

Titan's atmosphere simulation experiment using a continuous-spectrum UV-VUV synchrotron beamline

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Abstract

We report here a new reactor, named APSIS for Atmospheric Photochemistry SIMulated by Synchrotron, where a gas mixture ($\text{N}_2/\text{CH}_4=90/10$) at various pressures in the mbar range in the reactor is irradiated using the continuous-spectrum (60-350 nm) DISCO beam in the SOLEIL Radiation Facility. The photochemical products, *in situ* detected by quadrupole mass spectrometry, include C2, C3, C4 and probably C5 compounds. We compared the neutral productions in APSIS and other experiments with the INMS measurements.

1. Introduction

Titan, the largest moon of Saturn, is of great astrobiological interest, particularly in its upper atmosphere. In this atmospheric layer, the ongoing Cassini space mission revealed a complex chemistry resulting in the formation of N-bearing aerosols.

Since the formation mechanism of these species is still poorly understood, despite the numerous observations made by the Cassini Orbiter [1], complementary laboratory studies are realized in gas-phase reactors with an energy source initiating the primary ionization and dissociation processes of $\text{N}_2\text{-CH}_4$ gas mixtures. In the PAMPRE reactor [2], energy is deposited through electron impacts, whereas a VUV monochromatic synchrotron irradiation is used in the study of Imanaka and Smith [3].

In order to understand the *in-situ* observation better and try to reconcile plasma and synchrotron experiments, we designed a new reactor, APSIS - Atmospheric Photochemistry SIMulated by Synchrotron - installed on the DISCO beamline in SOLEIL Syn-

chrotron Radiation Facility, using a full-spectrum EUV-VUV photons, and using the same environmental conditions as the PAMPRE plasma reactor [4].

2. Experimental

The stainless-steel reactor is presented in Fig. 1. A non-reactive carrier gas, Helium, is continuously injected between the beamline and the APSIS chamber to prevent CH_4 to reach the synchrotron. A gas mixture of $\text{N}_2/\text{CH}_4=90/10$ is flowed at different fluxes, irradiated by continuous-spectrum photons (60-350 nm) of the DISCO beam and *in situ* analyzed by quadrupole mass spectrometry. The experiments are conducted at room temperature.

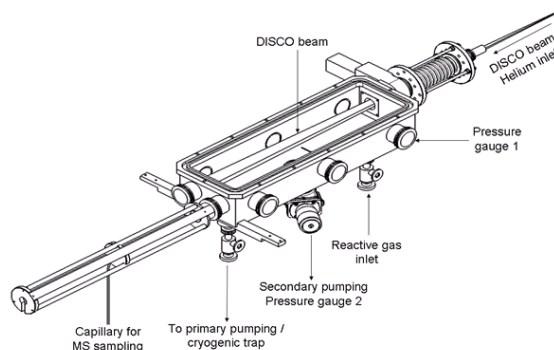


Figure 1: Schematic diagram of APSIS experiment.

In order to determine the absolute intensities of the peaks in the mass spectra, an alternative combination of least absolute deviation and least square deviation regressions for the MS is performed.

3. Results and discussions

The mass spectrometry MID analysis reveals that the system reaches its stationary state after a few hundred seconds irradiation. The analog scan spectra before and after ≈ 1 h irradiation are used for the analyses of the initial and stationary states, respectively. Spectra in difference are given on Fig. 2 for different influxes. Only the spectra for higher influxes (7 and 10 sccm) possess quantitatively significant intensities. The obvious C2, C3 and C4 band structures appear in the spectra (Fig. 2) (if the disturbance of N_2 at 28 and 29 m/z and of Ar at 40 m/z excluded) and there are also probably some productions in C5 region.

