

# Identifying the enigmatic Haystack and HASP ice clouds observed by CIRS in Titan's stratosphere

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## Abstract

Stratospheric ice clouds have been repeatedly observed in Titan's atmosphere by the Cassini Composite InfraRed Spectrometer (CIRS) since the Cassini spacecraft entered into orbit around Saturn fourteen years ago. However, their chemical composition is still undetermined. For some of them, co-condensation could be a formation mechanism. We present the laboratory experiments we have conducted and the results we have obtained with the aim to identify particularly two perplexing observed stratospheric clouds, the Haystack and the High-Altitude South Polar (HASP) ice clouds.

## 1. Introduction

In addition to the tropospheric convective methane clouds, a second type of cloud system is observed in Titan's stratosphere. Ices clouds of crystalline cyanoacetylene ( $\text{HC}_3\text{N}$ ,  $\nu_6$  band at  $506\text{ cm}^{-1}$ ) and dicyanoacetylene ( $\text{C}_4\text{N}_2$ ,  $\nu_8$  band at  $478\text{ cm}^{-1}$ ) are detected in CIRS far-infrared (far-IR) spectra, at high latitudes during the northern winter [1] [2]. CIRS far-IR data also show that during mid to late northern winter on Titan, thin nitrile ice clouds extend globally from  $85^\circ\text{N}$  to at least  $55^\circ\text{S}$ . These ices exhibit several overlapping broad-emission features due to low-energy lattice vibrations [3] (Table 1). Recently, a massive stratospheric ice cloud system, called the High-Altitude South Polar (HASP) cloud, has been discovered in Titan's early southern winter stratosphere at high southern latitudes [4]. Most of Titan's stratospheric ice clouds form as a result of vapor condensation processes, composed of pure organic cyanides (like  $\text{HC}_3\text{N}$  and  $\text{C}_4\text{N}_2$ ) but also of mixed nitriles and hydrocarbons. The first co-condensed nitrile ice feature dominated by a mixture of HCN and  $\text{HC}_3\text{N}$  ices, has been identified in the CIRS limb spectra, peaking at  $160\text{ cm}^{-1}$  [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. During co-condensation, the ice particles mixed together and are no longer isolated into successive shells of pure ices (layered ice). The presence of other CIRS-observed stratospheric ices, such as the unidentified Haystack peaking at  $\sim 220\text{ cm}^{-1}$  and the HASP peaking near  $200\text{ cm}^{-1}$  are puzzling since not any pure condensed vapor matches their emission features. In the present work, we have investigated if co-condensed mixed ices could contribute to the Haystack and HASP emission features.

Table 1: Spectral assignment of the stratospheric ice clouds detected by CIRS.

Stratospheric ices detected by CIRS	Far-IR emission features ( $\text{cm}^{-1}$ )
$\text{HC}_3\text{N}$	$506$ ( $\nu_6$ ) crystalline
$\text{C}_4\text{N}_2$	$478$ ( $\nu_8$ ) crystalline
Nitrile composite ice	$160$ (peak)
Haystack	$220$ (peak)
HASP	$200$ (peak)

## 2. Experimental methodology

We have performed experiments using the SPECTroscopy of Titan-Related ice AnaLogs (SPECTRAL) high-vacuum chamber set up at NASA Goddard Space Flight Center. The SPECTRAL chamber (Fig. 1) has been designed specifically for measuring laboratory transmission spectra of thin ice films of pure and mixed ices, at Titan-appropriate temperatures ( $70 - 130\text{ K}$ ) from the near to far-infrared region, i.e. from  $11700\text{ cm}^{-1}$  to  $50\text{ cm}^{-1}$ . The vapors were deposited at low temperatures from  $30\text{ K}$  to  $160$

K, and the resulting ice thicknesses were determined, the ice phase were analysed by FTIR spectroscopy and their optical constants computed.

