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HCN-C_6H_6 co-condensed ice cloud in Titan's stratosphere: Laboratory study of the CIRS-observed HASP cloud

Delphine Nna-Mvondo (1, 2), Carrie M. Anderson (1), Robert E. Samuelson (1, 3)

(1) NASA GSFC, Greenbelt, MD, USA, (delphine.nnamvondo@nasa.gov) (2) University of Maryland, Baltimore County (UMBC), Baltimore, MD, USA, (3) University of Maryland, College Park, MD, USA

Abstract

For thirteen years, the Cassini mission to explore Saturn and its icy moons has provided a large repository of data on Titan's atmosphere. Ice clouds have been repeatedly observed in Titan's stratosphere by the Cassini Composite InfraRed Spectrometer (CIRS). Pure nitrile ice clouds have been identified but the chemical composition of other observed ice clouds is still undetermined. We propose co-condensation to be a formation mechanism of these other clouds. With the aim to identify the High-Altitude South Polar (HASP) ice cloud, the most recently observed cloud during the early Titan's southern winter, we have conducted laboratory thin ice film spectroscopy of a series of organic mixed ices and found that a C_6H_6-HCN co-condensed ice, enriched in benzene, is the best chemical candidate for the HASP cloud.

1. Introduction

Observations from Cassini spacecraft orbiting Saturn revealed Titan to be one of the most Earth-like worlds we have encountered. Cassini's long mission enabled us to observe weather, seasonal changes and clouds formation on Titan and shed new light on the complexity of its atmosphere. In Titan's stratosphere, ice clouds of crystalline cyanoacetylene (HC_3N, ν_6 band at 506 cm^{-1}) and dicyanoacetylene (C_4N_2, ν_8 band at 478 cm^{-1}) have been detected at high latitudes during the northern winter in CIRS far-infrared (far-IR) spectra [1]. Recently, a massive stratospheric ice cloud system, called the High-Altitude South Polar (HASP) cloud, has been discovered in Titan's late southern fall stratosphere at high southern latitudes [2] [3]. Most of Titan's organic vapors condense to form successive ice shells on Titan's aerosol particles as the vapors cool while descending throughout Titan's stratosphere. However, depending on the vapor abundances, local atmospheric temperatures and saturation vapor pressures, these gases enter altitude regions in Titan's stratosphere where they can simultaneously saturate, and co-condensed (or mixed together) to form ice clouds (Fig. 1; [3]).

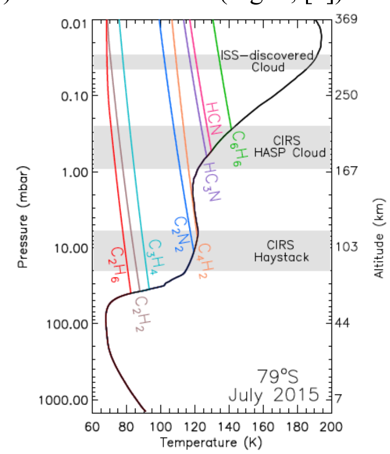

Figure 1: Titan's pressure-temperature-altitude profile (black curve) at 79◦S during late southern fall (July 2015) and vertical distributions for eight of Titan's stratospheric organic vapors (colored curves). The vapor abundances and temperature structure are determined from CIRS analyses during the July 2015 Cassini flyby. Figure from Ref. [3].

The HASP peaks near 200 cm^{-1} (Fig. 2) and not any pure condensed vapor matches its emission feature. Thus, we have investigated if a co-condensed mixed ice could contribute to the HASP emission features.

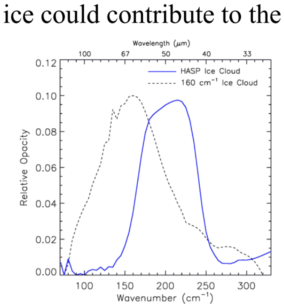

Figure 2: CIRS-derived spectral dependence of Titan's late southern fall HASP cloud (blue curve). As a comparison, the northern winter nitrile ice cloud (dashed curve) peaks at 160 cm^{-1}. Figure from Ref. [3].

