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Investigating Titan's C_6H_6 stratospheric ices and HASP cloud aging under long-UV radiations

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Abstract

The stratosphere of Titan is a complex environment in which solid particles as high altitude-produced aerosols and vapor phase compounds meet, submitted to long-UV photons. Climatic variations can induce conditions to allow vapor phase organics to condense leading to the formation of icy clouds. The most recent example is the High Altitude South Polar (HASP) cloud arising from benzene (C_6H_6) and hydrogen cyanide (HCN) co-condensation [2]. We present the results of laboratory experiments conducted to reproduce the condensation of these compounds as pure and co-condensed ices and also their behavior under low energy photons. The solid-state evolutions are monitored with *in situ* infrared spectroscopy and volatiles photo-products with GC-MS. We provide laboratory evidence that icy benzene and benzene-hydrogen mixes lead to the formation Titan's aerosol analogs along with volatiles photoproducts in conditions mimicking the stratosphere of Titan.

1. Introduction

Currently, Titan, the largest moon of Saturn has been revealed by Cassini-Huygens mission as the satellite with the more complex atmospheric chemistry of all solar system bodies. In addition to the production of complex carbon/nitrogen-based molecules and high altitude-produced aerosols, several stratospheric icy clouds have been reported by CIRS instrument. At these altitudes, variations of the temperature profile and saturation vapor pressures allow some of the gaseous compounds to condense, as pure ice, and in some cases to condense simultaneously. In particular, since 2011, Titan's meridional circulation has been reversed leading to an increase of benzene (C_6H_6) and hydrogen cyanide (HCN) mixing ratios at the southern pole of Titan. It occurred simultaneously to the drastic drop of the temperature under 120K at high altitudes (>250 km). These two climatic events have allowed these two molecules to condense resulting in the detection of pure benzene ice [1] and C_6H_6:HCN mixed ices which latter is responsible for the HASP cloud [2].

2. Objectives

The aim of this study was to investigate the photochemical aging of pure benzene ices as well as C_6H_6:HCN mixed ices. Therefore, we turn to laboratory experiments to simulate the condensation of these two molecules, first isolated and then condensed simultaneously with different mixing ratio, namely 4:1; 1:1 and 1:4. Then, we monitor their solid-state behavior under high-pressure vapor mercury lamp radiations (λ>230 nm) reproducing stratospheric long-UV exposure undergoing by these particles during their formation and beyond. The experimental set-up designed in our laboratory allow us to monitor either the solid phase by *in situ* FT-IR spectroscopy and the volatiles photo-products recovered with the help of analytical technique GC-MS [3].

3. Experimental setup

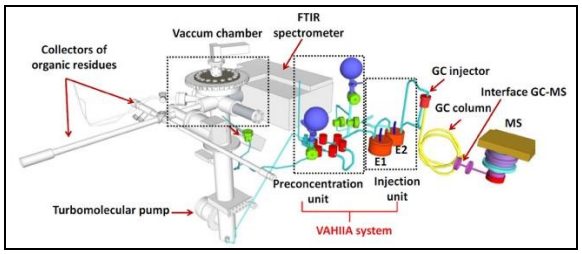

Figure 1: Schematic representation of AHIIA high vacuum chamber experiment developed in PIIM laboratory.

The gas mixture of interest is introduced in the vacuum chamber (i.e. 10^{-8} mbar) via spray nozzles and condense on a gold-platted surface cooled down to 70K, with the help of a cold head cryostat. Photolysis experiments have been performed using a high-pressure vapor mercury lamp. *In situ* spectra

(4000-500 cm^{-1}) were recorded in reflection-absorption (double-absorption) mode using a Fourier transform infrared spectrometer. The gaseous phase released during the warming-up was recovered thanks to a preconcentration loop from VAHIIA interface [3] between the vacuum chamber and the GC-MS.

4. Results

Our results demonstrate a photochemical activity of solid benzene under λ>230 nm radiations leading to the formation of both refractory material, which infrared spectrum at 300K is dominated by the contributions of CH sp^2 stretching modes, and volatiles photo-products. Benzene photochemical activity is drastically enhanced with the increasing amount of hydrogen cyanide in the mixes. The addition of this N-bearing molecule leads to the formation of nitriles/isonitriles derivatives as well as amines and cause a reversal of the sp^2/sp^3 ratio calculated from νCH deconvoluted contributions. As a consequence, the comparison of the UV-produced refractory phase for each ice with Cassini-Huygens VIMS/CIRS data highlights a better match for the one obtained from C_6H_6:HCN mixes. Moreover, GC-MS analyses performed for each experiment demonstrate a plethora of volatiles compounds produced by the photochemistry of an isolated benzene ice and poorly complexified by the addition of HCN in the initial ice.

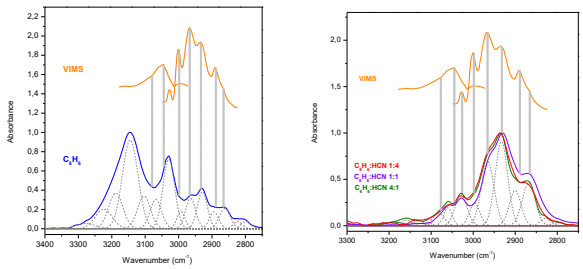

Figure 2: Comparison of pure C_6H_6/C_6H_6:HCN 1:4; 1:1; 4:1 mixing ratios) photopolymers deconvoluted infrared spectra recorded at 300K with VIMS data.

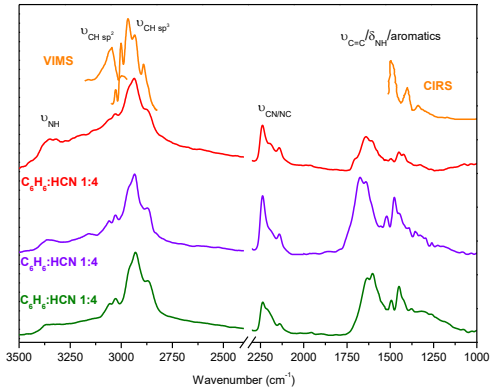

Figure 3: Comparison of C_6H_6:HCN (1:4; 1:1; 4:1 mixing ratios) photopolymers infrared spectra recorded at 300K with VIMS/CIRS data.

5. Outlooks

Aerosols present in the stratosphere are the one resulting from condensation processes at low altitude and those produced in the upper part of Titan's atmosphere. As we have studied the photochemical aging of C_6H_6:HCN ices considered as condensates, the next step is to study their behavior once they adsorbed at the surface of tholins.

Acknowledgements

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References

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