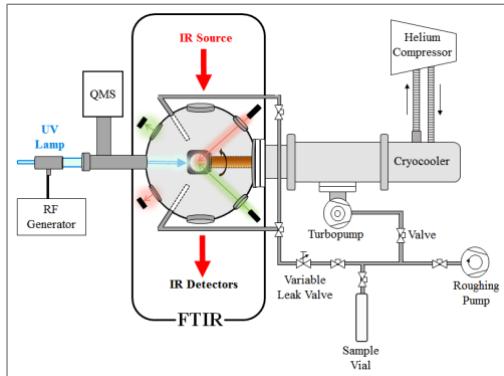
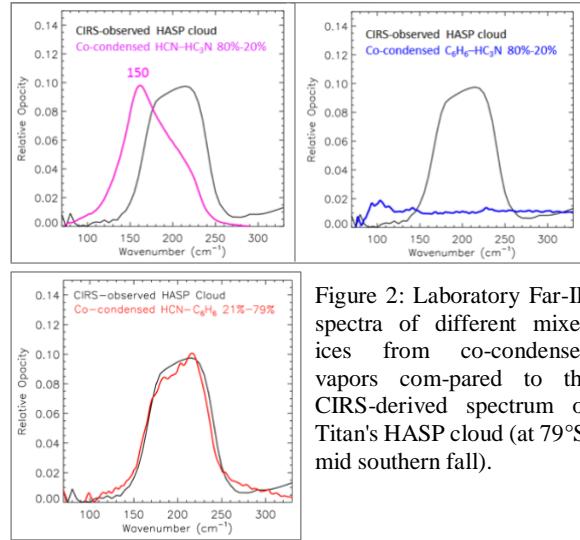


Figure 1: Schematic of the SPECTRAL high-vacuum chamber experimental setup at NASA GSFC.

### 3. Results

#### 3.1 Results: HASP study

We have co-condensed vapor mixtures of HCN-HC<sub>3</sub>N, C<sub>6</sub>H<sub>6</sub>-HC<sub>3</sub>N and C<sub>6</sub>H<sub>6</sub>-HCN at 110 K and analysed the resulting mixed ices (Fig. 2). HCN, HC<sub>3</sub>N, C<sub>6</sub>H<sub>6</sub> are gases co-condensing at the pressures, temperatures and altitude where the HASP cloud is observed.



The spectrum of co-condensed thin ice film from mixed vapors of 20% HCN- 80% C<sub>6</sub>H<sub>6</sub> deposited at 110 K is a good match for the HASP emission feature at 200 cm<sup>-1</sup>. This result demonstrates that the chemical composition of the HASP cloud is consistent with a mixed C<sub>6</sub>H<sub>6</sub>-HCN ice, formed via co-condensation.

#### 3.2 Results: Haystack study

Spectra of crystalline HCN ice and crystalline propionitrile (C<sub>2</sub>H<sub>5</sub>CN) ice obtained from pure vapors deposited at 110 K and 135 K, respectively were obtained (Fig. 3). They do not match the Haystack emission feature at 220 cm<sup>-1</sup>.

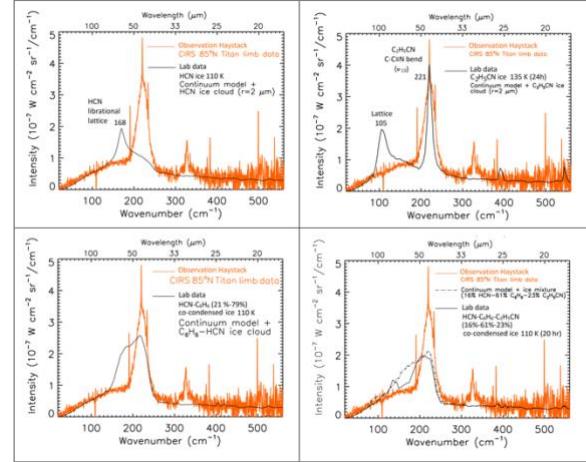


Figure 3: Laboratory Far-IR spectra of different mixed ices from co-condensed vapors compared to the CIRS-derived spectrum of Titan's Haystack cloud (at 85°N).

Comparing our laboratory spectra of different mixed ices containing HCN, C<sub>6</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>5</sub>CN to the CIRS data (Fig. 3), we do not find any good match for the Haystack emission feature yet, but further experiments with other co-condensed ices are currently in progress.

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