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Laboratory investigation of nitrile ices of Titan's stratospheric clouds

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Abstract

Titan's mid to lower stratosphere contains complex cloud systems of numerous organic ice particles comprised of both hydrocarbon and nitrile compounds. Most of these stratospheric ice clouds form as a result of vapor condensation formation processes. However, there are additional ice emission features such as dicyanoacetylene (C_4N_2) and the 220 cm^{-1} ice emission feature (the "Haystack") that are difficult to explain since there are no observed vapor emission features associated with these ices. In our laboratory, using a high-vacuum chamber coupled to a FTIR spectrometer, we are engaged in a dedicated investigation of Titan's stratospheric ices to interpret and constrain Cassini Composite InfraRed Spectrometer (CIRS) far-IR data. We will present laboratory transmittance spectra obtained for propionitrile (CH_3CH_2CN), cyanogen (C_2N_2) and hydrogen cyanide (HCN) ices, as well as various combinations of their mixtures, to better understand the cloud chemistry occurring in Titan's stratosphere.

1. Introduction

In Titan's stratosphere, at altitudes spanning 60 to ~200 km, and temperatures between about 70K and ~150K, condensed nitriles (and hydrocarbons) constitute a second type of Titan cloud system; this is in addition to the tropospheric convective methane clouds. Stratospheric ice clouds of cyanoacetylene (HC_3N) and dicyanoacetylene (C_4N_2) are observed in CIRS far-infrared spectra at high latitudes during the northern winter [1], as sharp emission features peaking at 506 cm^{-1} and 478 cm^{-1}, respectively. Spectrally broad ice emission features in Titan's stratosphere are also observed in CIRS spectra [2], peaking at 220 cm^{-1} (termed the "Haystack") and at 160 cm^{-1}, the latter feature identified as a nitrile composite ice. Whereas HC_3N vapor in the far-IR is observed at 499 cm^{-1}, and explains the formation of its condensate at 506 cm^{-1}, the presence of C_4N_2 ice and the Haystack remain puzzling since there are no associated vapor emission features to explain these ices to form from vapor condensation processes [3]. Anderson *et al.* [3] have postulated that Titan's stratospheric C_4N_2 and the Haystack ices may form through solid-state (photo)chemistry, in a similar way to the formation of nitric acid trihydrate in the terrestrial polar stratosphere. For the 160 cm^{-1} nitrile composite ice emission feature, Anderson and Samuelson [2] showed that it may arise from lattice/libration vibrations of a combination of nitrile ices, notably that of HCN and HC_3N, with possible contributions from additional trace nitrile ices. Here we present our laboratory efforts so far towards the identification of the chemical composition of Titan's Haystack and nitrile composite ices features.

2. Laboratory experiments

All experiments are conducted in the Spectroscopy for Planetary Ices Environments (SPICE) laboratory at NASA GSFC. Transmission spectroscopy is performed with the SPECtroscopy of Titan-Related ice AnaLogs (SPECTRAL) high-vacuum chamber (Fig. 1) in order to measure the near- to far-infrared spectroscopic and optical properties of thin films of pure and mixed ices of propionitrile, cyanogen and hydrogen cyanide. Transmittance spectra of thin ice films (≤10 µm thick) are acquired from 50 cm^{-1} to 11700 cm^{-1} at low dosing temperatures ranging from 30K to 160K. HCN and C_2N_2 were previously synthesized by thermal reaction of potassium cyanide with stearic acid and by thermal

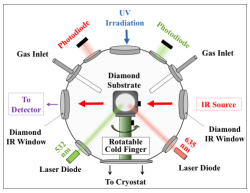


Figure 1: Schematic illustration of the SPECTRAL high-vacuum spherical sample chamber used for the experiments.

decomposition of silver cyanide, respectively. Propionitrile was provided commercially. The samples were purified by several cycles of freeze-pump-thaw under a cooling bath of ethanol and liquid nitrogen (-116˚C).

3. Results

3.1. Pure nitrile ices

For pure HCN and C_2N_2 ices, there is a clear transition in ice phase from amorphous to crystalline. This is evidenced by an increase of the band intensity of the lattice mode libration at 166 cm^{-1} for HCN and the C-C≡N asymmetric bend (ν_5) at 237 cm^{-1} for C_2N_2. Both nitriles show a peak wavenumber shift and also there is a split of the C_2N_2 absorption band (Fig. 2).

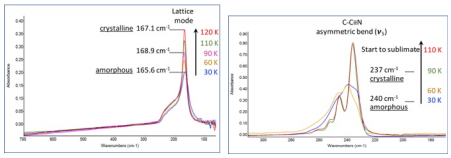


Figure 2: Far-IR spectra of pure HCN ice (2 µm film) dosed at 30K, 60K, 90K, 110K, 120K (left) and pure C_2N_2 ice (3 µm film) dosed at 30K, 60K, 90K, 110K (right).

On the other hand, for propionitrile ice, we observe peculiar temperature-driven ice phases compared to that of C_2N_2 and HCN ices (Fig. 3). The presence in the methyl molecule (-CH_3) and methylene (-CH_2) groups, which have low barriers to rotation around single bonds, produces several orientations and reordering of these groups in the solid phase ice structure. Consequently, several phase transitions are observed in the far-IR spectra at different temperatures, until the final stable crystalline phase is achieved.

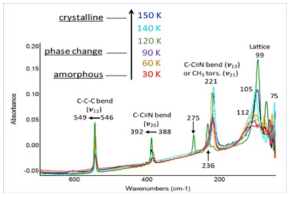


Figure 3: Far-IR spectrum of pure CH_3CH_2CN ice (3-10 µm film) dosed at 30K, 60K, 90K, 120K, 140K, 150K.

3.2. Mixed nitrile ices

For the HCN/C_2N_2 ice mixture, we observe that the HCN libration mode (168 cm^{-1} at 110K) disappears when C_2N_2 prevails in the ice mixture (Fig. 4). We note that for the HCN/CH_3CH_2CN ice mixture, this libration mode significantly broadens when CH_3CH_2CN prevails in the mixture (Fig. 4).

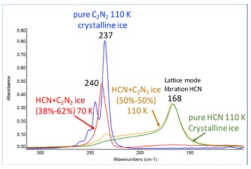
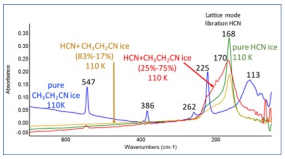


Figure 4: Far-IR spectra of HCN/C_2N_2 (top) and HCN/CH_3CH_2CN (bottom) ice mixtures compared to spectra of pure HCN, C_2N_2 and CH_3CH_2CN ices.



4. Conclusion

We have demonstrated our first attempts of many to ultimately reproduce and identify the CIRS Titan far-IR stratospheric ice observations. In our initial attempts of just a few compounds, we find that the spectral feature of the HCN libration mode (166 – 169 cm^{-1}) can be drastically altered by the surrounding molecule when mixing occurs. These nominal results indicate that the HCN/C_2N_2 ice mixture does not match the spectral shape and wavenumber peak position of the Haystack emission feature, or that of the nitrile composite ice. This is also true of the HCN/CH_3CH_2CN ice mixture even though it shows a broad absorption band at 170 cm^{-1}, which better resembles the Haystack than the previous mixture.

Acknowledgements

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