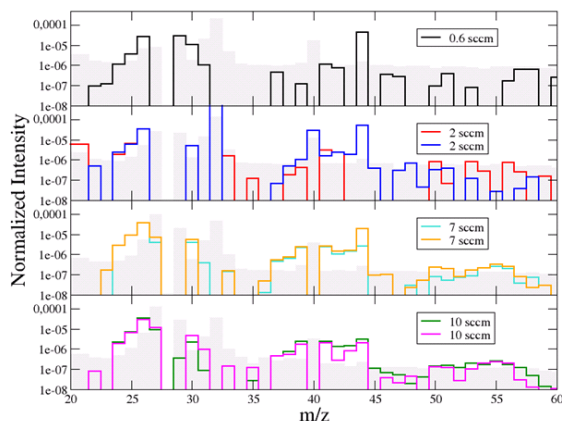


Figure 2: Difference between the MS of the initial state and the state after ≈ 1 h irradiation obtained at various gas influxes in the APSIS reactor. Grey bars represent the fit errors of all m/z units.

In Fig. 3, we compare the neutral productions in (a) the INMS measurements with (b) the PAMPRE experiment [2], (c) the synchrotron study at 60 nm [3] and (d) the APSIS experiment. A general decrease of the intensities with the size of the detected species is observed in all spectra, but with various orders of magnitude, due to different energy deposition efficiencies. The product mixing ratios in (b) and (c) are one order of magnitude higher than in Titan atmosphere and about one order of magnitude lower in (d).

More important is the distribution among the products, in particular the ratio between the intensities at $m/z=26$ and 27, corresponding on a first approach to the mixing ratios of C_2H_2 and HCN. Both (b) and (c) measure a significantly higher intensity of the peak at $m/z = 27$, and it is the opposite in the INMS and in the APSIS neutral mass spectra. Another N-bearing species, C_2N_2 , is detected in Titan and in the APSIS

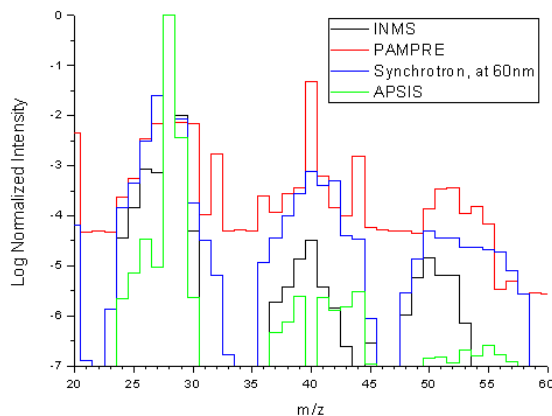


Figure 3: Mass spectra of neutral species in (a) Titan atmosphere measured by the INMS [1], (b) the PAMPRE plasma discharge study [2], (c) a synchrotron experiment at 60 nm reported in [3], and (d) the APSIS experiment at 10 sccm (the intensities at $m/z=28$ and 29, corresponding to N_2 , added artificially for convenience in comparison).

and (b), but not in (c). Therefore, in spite of systematic lower productions, it seems that the APSIS experiment is more realistic to reproduce qualitatively Titan photochemistry. This reactor provides a new complementary tool to simulate Titan atmospheric reactivity.

4. Conclusion

A new reactor, APSIS, Atmospheric Photochemistry Simulated by Synchrotron, has been designed to simulate planetary atmospheric photochemistry processes. This setup produces species with two up to five heavy atoms. The C2 hydrocarbons are the major products, but nitrogen bearing species such as HCN and C_2N_2 were also detected, in agreement with Titan observations.

References

- [1] J.H. Waite Jr., D.T. Young, T.E. Cravens, A.J. Coates, F.J. Crary, B. Magee, and J. Westlake. *Science*, 316:870-875, 2007.
- [2] N. Carrasco, T. Gautier, E. Es-sebbar, P. Pernot and G. Cernogora. *Icarus*, 219:230-240, 2012.
- [3] H. Imanaka and M.A. Smith. *Proc. Natl. Acad. Sci. USA*, 107:12423-12428, 2010.
- [4] Z. Peng *et al.* Titan's atmosphere simulation experiment using a continuous-spectrum UV-VUV synchrotron beamline, in preparation, 2012.