CHARACTERIZING PROPYNE, A RELEVANT MOLECULE TO TITAN'S ATMOSPHERE AND SURFACE. T. C. Marlin[1,2], M. L. Cable[1], T. Vu[1], M. Choukroun[1], M. Ugelow[3], H. E. Maynard-Casely[4], R. Hodyss[1], C. Anderson[3]. [1]NASA Jet Propulsion Laboratory, California Institute of Technology (4800 Oak Grove Drive, Pasadena, CA 91109); [2]Division of Geological and Planetary Sciences, California Institute of Technology (1200 E California Blvd, Pasadena, CA 91125); [3]NASA Goddard Space Flight Center (8800 Greenbelt Road, Greenbelt, MD, 20771); [4]Australian Nuclear Science and Technology Organisation (Locked Bag 2001, Kirrawee DC, NSW, 2232, Australia).

Introduction: With its large size, dense atmosphere, hydrologic cycle, and diverse surface features, the Saturnian moon Titan is one of the most unique of the outer Solar System satellites. Although the main atmospheric constituents molecular nitrogen and methane are not themselves very reactive, energetic particles from Saturn's magnetosphere and photons break apart these neutral atmosphere components. Ionized fragments then recombine to form a diverse and complex array of molecules [1,2].

Study of these photochemically produced molecules is critical in order to understand the mechanics of Titan's atmosphere, including stratospheric clouds. *Cassini*'s CIRS (Composite InfraRed Spectrometer) instrument detected six distinct ice emission features; each corresponds to a different type of cloud with unique chemical, latitudinal, and seasonal profile [3]. The clouds in Titan's stratosphere are incredibly complex- most are thought to be composed of co-condensed ice mixtures. The chemical compositions of clouds in Titan's atmosphere is related to the satellite's temperature-pressure profile and corresponding chemical abundances. Different species are more likely to be present and condense out at different locations in the atmosphere. The phenomenon of co-condensing is particularly relevant as the infrared spectrum of a mixture of co-condensed species cannot be fully accounted for by the weighted sum of the individual chemical species' spectra [4]. Thus, it seems that the co-condensation process is leading to inter-species interaction and potentially molecular structural modification, further underlining the need for experimental work on these stratospheric co-condensed clouds. Some laboratory work has been conducted thus far to compare CIRS-acquired spectra to experimentally generated "cloud" co-condensates with varying ratios of molecules based on Titan's pressure-temperature profile [e.g. 5]. However, before extensive work can be conducted, individual ice species that may be present in stratospheric clouds need to be characterized. Here, we present data on propyne (C_3H_4), which has been minimally characterized to date. Propyne, a photochemically-produced species in Titan's stratosphere, is expected to condense out at lower stratospheric altitudes and may be a trace species present in stratospheric co-condensed clouds.

A joint-effort CDAP (*Cassini* Data Analysis Project) between NASA Goddard and NASA JPL-Caltech on Titan's stratospheric ice clouds allows a variety of analogue experiments and computational approaches, including FTIR spectroscopy, Raman spectroscopy, cryogenic X-ray diffraction (XRD).

Experimental: Lab-based Raman spectroscopy permits investigation and characterization of the molecular bonds and chemical environments of these species. With the vacuum cryostage, data relevant to Titan's clouds can be gathered. Additionally, with the cryostage at atmospheric pressure, propyne that has potentially been deposited upon Titan's surface can be studied and characterized. By gathering Raman data across varying time and temperature points, an understanding of formation kinetics and stability of various Titan-relevant ices can be acquired. Finally, the collection and analysis of XRD (from laboratory and synchrotron source) has allowed elucidation of bulk structural properties, such as crystalline structure and thermal expansion.

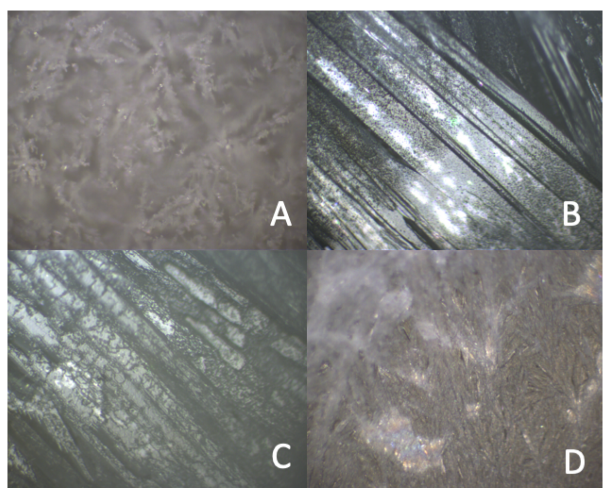

Figure 1. Solid propyne under different formation procedures. (A): 90 K; condensed from gas phase at 90 K. (B): 93 K; cooled rapidly from liquid at 173 K. (C): 93 K; cooled slowly from liquid (in ten degree increments). (D): 90 K; condensed from gas phase at 90 K, annealed at 163 K, re-cooled to 90 K.