2. Laboratory thin ice film spectroscopy of co-condensed ices

The experiments were performed using the SPECtroscopy of Titan-Related ice AnaLogs (SPECTRAL) high-vacuum chamber (Fig. 3) at NASA GSFC [4]. The SPECTRAL chamber is aimed to investigate on the physico-chemical and optical properties of pure, layered and co-condensed organic ices that can form in planetary atmospheres (and surfaces). We can follow how ices evolved optically and chemically with the temperature and time [5], using a Fourier Transform Infrared spectrometer coupled to the chamber, varying the temperatures from 20 K to 200 K and under high-vacuum (4×10^{-8} mbar).

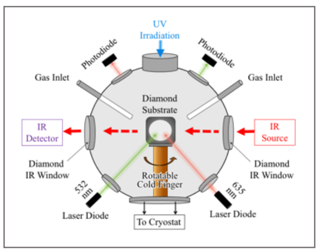

Figure 3: Schematic cross section of the high-vacuum SPECTRAL chamber. The spherical chamber is integrated inside the sample compartment of the FTIR spectrometer. Figure from Ref. [4].

For the study on Titan's HASP cloud, we have co-condensed vapor mixtures of HCN-HC_3N, C_6H_6-HC_3N and C_6H_6-HCN at 110 K and carried out quantitative thin ice film infrared transmission spectra of those ices from the far- to mid-IR spectral range (50 cm^{-1} to 8000 cm^{-1} / 200 - 1.25 µm). Double laser interferometry technique was used to determine the thickness of the ice films in order compute the complex indices of refraction, n and k. Laboratory data were then incorporated in radiative transfer modelling to match CIRS observations.

3. Results and first conclusion

Because HCN, HC_3N, C_6H_6 are gases co-condensing at the pressures, temperatures and altitude where the HASP cloud is observed (see Fig. 1), we have co-deposited vapor mixtures of HCN-HC_3N, C_6H_6-HC_3N and C_6H_6-HCN at 110 K. The resulting co-condensed ices are shown in Fig. 4.

We have found that the spectrum of co-condensed HCN-C_6H_6 ices enriched in C_6H_6 (80-85% C_6H_6) at 110 K is a good match for the HASP emission feature at 200 cm^{-1}. This result demonstrates that the chemical composition of the HASP cloud is consistent with a mixed C_6H_6-HCN ice formed via co-condensation and not from layered ices.

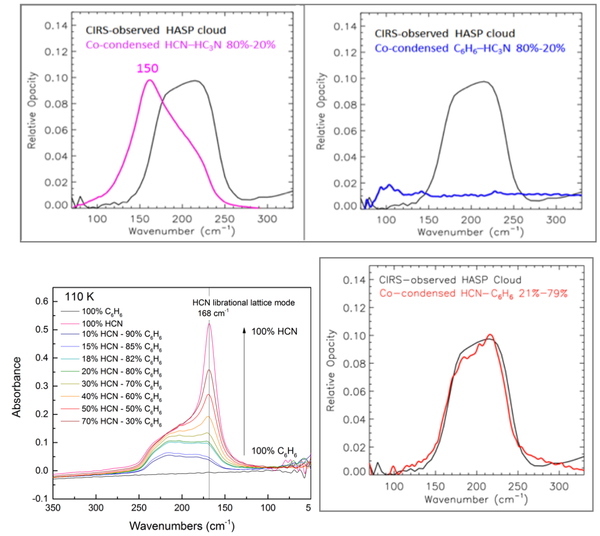

Figure 4: CIRS-derived spectral dependence of Titan's HASP cloud discovered at mid stratospheric altitudes during late southern fall at 79°S (July 2015) (Black curves) compared to co-condensed thin ice films (vapors deposited at 110 K). The left lower panel shows laboratory Far-IR spectra we have collected for several HCN-C_6H_6 co-condensed ices with different mixing ratio.

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