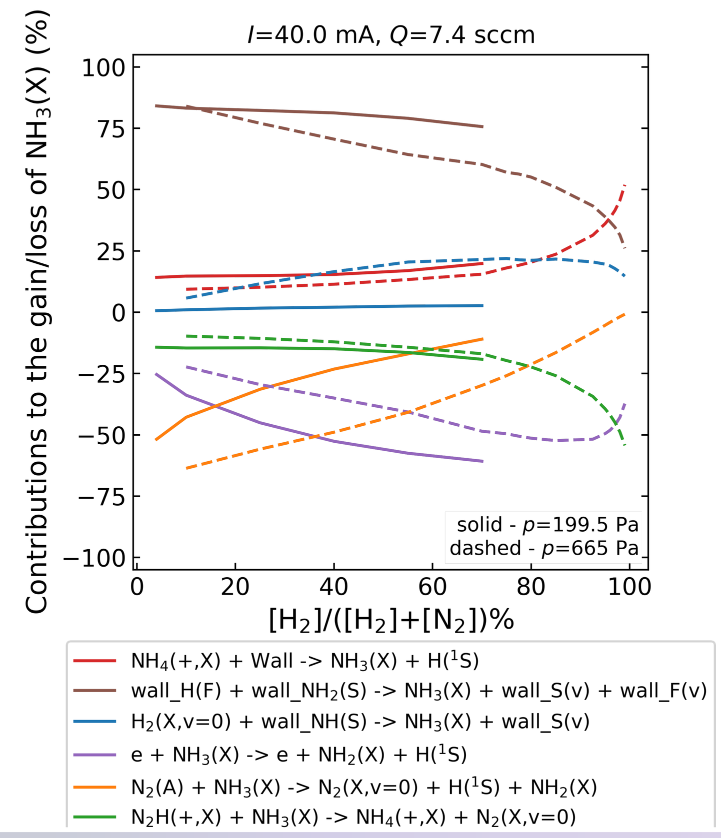
Neutral atoms densities



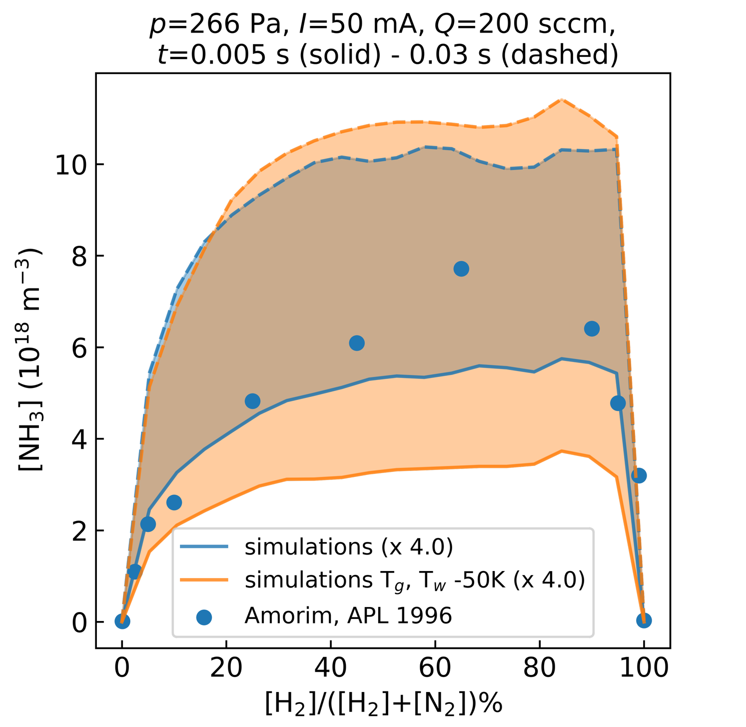
Ammonia density



Gain/Loss mechanisms



Residence time/gas temperature effect



Results and discussion

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

The **"Plasma characteristics"** panel shows results of ***E/N*** as a function of either ***NR*** or the **concentration of H_2**, at different pressures [3,4,6]. For comparison, we also show results of the **N_2^+(B) density** for various H_2 concentrations [7]. Model predictions tend to overestimate the values of E/N in N_2-H_2 mixtures, while showing good agreement for pure H_2 and pure N_2 (particularly at lower pressures). The gas temperature T_g has a relevant impact on the results, as demonstrated by the experimental error bars (obtained using an uncertainty of 50 K in T_g).

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 H_2 concentration [6,7]. Simulations show a very good qualitative agreement with the experiment, mainly due to:
(i) the choice of the surface activation and desorption energies of N and H;
(ii) reaction N_2(A) + H(^{1}S) -> N_2(X,v*) + H(^{1}S), responsible for the steep increase of [N];
(iii) the neutral-transport model and parameters, controlling the smooth decrease of [N] with H_2 concentration.

Simulations of "**Ammonia density**" at different H_2 concentrations show good qualitative agreement with experimental measurements [5,6], although the absolute values are underestimated by a factor of ~4-10x. Simulations reproduce the maximum NH_3 density at ~70% H_2. At high flow rates, the discrepancy is reduced when accounting for the short residence time t in the discharge and the uncertainty in the gas temperature, as illustrated in the "**Residence time/gas temperature effect**" figure. Here, the shaded bands represent calculated [NH_3] for t = 5 ms - 30 ms and T_g – 50 K.

NH_3 production is dominated by LH, NH_4^+ wall recombination, and ER processes, whereas its **destruction** is primarily due to electron-impact reactions and collisions with N_2(A) and N_2H^+, as illustrated in the "**Gain/Loss mechanisms**" figure.
The microkinetic mesoscopic surface model captures ammonia production via plasma-surface interactions, showing that the physisorption of N, H atoms on vacant physisorption sites F(v) enables key reaction pathways that strongly depend on the surface state.

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