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# APSIS: a Titan's atmosphere simulation experiment using a continuous-spectrum UV synchrotron beamline

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## Abstract

A new reactor has been designed for experimental simulation of Titan's atmospheric photochemistry and installed at SOLEIL Synchrotron Radiation Facility whose DISCO continuous-spectrum UV beamline is used as the energy source. The products of the photochemistry are detected *in situ* by mass spectrometry and *ex situ* by the GC-MS analysis of a cryogenic trap experiment. The formation of $C_2H_2$, HCN, $C_2H_4$, $C_2H_6$, $CH_3CN$ and $C_2N_2$ is observed and confronted with results of other Titan's photochemical simulation experiments.

## 1. Introduction

Titan, the biggest moon of Saturn, is of great astrobiological interest, particularly due to its upper atmosphere (ionosphere), mainly composed of nitrogen ($\simeq$98%) and methane ($\simeq$2%), where a complex chemistry is initiated by the solar EUV-VUV irradiation. This leads to the formation of a lot of organic species, including N-bearing ones. However, despite the observations by the Cassini Orbiter [1], the formation mechanism of these species is still poorly understood. This motivates a variety of studies, such as photochemical modeling [2], kinetics of specific reactions of interest for Titan, and experimental simulations [3, 4]. The last kind of studies is usually realized in a gas-phase reactor with an energy source initiating the global chemistry, such as RF plasma in the PAMPRE reactor, where energy is deposited through electrons [3], or monochromatic synchrotron radiation in the study of Imanaka and Smith [4]. However, electronic impact is never equivalent to photolysis in terms of cross-section and branching ratios and monochromaticity contradicts the continuous solar spectrum. In this study, we present a new reactor APSIS - Atmospheric Photochemistry SImulated by Synchrotron - installed on the DISCO beamline in SOLEIL Synchrotron Radiation Facility, using its full-spectrum EUV-VUV photons (60 - 350 nm). The results of different experiments simulating Titan's atmospheric photochemistry is also compared.

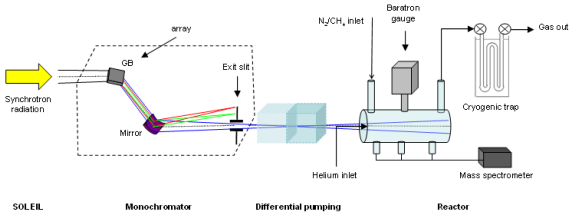


Figure 1: Schematic diagram of APSIS experiment.

## 2. Experimental

The DISCO beamline provides a radiation flux not significantly dependent on the wavelength. A gas mixture of $N_2$ / $CH_4$ = 90 / 10 is flowed into the stainless steel reactor. In order to avoid pumping the mixture toward the beamline, we add helium as a carrier gas (transparent in the wavelength range of DISCO beamline) from the beamline into the reactor (Fig. 1). The experiments are conducted under the total internal pressure of 4 - 7 mbar, including a reactants' partial pressure of $\simeq$1 mbar, but always at room temperature. The products are analyzed in two ways: *in situ* detected by a quadrupole mass spectrometer and condensed in a cryogenic trap between the exit of the reactor and the pump and then *ex situ* analyzed by GC-MS (Fig. 1).

## 3. Results and discussions

It appears in the mass spectrum of the APSIS experiment's stationary state that the product formation seems less efficient than in Imanaka and Smith's reactor. Only the ion signals at m/z of 25, 26, 27, 38, 39, 40, 41 and 52 increase (Fig. 2), whereas Imanaka and Smith observed a nearly continuous mass spectrum in the 35 - 100 m/z range [4]. The obvious difference could be roughly explained by the energy/matter ratio. In Imanaka and Smith's experiment, the radiation intensity is about 100 times greater than in APSIS, and the reactant mixture is much more rarefied (pressure of several hundredth mbar). Consequently, larger amount of highly reactive species (radicals and ions) are produced per unit of matter, hence larger amount of heavier species are likely to form.

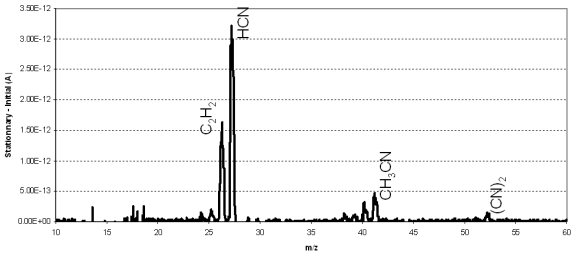


Figure 2: Intensity increase (product formation) of the final mass spectrum in comparison to the initial one.

On the other hand, too many products may scramble the MS analysis. Typically, in the mass spectra of [4], the authors could not identify the products' chemical formula but only their carbon atom number. Furthermore, the peaks corresponding to the N-bearing products are completely hidden in the packets. This is avoided in the APSIS experiment, where the product formation is less efficient: only the most efficiently formed products are highlighted. The attribution of the peaks in the differential mass spectrum can be easily and clearly done: the peaks at m/z of 25 and 26 to $C_2H_2$, 27 to HCN, 38, 39, 40 and 41 to $CH_3CN$ and 52 to $(CN)_2$. Moreover, the *ex situ* GC-MS analysis confirms the formation of $C_2$ species and N-bearing species (Fig. 3), giving prominence to the nitrile chemistry in Titan's upper atomsphere, in agreement with [3]. The chromatogram also shows peaks corresponding to $C_3$ hydrocarbons, but this possible production has to be further confirmed.

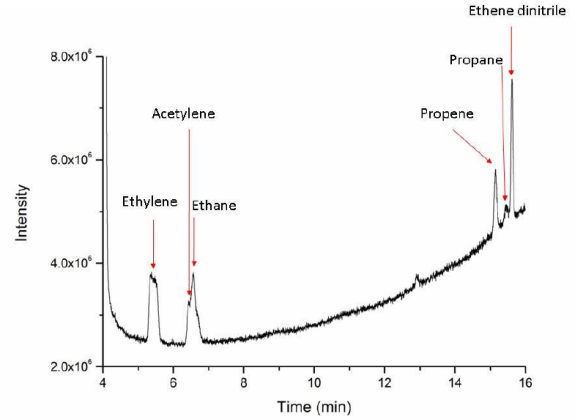


Figure 3: Chromatogram obtained by direct GC-MS analysis of a cryogenic trap experiment. Separation was performed on a QPlot column (30m x 0.25mm x 0.10 $\mu$m) in splitless mode with an helium flow of 1.0 mL/min.

## 4. Conclusion

A Titan's atmospheric photochemistry simulation experiment using a continuous-spectrum EUV-VUV photons is conducted for the first time to our knowledge, through a photoreactor (APSIS) under the irradiation of a synchrotron beamline. Though less efficient than in Imanaka and Smith's reactor [4], the formation of the organic species, $C_2H_2$, HCN, $C_2H_4$, $C_2H_6$, $CH_3CN$ and $(CN)_2$ in APSIS is neatly confirmed by *in situ* mass spectrometry and *ex situ* gas-phase chromatography. This validates the approach of the experiment and the importance of nitrile chemistry. Further experiments based on the APSIS setup should be pursued, *e.g.* study of the effect of different wavelength ranges of the UV source and photolysis experiment of pure methane.

## References

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