Plasma-surface coupled modelling of N_2-H_2 DC discharges for ammonia production

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

[1] *Instituto de Plasmas e Fusão Nuclear, Instituto Superior Técnico, Universidade de Lisboa, Lisboa, PORTUGAL*
[2] *LPP, École Polytechnique, Sorbonne Université, Institut Polytechnique de Paris, CNRS, FRANCE*
[3] *Centro de Física das Universidades do Minho e do Porto, Braga, PORTUGAL*
[4] *Faculdade de Engenharia, Universidade do Porto, Porto, PORTUGAL*

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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.

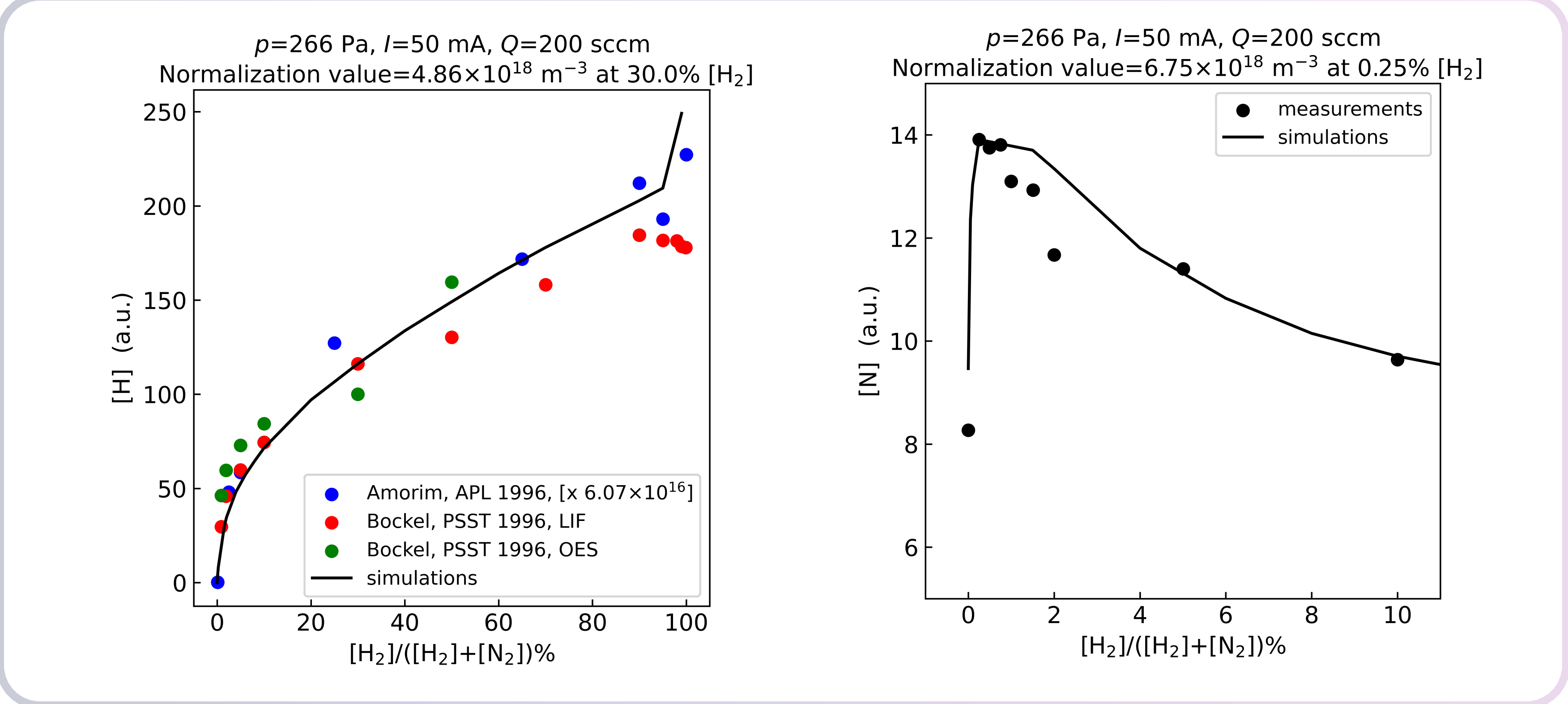
We present follow-ups of our research program on nitrogen-hydrogen plasmas, based on a **very complete kinetic scheme** for this system, which was **revised and validated** using complementary modelling and diagnostics analyses.