Work conducted at JPL thus far has largely focused on characterization of propyne via Raman spectroscopy and XRD. Raman work has focused on temperatures between 163K and 77K at both atmospheric pressure and under vacuum/low pressure conditions (4 µTorr). Varying deposition methods have been explored, including deposition from gas phase at low temperature (77 K), both rapid and slow freezing from liquid, and annealing. Sequential deposition and co-condensation with methane and ethane have also been performed.

The morphology of solid propyne is not consistent across deposition methods. As can be seen in Figure 1, different deposition methods lead to starkly different apparent structures and aggregation patterns, from frostlike to prismatic.

Under ambient pressure, two solid phases of propyne have been tentatively identified, one present at high temperatures and one at lower temperatures. The region that is most highly diagnostic is from 330 cm^{-1} to 700 cm^{-1}: the C≡C-C bending mode (at approximately 340 cm^{-1}) and the C-H bending mode (at approximately 660 cm^{-1}) (Figure 2). The patterns of peaks within these regions vary widely with temperature and deposition method, and are indicative of different molecular environments for propyne.

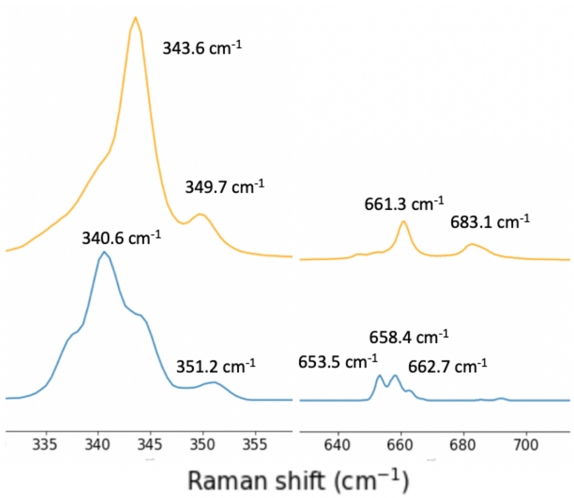

Figure 2. Diagnostic regions of proposed solid phases of propyne. High temperature (163 K)- orange, and low temperature (77 K)- blue.

The Raman data has been supplemented by collection of XRD data (Figure 3) to further characterize low temperature behavior of propyne. The data suggest that a singular phase of propyne is observed between 85 and 120 K (potentially the proposed "low temperature" phase of propyne identified in the Raman data).
It has not yet been determined whether the phases observed are both crystalline or crystalline and amorphous; additional Raman spectroscopy and XRD experiments will be conducted to further study this.

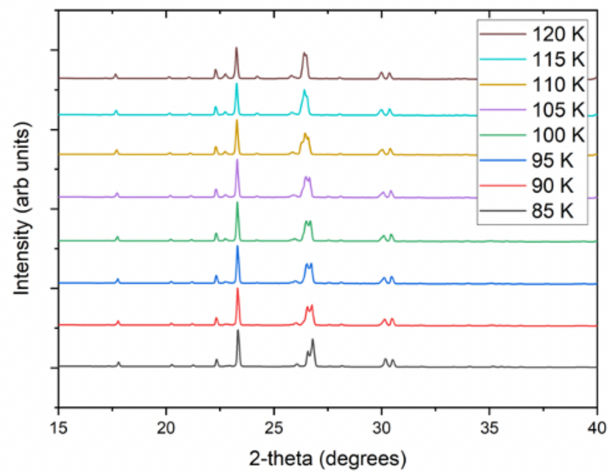

Figure 3. XRD from JPL laboratory source (λ = 1.54 Å) of propyne between 85-120K at ~1 bar. Variable temperature XRD of propyne which, coupled with higher resolution synchrotron measurements, have enabled the discovery of the crystal structure of propyne and the determination of its density. The XRD at ~1 bar demonstrates no phase transition in the 85-120 K range.

The existence of two temperature phases is intriguing within the context of temperature and pressure variation in Titan's atmosphere and on its surface. According to Titan's pressure-temperature profile, propyne is expected to condense at 92 K. If propyne is deposited on Titan's surface, it would likely also exist in the low-temperature phase as Titan's average surface temperature is 90 K [1]. However, with Titan's incredibly dynamic nature, it is possible that surface deposits of propyne may exist in high temperature phases as well, whether through phase-trapping, localized hot spots on the surface, or further in Titan's warmer interior. Thus, continued characterization of propyne and its potential solid phases is key for an understanding of Titan's atmosphere, surface and subsurface.

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