Investigations of Titan's Stratospheric Ice Cloud Chemistry using the NASA-GSFC SPECTRAL Chamber.

J. L. McLain[1,2] and C. M. Anderson[2], D. Nna-Mvondo[2,3]. [1]University of Maryland College Park (jason.l.mclain@nasa.gov), [2]NASA Goddard Space Flight Center (carrie.m.anderson@nasa.gov,), [3]Universities Space Research Association (delphine.nnamvondo@nasa.gov).

Introduction: Laboratory near-to-far IR transmission spectra of thin film ices are obtained with the SPECtroscopy of Titan-Related ice AnaLogs (SPECTRAL) high-vacuum chamber (Figure 1) at NASA Goddard Space Flight Center (GSFC). A Nicolet iS50 FTIR Spectrometer has been coupled to a spherical vacuum chamber to allow in-situ spectroscopy of the icy samples. The IR beam is transmitted through the vacuum chamber through two CVD-grown diamond vacuum windows and a diamond sample substrate. The temperature of the substrate is controlled and maintained by a closed cycle helium cryostat equipped with a resistive heater. The main goal is to interpret and identify the ice emission features of Titan's stratospheric clouds observed by the Cassini Composite InfraRed Spectrometer (CIRS), and to study and better understand the chemical processes involved in the formation of some of Titan's stratospheric clouds.

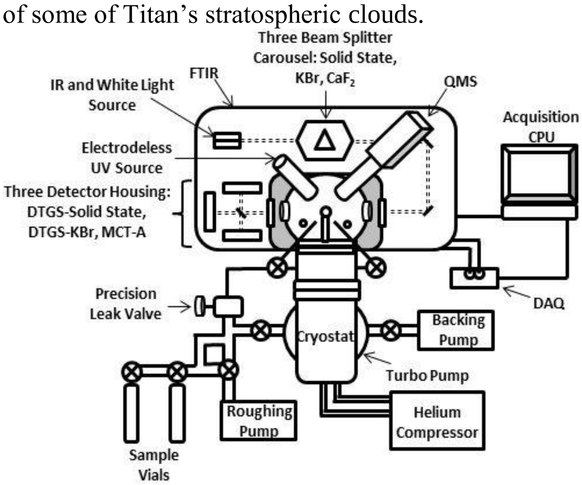

Fig. 1. The NASA SPECTRAL Chamber coupled to the Nicolet iS50 FT-IR Spectrometer.

Experiments are typically performed by varying the ice deposition parameters such as the substrate temperature ($14 \text{ K} \leq T \leq 200 \text{ K}$) and the dosing rate (with a precision leak valve). Precise control of these parameters allow the growth of very reproducible, pristine ice thin films. The structure of the ice (crystalline, amorphous, or a mixture) significantly affects its far-IR transmission spectrum from ~50-600 cm^{-1}, and specific spectral features help to discriminate if the ice is in an amorphous or crystalline phase. The diamond substrate and vacuum windows are transparent to the full range of the IR (near-to-far), which allows us to also examine the ice spectral signatures in the mid and near-IR (600-11700 cm^{-1}) during a single experiment by automatically swapping the iS50 detectors and beam splitters.

Depending on the ice film's chemical characteristics and optical properties, a set of experiments is performed with various film thicknesses in order to precisely identify the ice absorption features or libration strengths of the sample. Independent fringe measurements are performed during the ice deposition by specular scattering of two 532 nm and 635 nm diode lasers in order to compute the thickness and refractive index, n_0, of the ice film. Typically, an ice thickness of a few microns is sufficient to obtain a detailed IR spectrum. Once the film thickness and n_0 of the ice film is computed, the optical constants of the ice is determined by the Kramer-Kronig integration procedure.

Specific IR emission features for one ice can be altered significantly when the ice is mixed or diluted. For example, radiative transfer analyses of Cassini CIRS observations revealed a spectral shift and broadening of the C_4N_2 ice emission feature at 478 cm^{-1} when adopting optical constants for an HCN/C_4N_2 ice mixture. Optical constants for pure C_4N_2 ice were also evaluated but a much better fit to the CIRS spectra was found when using the diluted C_4N_2 ice mixture [1].

Chemical Synthesis: Due to their high reactivity, nitrile gases observed in Titan's atmosphere are not available for purchase from commercial sources. Therefore, we first synthesize them in the laboratory, followed by a purification process, in order to study the spectral properties of the pure ice compounds, free of any contamination. A high vacuum synthesis manifold has been designed and built to perform these syntheses. We have synthesized and purified the following nitrile gases: HCN, C_2N_2, HC_3N and C_4N_2. Pure compounds and mixed samples are kept frozen at 190 K in a vacuum tight vial, protected from the UV light and used quickly to avoid polymerization and additional reactions.

Ice Chemistry: The spherical chamber is equipped with an electrode-less Hg-UV lamp to irradiate the icy thin films and initiate chemical reactions. The reactants and reaction products are directly monitored with the FTIR, as well as with a quadrupole mass spectrometer (Pfeiffer PrismaPlus QMG 200) while heating the ices. UV irradiation experiments are underway to study the reactivity of the nitrile ices.

References:

[1] C.M. Anderson et al., (2016) GRL 3088-3094.