Experiments

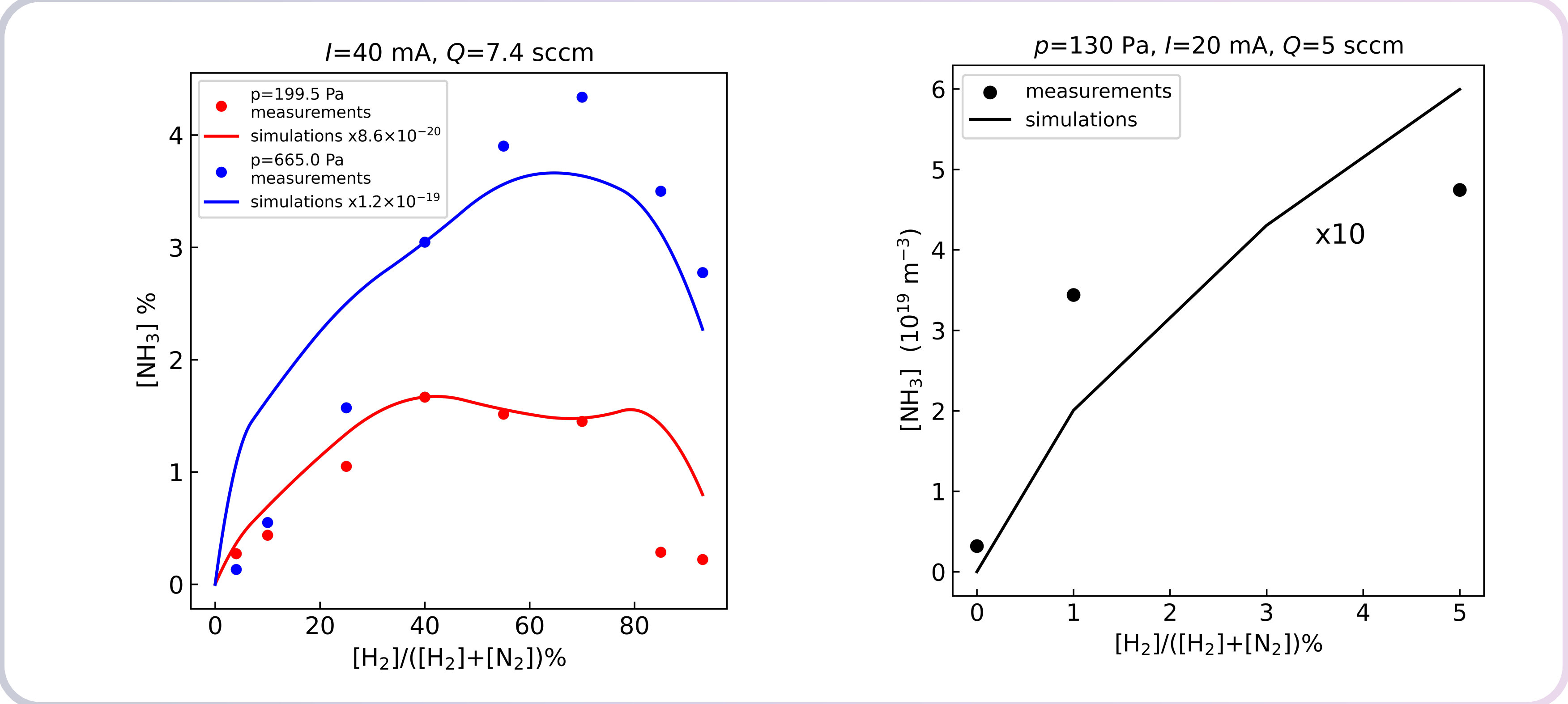
We model **cylindrical DC glow discharges** (L≈20-50 cm long and R≈1 cm radius), produced in N_2-H_2 gas mixtures at various H_2 concentrations (0-100%), gas flows (Q = 0-600 sccm), pressures (p = 30-600 Pa) and discharge currents (I_{dc} = 5-100 mA).

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 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.

