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# Investigating the chemical pathways to PAH- and PANH-based aerosols in Titan's atmospheric chemistry

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## Abstract

## 1. Introduction

A complex organic chemistry between Titan's two main constituents, $N_2$ and $CH_4$, leads to the production of more complex molecules and subsequently to solid organic aerosols. These aerosols are at the origin of the haze layers giving Titan its characteristic orange color.

In situ measurements by the Ion Neutral Mass Spectrometer (INMS) and Cassini Plasma Spectrometer (CAPS) instruments onboard Cassini have revealed the presence of large amounts of neutral, positively and negatively charged heavy molecules in the ionosphere of Titan [2,10]. In particular, benzene ($C_6H_6$) and toluene ($C_6H_5CH_3$) [9], which are critical precursors of polycyclic aromatic hydrocarbon (PAH) compounds, have been detected, suggesting that PAHs might play a role in the production of Titan's aerosols. Moreover, results from numerical models [5,8] as well as laboratory simulations [3,4] of Titan's atmospheric chemistry are also suggesting chemical pathways that link the simple precursor molecules resulting from the first steps of the $N_2$-$CH_4$ chemistry ($C_2H_2$, $C_2H_4$, HCN…) to benzene, and to PAHs and nitrogen-containing PAHs (or PANHs) as precursors to the production of solid aerosols.

## 2. The Titan Haze Simulation Experiment

The aim of the Titan Haze Simulation (THS) experiment is to study the chemical formation pathways, in Titan's atmosphere, from the simple gas phase molecules to the more complex gas phase precursors of aerosols; and more specifically, to investigate the role of PAHs and PANHs, among other hydrocarbons, in these chemical pathways. In the THS experiment, Titan's atmospheric chemistry is simulated by a plasma jet expansion at pressure and temperature conditions close to those of Titan's atmosphere in the regions where aerosols are formed.

Here, we present the results of ongoing studies on different aspects of Titan's chemistry using various gas mixtures: from $N_2$-$CH_4$ gas mixtures at different $CH_4$ concentrations to more targeted gas mixtures including trace elements present in Titan's atmosphere such as, for example, $N_2$-$C_2H_2$, $N_2$-$C_6H_6$ and $N_2$-$C_2H_2$-$C_6H_6$ to study specific pathways to the production of PAHs and PANHs and large organic aerosols.

## 3. Experimental setup

The THS experiment is conducted on the NASA Ames Cosmic Simulation Chamber (COSmIC), which is composed of a Pulsed Discharge Nozzle (PDN) expansion coupled to two high-sensitivity, complementary *in situ* diagnostics: a Cavity Ring Down Spectroscopy (CRDS) system and a Reflectron Time-Of-Flight Mass Spectrometer (ReTOF-MS).

The PDN-produced species are cooled in the supersonic jet expansion where the temperature (~100-150K) and pressure (~0.2 mbar) conditions are close to Titan's atmospheric conditions. The ReTOF allows the real-time detection of the different species (neutral, ions and radicals) present in the discharge, separating them according to their mass/charge ratio. The CRDS, on the other hand, allows the detection of a specific, targeted, species from its spectroscopic absorption signature. The THS experimental setup is described in detail in [6].

## 4. Results and discussion

Different gas mixtures have been used in the THS to observe the differences in chemical pathways and the formation and destruction of molecules depending on the initial species injected in the PDN. Figure 1 shows the mass spectra obtained in four gas mixtures: (a) $N_2$-$CH_4$, (b) $N_2$-$C_2H_2$, (c) $N_2$-$C_6H_6$ and (d) $N_2$-$C_2H_2$-$C_6H_6$.

In the $N_2$-$CH_4$ plasma, masses corresponding to the fragment ions of $CH_4$, i.e. $CH_3^+$, $CH_2^+$, $CH^+$ and $C^+$ were detected as well as $N_2^+$ and molecules at masses m/z=27 and 29 which can either be $C_2H_3^+$ or $HCN^+$, and $C_2H_5^+$ or $N_2H^+$, respectively. Argon was also present in this experiment and was also detected at m/z=40 ($Ar^+$) and m/z=20 ($Ar^{2+}$). No larger molecule was detected in this experiment. This is thought to be due to the high concentration of $CH_4$ in the mixture resulting in high concentrations of H and $H_2$ in the plasma, which inhibit the chemistry [1,7]. New experiments with lower concentrations of $CH_4$ in $N_2$ are underway.

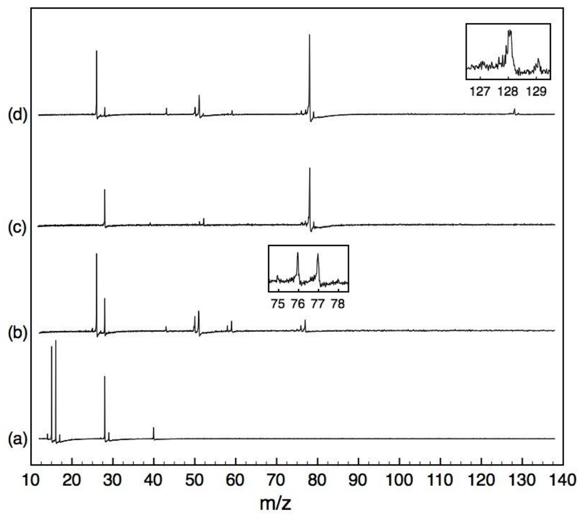


Figure 1: ReTOF mass spectra of (a) $N_2$-$CH_4$, (b) $N_2$-$C_2H_2$, (c) $N_2$-$C_6H_6$ and (d) $N_2$-$C_2H_2$-$C_6H_6$ plasmas in the THS experiment.

In the $N_2$-$C_2H_2$ plasma, new reaction pathways lead to the production of molecules of higher masses, the most abundant being at masses m/z=50 ($C_4H_2^+$ or $C_3N^+$), m/z=51 ($C_4H_3^+$ or $HC_3N^+$), m/z=59 ($C_4H_{11}^+$ or $N(CH_3)_3^+$), m/z=76 ($C_6H_4^+$) and m/z=77 ($C_6H_5^+$). The $N_2$-$C_6H_6$ plasma does not exhibit reaction pathways that produce molecules of masses higher than the benzene, $C_6H_6$, injected. However when mixing both $C_2H_2$ and $C_6H_6$ in $N_2$, new chemical reactions occur that lead to the production of molecules of mass m/z=128. CRDS measurements are being carried out to identify them.


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