Simulation of Titan's atmosphere using N_2-CH_4 afterglow plasma : formation of HCN and NH_3

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INTRODUCTION

Molecular nitrogen and methane are the main precursors of Titan's atmospheric chemistry driven by high energy electrons from Saturn's magnetosphere and solar UV photons.

A great number of laboratory experiments have been carried out to mimic Titan's atmospheric chemistry. But, up to now, N_2/CH_4 mixtures have been submitted to a unique type of energy source: UV light, high energy particles or electric discharges.

We are developing a new program of simulations [1] aiming to **improve the representativeness towards Titan's condition in term of energy deposition** which consists in submitting a N_2/CH_4 mixture in a flow reactor to both electrons (microwave plasma discharge) and photons (Lyman-alpha delivered by a continuous H_2/He lamp).

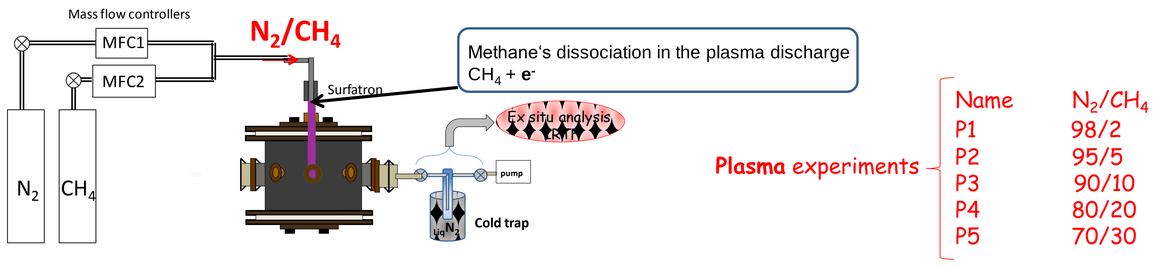
In a first step, N_2/CH_4 chemistry has been initiated using microwave **plasma** discharges or **afterglow plasma** discharges.

A detailed kinetic model has been developed to **simulate the results obtained for the post-discharge experiments**. Theoretical predictions are then compared to experimental measurements.

EXPERIMENTAL

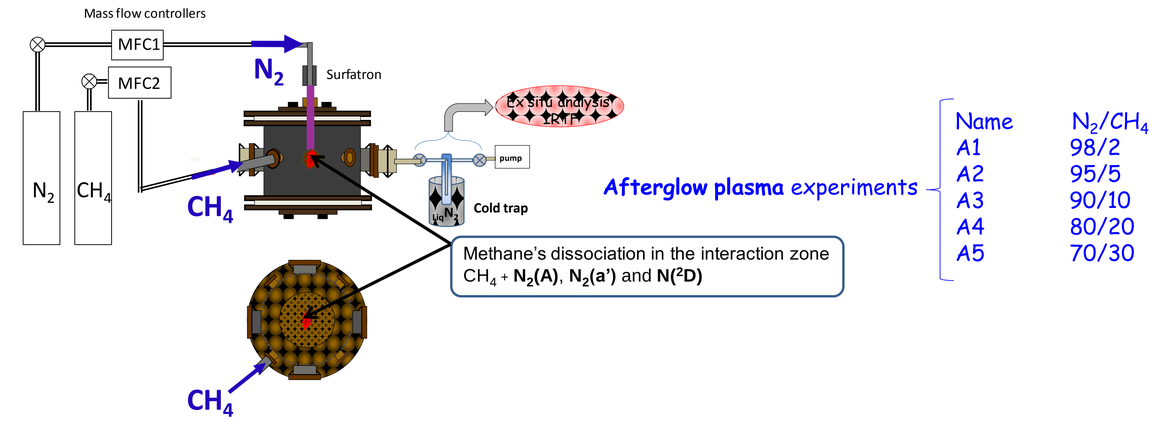
Titan's experimental simulations have been undertaken using N_2/CH_4 **plasma** (figure 1a) as well as N_2/CH_4 **afterglow plasma** (figure 1b) with different mixing ratio of N_2 and CH_4.
Ex-situ qualitative and quantitative analysis of the resulting gas mixture recovered in a cold trap has been performed, for the first time, by IRTF spectroscopy.