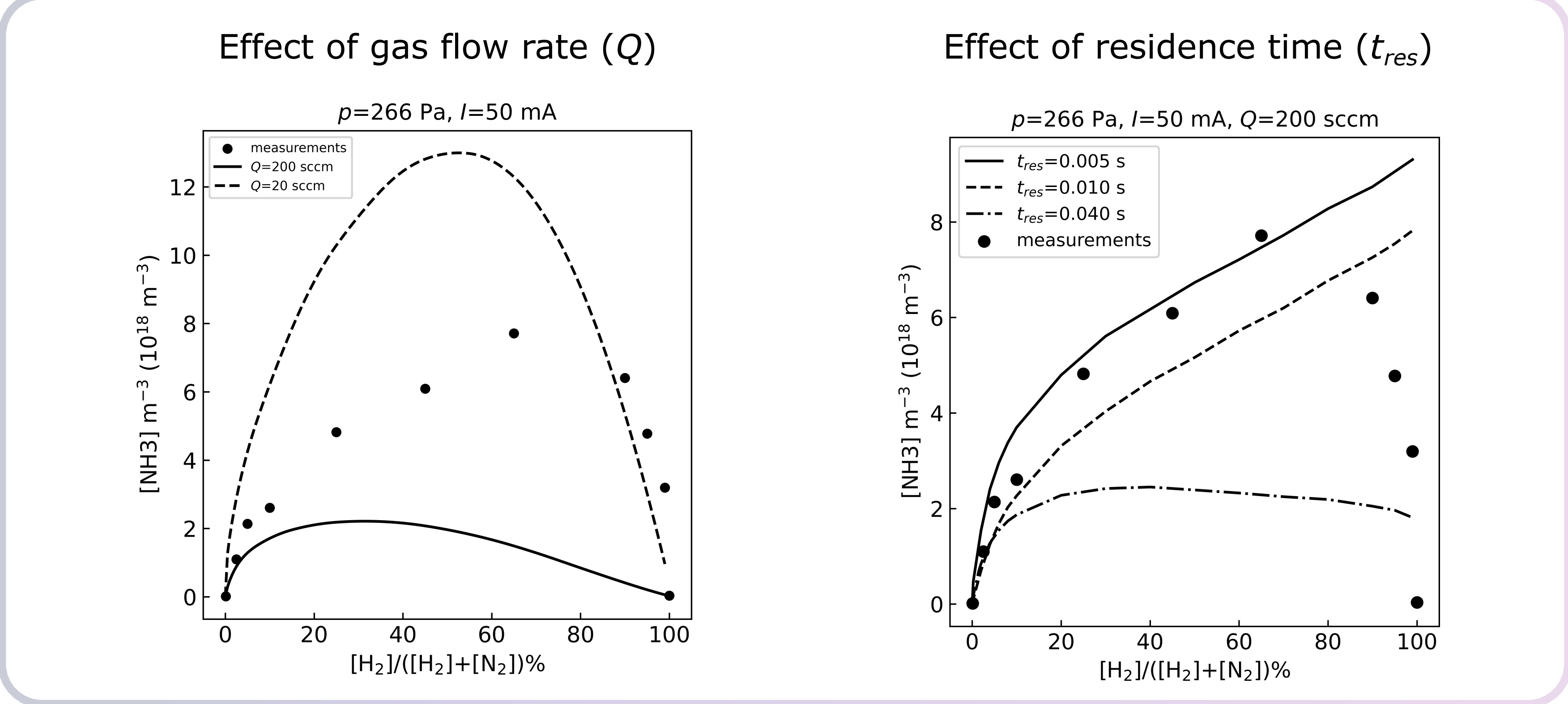
Neutral atoms densities



Ammonia density



Effect of gas flow rate/residence time on ammonia density



Simulations

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

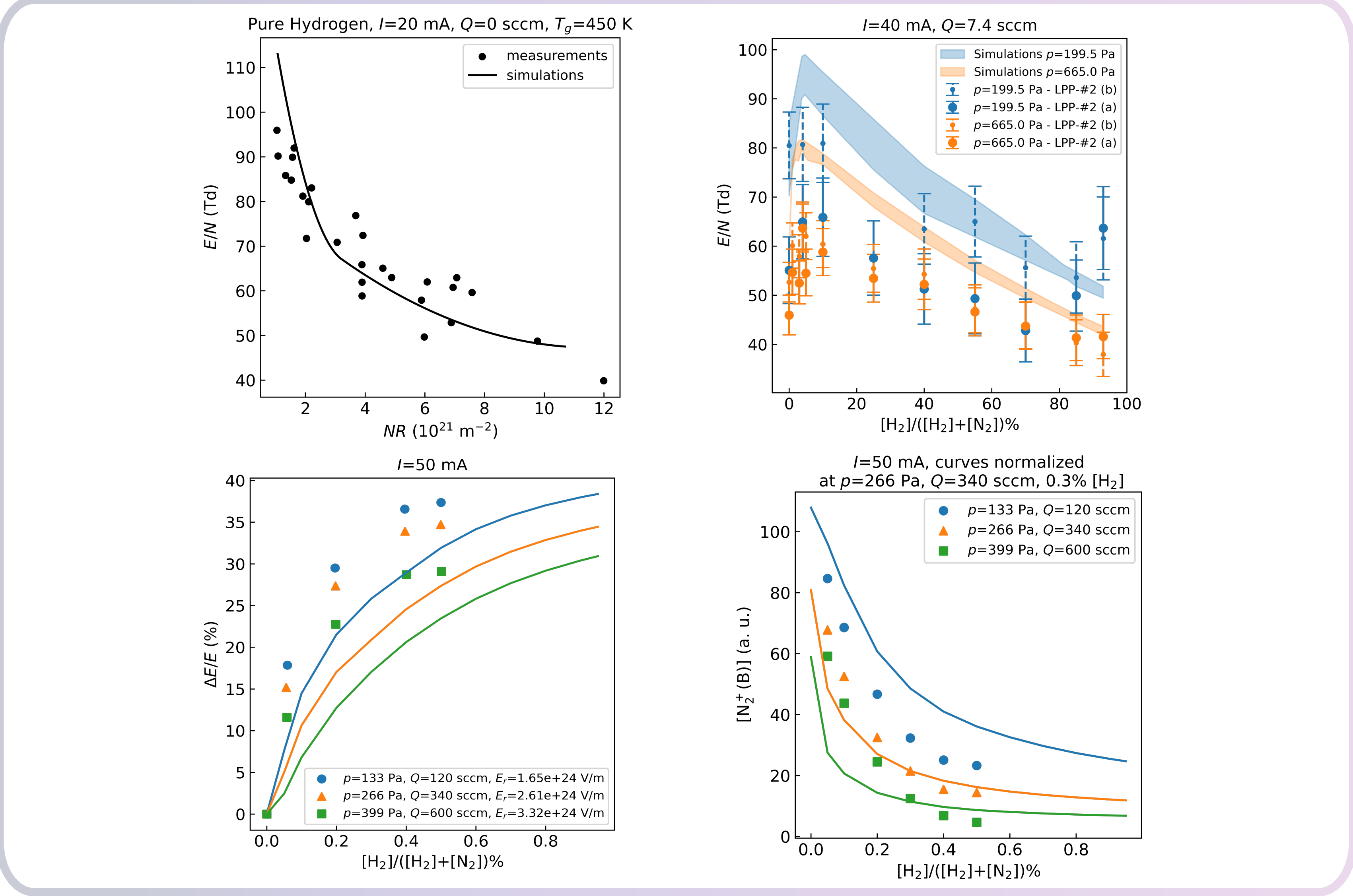
- **LoKI-B** that solves a space-independent form of the two-term **electron Boltzmann equation** (EBE) for non-magnetised non-equilibrium low-temperature plasmas excited by DC/HF, or time-dependent (non-oscillatory), electric fields, using electron-scattering cross sections that can be downloaded from 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 $N_2(X, v=0\text{-}44)$, $H_2(X, v=0\text{-}14)$, 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.*** [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} m^{-2}.

Plasma characteristics



Results and discussion

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

The **"Plasma characteristics"** panel shows results of ***E/N* and *ΔE/E*** as a function of either NR or the concentration of H_2, at different pressures [4,6]. For comparison, we also show results of the **$N_2^+(B)$ density** for various H_2 concentrations [6]. Model predictions tend to overestimate the values of E/N for pure N_2 (used to calculate the reference electric field E_r in the lower-left figure), while showing good agreement for pure H_2. 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 N_2(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 H_2 concentration [4,5]. In this case, simulations show good qualitative agreement with the experiment.

Simulations of **"Ammonia density"** at various H_2 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 **$[NH_3]$ 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 NH_3** (~40%), rivaling losses from electrons, N_2(A) and N_2H^+ collisions (~20% each). The mesoscopic surface kinetic model effetively 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 NH_4^+ .

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