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Photochemistry of HCN Ice on Tholins Simulated in Titan's Lower Atmosphere Conditions

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Abstract

Titan's organic atmospheric chemistry is unique in the Solar System. Revealed by the Voyager and ongoing Cassini Missions, a variety of latitudinal and altitudinal-changing trace species broken down from the initial $N_2 - CH_4$ $(98 - 2\%)$ composition, are found in Titan's atmosphere in the gas phase [1] and as ices (e.g. C_4N_2, HCN) above the poles [2]. Hydrogen cyanide (HCN) is the most common nitrile trace volatile [1,2] and is known to reach condensation point at stratospheric altitudes [3]. Furthermore, high-energy irradiation in the upper atmosphere (≈1400 km) initiates gas phase reactions known to produce the thick aerosol layers [4]. These aerosols precipitate down to the surface while interacting with the gas medium and are subject to potential condensation of trace species such as HCN onto their surface [5]. The reactivity of HCN is still quite unknown and its potential for prebiotic chemistry pertains to Titan conditions [6,7,8]. Thus, we investigate whether the irradiation reaching Titan's lower atmosphere and near-surface conditions be reactive enough to induce photochemical reactions of condensed HCN ice. To do tackle question, we turn to laboratory simulations of HCN ice deposits on tholins irradiated at wavelengths relevant to low-altitude and near-surface conditions. Ice analysis is performed with *in situ* Fourier-Transform Infrared and UV-VIS spectroscopy.

1. Introduction

1.1 Gas and solid phase chemistry

Saturn's moon Titan displays a unique atmospheric chemistry that is both initiated in the upper atmosphere and further complexified in the vertical column [4]. Direct monitoring of seasonal clouds from Earth-based observations helped us infer their transient locations [9], or compositional characteristics as in the case of hydrogen cyanide HCN [10,11,12] with the rise of ground-based observation techniques such as ALMA. Atmospheric studies with the Voyager 1 mission were able to identify several organic molecules [13,14,15]. Later, the Cassini-Huygens (NASA/ESA) mission provided us with a more precise atmospheric characterization of the composition, winds and temperatures, while the Huygens lander was able to determine the composition of the aerosol particles *in situ*. Further, the presence of organic ice condensation in Titan's atmosphere has been well established since Voyager, but its formation mechanism and potential for chemical reactivity still unknown, especially in the lower altitudes.

1.2 Stratospheric condensation

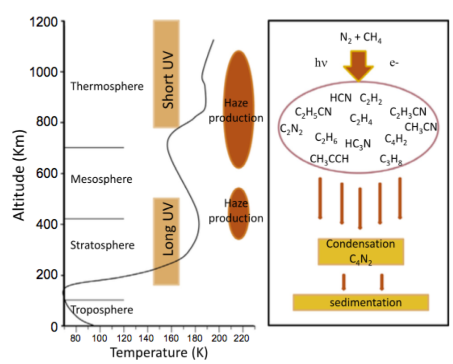

Figure 1: Titan's temperature profile against some important nitrile and hydrocarbon species detected in the atmosphere, from [17]. As also shown in [3], most species reach their condensation point in the lower stratosphere and high troposphere, which can then precipitate to the surface.

C_4N_2 and HCN ices for example were detected above Titan's northern pole, while the presence of HCN clouds [16] seems to be non trivial. [3] have developed a 1D microphysics model pertaining to the condensation of Titan's most abundant hydrocarbon and nitrile species. These ices can have relatively long timescales as they precipitate down to the surface. Hydrogen cyanide HCN is thought to start condensating at low-stratosphere and high-troposphere altitudes, where particles could coat aerosols or form condensed ice particles. [5] reported these condensation mechanisms of photo-produced tholins from C_4N_2 ice photolysis, whereby articles can either exist in an isolated state, as a molecular aggregate, or condensed onto the surface of larger aerosols.

2. Experimental modeling

We use the Titan Organic Aerosol Spectroscopy and chemisTry (TOAST) setup of JPL's Ice Spectroscopy Laboratory (ISL). Tholins were produced with the PAMPRE setup at LATMOS, using different CH_4 concentrations, to see their influence on any potential HCN ice chemical interaction. HCN is produced using stearic acid and KCN, heated and kept at low-controlled pressure. The ice deposition is done at low temperatures ($< 80K$) on $[CH_4]_0 = 1\%$, $[CH_4]_0 = 5\%$ and $[CH_4]_0 = 10\%$ samples. The tholins are then irradiated using long-UV irradiation and analyzed *in situ* with IR (covering 1 micron to 20 microns) and UV-VIS spectroscopy.

3. Summary and Conclusions

Using our laboratory simulations relevant to Titan's lower atmosphere and surface conditions, the role of HCN condensates seems to be important. HCN ice deposited on $[CH_4]_0 = 10\%$ tholins seems to go through a photo-depletion stage, while infrared spectra may hint at a possible production at 2250-2200 cm^{-1} (4.4 - 4.5 μm). UV-VIS-NIR spectroscopy displays uncharacterized production features after just a 1h irradiation ($\approx 10mW$).

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