METHANE, ETHANE AND NITROGEN LIQUID STABILITY ON TITAN. J. Hanley[1], L. Pearce[2,3], G. Thompson[2], W. Grundy[1], H. Roe[1], G. Lindberg[2], S. Dustrud[2], D. Trilling[2], S. Tegler[2]. [1]Lowell Observatory, Flagstaff, AZ (jhanley@lowell.edu), [2]Northern Arizona University, Flagstaff, AZ, [3]University of Texas, Austin, TX.

Introduction: The Physics and Astronomy Department at NAU hosts the Astrophysical Ice Laboratory, which is dedicated to studying ices under controlled temperatures and pressures [1-5]. Simple molecules like CH_4, H_2O, N_2, CO, CO_2, O_2, CH_3OH, C_2H_6, and NH_3 are important geological materials in the cold, outer regions of the solar system. Their mobility and distinct material properties enable geological activity and produce a spectacular variety of exotic landforms, even at extremely low temperatures. But frustratingly little is known of the basic mechanical and optical properties of these volatile ices, and especially of their mixtures.

Many outer solar system bodies are likely to have a combination of methane, ethane and nitrogen. In particular, the atmosphere and lakes of Titan are known to consist of these species. Understanding the past and current stability of these lakes requires characterizing the interactions of methane and ethane, along with nitrogen, as both liquids and ices. Previous studies have shown that the freezing point of methane is depressed when mixed with nitrogen [6]. Our cryogenic laboratory setup allows us to explore ices down to 30 K through imaging and transmission spectroscopy. Our recent work has shown that although methane and ethane have similar freezing points (~91 K), when mixed they can remain liquid down to 72 K. We will present new results exploring the ternary system of methane, ethane and nitrogen. In particular we will explore the effect of nitrogen on the eutectic of the methane-ethane system.

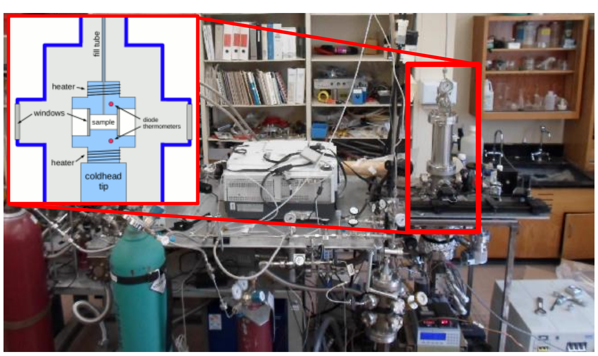

Figure 1. *Photo of laboratory setup. Inset: Schematic of the cell.*

Methodology: Within the laboratory setup (Fig 1), volatile ices are condensed as thin ice films on a cold mirror, or within an enclosed cell (Fig 1 inset). Cooling is provided by closed-cycle helium refrigerators, within vacuum chambers for insulation. Cryogenic ice samples are studied via various analytical techniques including visible and infrared transmission spectroscopy and photography (e.g. Fig 2A-B). Mass spectrometers are capable of monitoring changes in composition. Freezing points are measured as when ice is first seen visually.

Concurrently with the freezing point measurements we acquire transmission spectra of these mixtures to understand how the spectral features change with concentration and temperature.

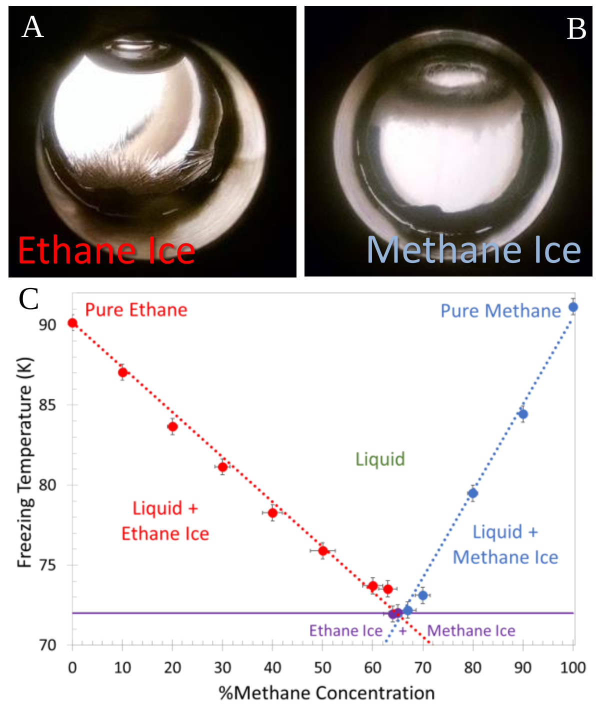

Figure 2. *Freezing points of solutions with varying methane/ethane concentrations. (A-B) Images of mixed methane and ethane solutions at their freezing points. Ethane ice freezes first (A) when the concentration falls on the ethane liquidus (red line in C), whereas methane ice forms on the top of the solution (B) when on the methane liquidus (blue line).*

Results: Any mixing of methane and ethane together will depress the freezing point of the lake below Titan's surface temperature, preventing them from fully freezing (Fig. 2C). Also, when ethane ice forms, it freezes on the bottom of the liquid (Fig 2A), while methane ice freezes at the top of the liquid (Fig 2B), implying ethane ice is denser than the solution, while methane ice is less dense; this holds for all concentrations. In addition, which ice forms first is dependent on the initial concentration of the solution. If it starts along the ethane liquidus (red line Fig 2C), ethane ice will form first, while the reverse is true for methane (blue line).

