

# Modeling of Atmospheric Photochemistry SImulated by Synchrotron setup

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## Abstract

A preliminary modeling of a new photoreactor for experimental simulation of Titan's photochemistry is developed. This study confronts experimental results with those of a 1D neutral photochemical model and its improved versions: the ones with ion-molecule reaction included and with ion-molecule reaction and dissociative recombination included. Finally, a 2D ion-neutral model is taken into account and gives a result in qualitative agreement with the experimental observations.

## 1. Introduction

Recently, a reactor, named APSIS (Atmospheric Photochemistry SImulated by Synchrotron), experimentally simulating Titan's atmospheric photochemistry, has been installed in SOLEIL Synchrotron Radiation Facility [1]. In this photoreactor, a gas mixture of  $\text{N}_2/\text{CH}_4=90/10$  is irradiated with the DISCO EUV-VUV beamline, initiating complex radical and ionic chemistry and then resulting in the formation of heavier organic species, detected by *in situ* mass spectrometry.

The spectrum of the DISCO beamline is much more uniform than the solar spectrum and has no peak at Ly- $\alpha$  (Fig. 1), at which cross-section and branching ratio of methane photolysis have been intensively studied. We have very little knowledge of methane photolysis branching ratios at other wavelengths, which play a dominant role in APSIS, leading to the invalidation of a common hypothesis in Titan's photochemical models that methane photolysis out of Ly- $\alpha$  produces only  $\text{CH}_3$  [3]. Nevertheless, an interpolation/extrapolation model of the accurate experimental results of methane photolysis branching ratios at 118.2 nm and Ly- $\alpha$  obtained by Gans *et al.* [2] has been established to estimate these branching ratios at different wavelengths [3]. Based on the wavelength-dependent branching ra-

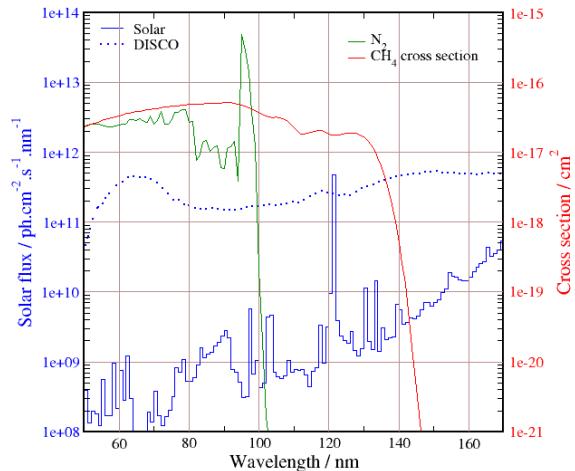


Figure 1: Solar spectrum and that of the DISCO synchrotron beamline and photoabsorption cross-section of  $\text{N}_2$  and  $\text{CH}_4$ .

tios, we perform the modeling for APSIS photoreactor to understand the formation mechanism of various organic species in it.

## 2. Model

We started with an 1D transport-reaction neutral photochemical model in which neutral species' production by photolysis, radical reactions, axial diffusion and advection corresponding to the gas flow in the experiments are included (Run 1 in Tab. 1). Supposing the radial uniformity, we applied a reduced flux to mimic a case in which the photons, concentrated in a cross-section of  $\simeq 1 \text{ cm}^2$  in experiments, are uniformly distributed in the whole photoreactor's cross-section ( $96 \text{ cm}^2$ ). This resulted in no noticeable consumption of  $\text{CH}_4$ . Then, ionic processes, *i.e.* ions' production by photolysis, ion-molecule reactions (Run 2), discharge by collisions with the reactor's internal surface and dissociative recombination (Run 3) were

Table 1: Processes in consideration other than the reference 1D model (Run 1) and percentage of consumed  $\text{CH}_4$  in different modeling runs. The percentages of consumed  $\text{CH}_4$  in experiments are also shown for comparison.

Run	Process(es) added	$\text{CH}_4$ consumed (%)
1	reference	<1
2	ion-molecule reaction	$\simeq 100$
3	ion-molecule reaction, ion-surface collision, dissociative recombination	$\simeq 100$
4	ion-molecule reaction, ion-surface collision, dissociative recombination, radial diffusion	$\simeq 30$
Exp.		4-7

successively introduced through a pseudo-ion strategy encompassing all ionic processes consuming  $\text{CH}_4$ . In spite of its overestimation of the  $\text{CH}_4$  consumption, this strategy facilitates our preliminary study. Finally, we designed a 2D model by explicitly considering the non-irradiated space and matter transport between this space and the irradiated column (Run 4).

### 3. Results and discussions

We compared the primary quantities measured in the experiments, percentages of consumed  $\text{CH}_4$  (4% - 7%), to the calculated ones after at least 500 s of irradiation when the system is close enough to the stationary state for a preliminary study (Tab. 1).

The percentage of consumed  $\text{CH}_4$  obtained in the reference 1D neutral model with reduced radiation flux is negligible, indicating that the ion-molecule reactions not radical reactions should play a dominant role in  $\text{CH}_4$  consumption. If ionic processes are introduced, however, a radially uniform 1D model is not suitable to describe the reactor, because nearly all of  $\text{CH}_4$  is consumed by ion-molecule reactions (Run 2) even though discharge by ion-surface collisions and dissociative recombination are included in the model (Run 3). To obtain a qualitatively satisfactory result, we need to take into account radial diffusion in the reactor (Run 4). In this case, the ions are confined to a narrow column (and reactive species are formed only near the head of the reactor in any case) (Fig. 2), which makes dissociative recombination more kinetically favorable and decreases thus the total number of ions and the consumption of  $\text{CH}_4$  by ions.

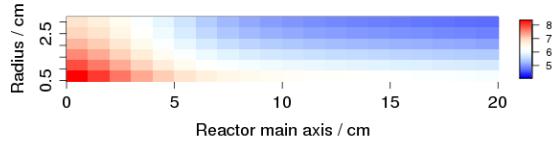


Figure 2: 2D concentration distribution of the pseudo-ion in Run 4. The color bar corresponds to the logarithm of the concentration (in  $\text{molecules.cm}^{-3}$ ).

### 4. Conclusion and perspectives

In this study, a new photoreactor (APSiS), which mimics photochemistry in Titan's atmosphere, is modeled with the support of a new description of methane full-spectrum photolysis [3]. This modeling study is achieved by steps to identify the influence of different processes on the model output. In APSiS, there is a very heterogeneous structure controlled by radial diffusion: the non-irradiated space essentially plays a role of gas container while nearly all reactions of interest take place in the irradiated column, where the relatively intense radiation leads to a very high ionic/electronic density, hence a crucial contribution of ion-molecule reactions to gas reactants' consumption and a significant contribution of dissociative recombination to ions' consumption.

Note that this study is still preliminary. The calculated percentages of consumed  $\text{N}_2$  and  $\text{CH}_4$  are not yet in quantitative agreement with the observations. We will take into account more reactions as well as uncertainties on the photolysis and rate constants and quantify the effect of different processes, so as to explain the product formation and consequently experimental results, for example *in situ* mass spectra.

### References

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