1a)



Plasma experiments	Name	N_2/CH_4
	P1	98/2
	P2	95/5
	P3	90/10
	P4	80/20
	P5	70/30

1b)



Afterglow plasma experiments	Name	N_2/CH_4
	A1	98/2
	A2	95/5
	A3	90/10
	A4	80/20
	A5	70/30

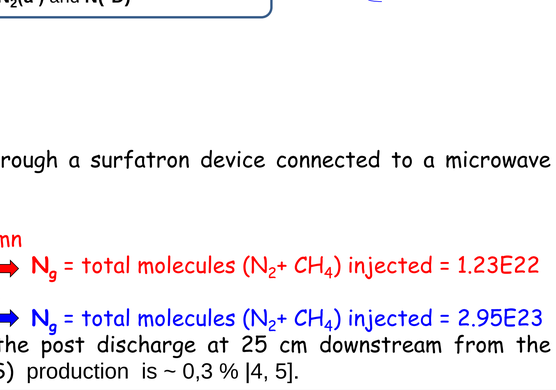
Microwave plasma discharge generated in a quartz tube through a surfatron device connected to a microwave generator at 2.45 GHz with an output of **100W**.
Total pressure in the simulation chamber = **4.8 mb**
Total flow rate = **50 sccm** duration of PX experiments = 10 mn
➡ N_g = total molecules (N_2+ CH_4) injected = 1.23E22
duration of AX experiments = 4 h
➡ N_g = total molecules (N_2+ CH_4) injected = 2.95E23
In the afterglow plasma experiments, CH_4 is injected in the post discharge at 25 cm downstream from the nitrogen plasma discharge. At this point, the efficiency of $N(^4S)$ production is ~ 0,3 % |4, 5].

KINETIC MODEL

A self-consistent kinetic model for the afterglow of a flowing microwave discharge in pure N_2, in which various percentages of CH_4 are introduced has been developed by Pintassilgo and co-workers [2,3,4]. This model has two separate modules, one for the discharge and another for the post-discharge, the stationary solutions obtained in the first module being the initial conditions for the second one.

The first module considers the various atomic and molecular species produced in the discharge, i.e. ions, neutral species such as ground state $N(^4S)$ and metastables $N(^2D)$, $N(^2P)$ or $N_2(A^3\Sigma_u^+)$ and $N_2(a'^1\Sigma_u^-)$. The latter may be either carried out to the post discharge or created in the post-discharge. Their concentrations and time evolutions are studied thanks to the second module of the model by considering a system of coupled time-varying kinetic master equations in which the electron impact processes can be neglected since they play a very minor role.

In the post-discharge, the nitrogen metastables mentioned above are able to dissociate methane producing CH_3, CH_2, CH radicals.
These species along with H and H_2 further react with atomic nitrogen $N(^4S)$ to produce more complex species, to produce more complex species starting with HCN.
Additionally, the model takes into account reactions leading to NH_3 via NH_2 radical.



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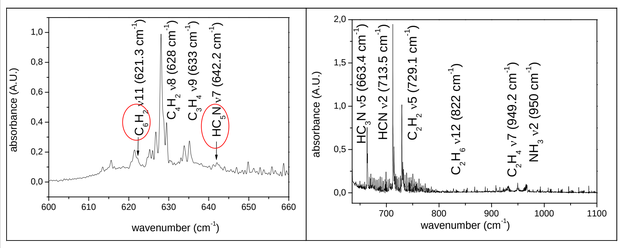
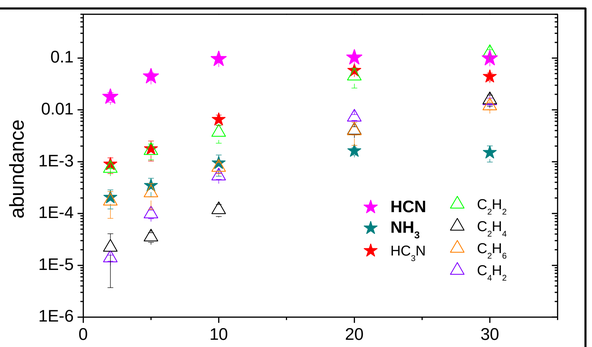
RESULTS

Plasma experiments



Samples of the FTIR spectrum obtained for P5 (N_2/CH_4: 70/30) experiment

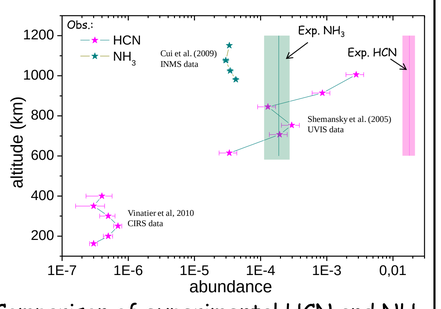


Abundances of various CH_4 mixing ratio [P1-P5]

Determination of N_x (number of molecules X formed) → Abundance of X = $\frac{N_x}{N_g}$

The experimental results are consistent with those obtained for previous plasma simulations (Coll et al, 1995) and are in relative good agreement with the observational data in the upper atmosphere of Titan (900 to 1200 km) but…

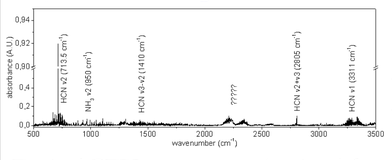
Plasma experiments	Titan's upper atmosphere (>500km)
high energetic electrons	high energetic electrons + photons
T gas ~ 1000K [5]	T lower than 180 K



Comparison of experimental HCN and NH_3 abundances with Titan observations

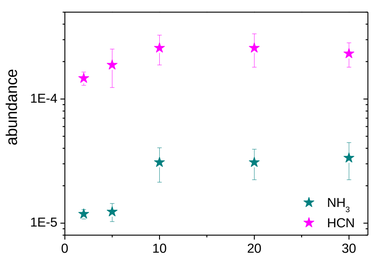
➡ **Such microwave plasma** experiments can not be considered as representative simulations of Titan's atmosphere.

Afterglow plasma experiments (representativeness towards Titan's temperature improved as T gas ~ 300K)



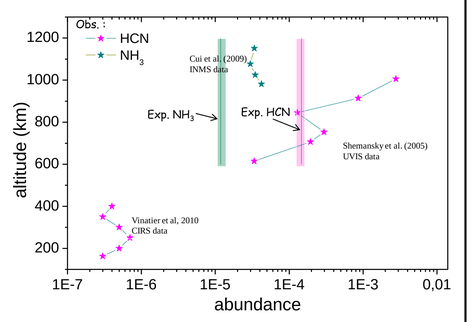
Typical FTIR spectrum obtained for A5 (N_2/CH_4: 70/30) experiment

Abundance of X = $\frac{N_X}{Ng}$



Abundances of HCN and NH_3 obtained for experiments [A1-A5]

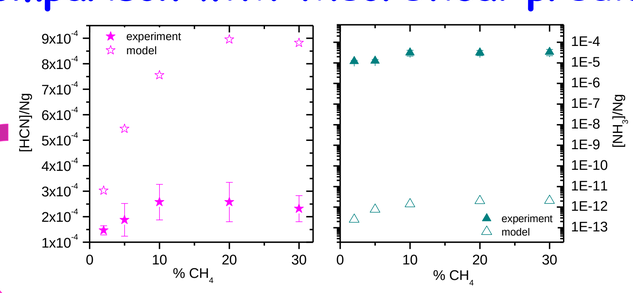
	P1	P5
NH_3	2.04E-4 ± 8.1E-5	1.50E-3 ± 5.1E-4
HCN	1.70E-2 ± 3E-3	9.80E-2 ± 9.2E-3



Comparison of experimental HCN and NH_3 abundances with Titan observations
Agreement exp/obs data improved

➡ Unlike plasma experiments, only two main species are observed here: HCN and NH_3

Comparison with theoretical predictions



In the model, NH_3 is underestimated by more than 6 order of magnitude for all experiments

HCN is overestimated by a factor of 2 and 5 respectivelly for A1 (N_2/CH_4: 70/30) and A5 (N_2/CH_4: 70/30) experiment

Conclusion

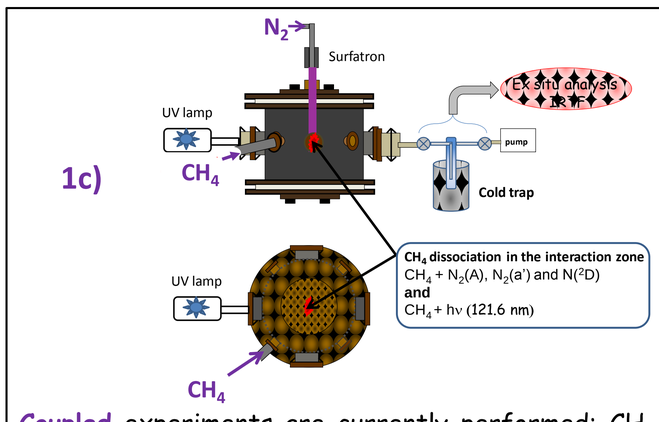
In the chemical scheme used to describe the evolution of the post discharge, the most efficient reactions lead to the formation of HCN as well as N_2 regeneration.

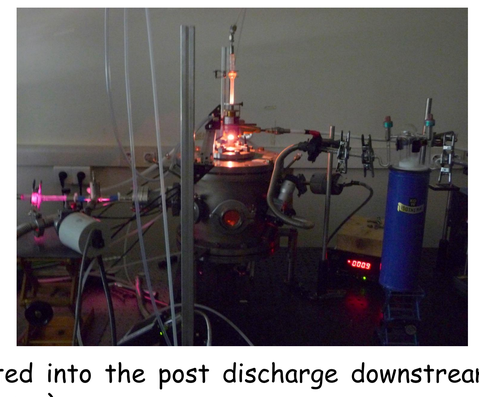
The reactions involved in the formation of NH_3 (in red in the scheme) are too slow in the gas phase to reproduce the experimental abundance of this compound.

Therefore, surface processes must be taken into account in the model in order to reproduce the production of NH_3.

WORK IN PROGRESS

1c)





Coupled experiments are currently performed: CH_4 injected into the post discharge downstream from the N_2 discharge is submitted to UV photons (H_2/He lamp).