Nitrogen was added to the methane-ethane system in a systematic process. We mapped the freezing point as a function of nitrogen concentration, holding the methane:ethane ratio constant in the remainder of the solution at the eutectic ratio (64% methane:36% ethane). For example, if the total solution was 30% nitrogen, the remainder would be 44.8% methane and 25.2% ethane. The results of these experiments are shown in Figure 3. As the nitrogen concentration increases from zero, the freezing point of the system increases until a maximum at 65% N_2, 22.4% CH_4, 12.6% C_2H_6 and 81 K. It then drops back off to the freezing point of pure nitrogen at 63 K.

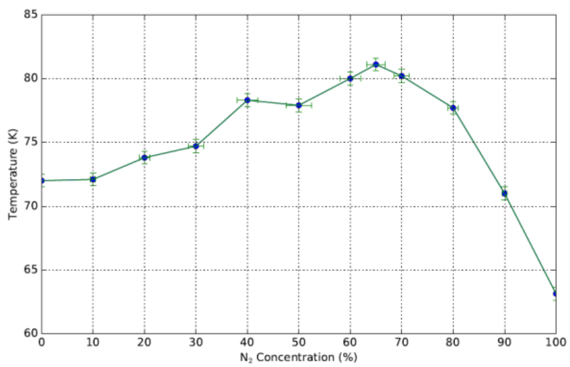

Figure 3. *Freezing points of nitrogen-ethane-methane mixtures for varying amounts of nitrogen and a constant remainder ratio of 64% methane:36% ethane.*

In order to measure the freezing point of the liquid solution between 60-70% nitrogen, we had to go to higher pressures to reach the dew point before the freezing point. By doing this, we encountered a strange phenomenon. At high pressure we find that the ternary creates two separate liquid phases (Fig 4A-B). Through spectroscopy we determined the bottom layer to be nitrogen rich, and the top layer to be ethane rich (Fig 4C). We are further exploring at what pressures and temperatures these effects occur.

Implications: Understanding the freezing points of combinations of these species has implications for not only the lakes on the surface of Titan, but also for the evaporation/condensation/cloud cycle in the atmosphere, as well as the stability of these species on other outer solar system bodies. These results will help interpretation of future observational data, and guide current theoretical models.

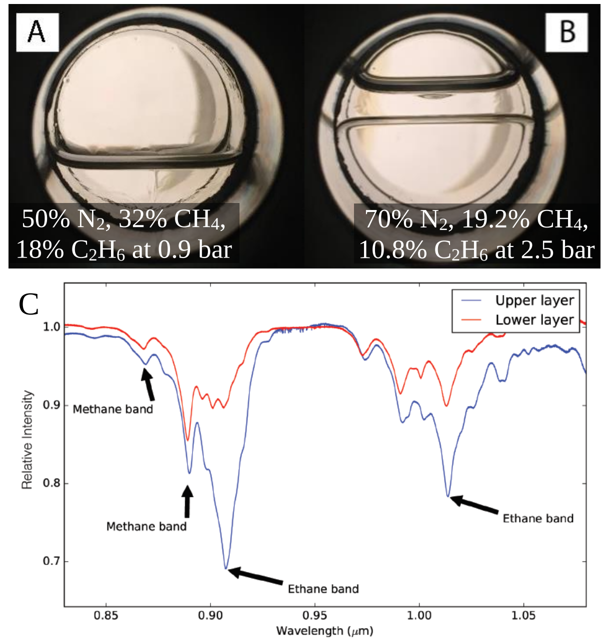

Figure 4. *Images taken at low (A) and high (B) pressure. (C) Spectra of the top and bottom layer from experiment B.*

Future Goals: The ices that can be created in the lab are useful to a variety of outer solar system bodies. For instance, mixtures of CO and N_2 are found on both Pluto and Triton, and spectral features acquired in the lab may aid in their identification [5]. We intend to continue to characterize the ternary of methane-ethane-nitrogen. We will also add other hydrocarbons and materials likely in Titan's atmosphere and surface to determine how their presence effects stability and spectral properties.

We would like to be able to study not only the spectroscopic properties of these materials at low temperatures, but the physical properties as well. These include density, viscosity, speed of sound, vapor pressure, refractive index, compressibility, thermal and electrical conductivity, and diffusion rates.

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References: 1. Tegler S.C. et al. (2012) *The Astrophysical Journal*, *751*, 76. 2. Grundy W.M. et al. (2011) *Icarus*, *212*, 941-949. 3. Roe H.G. and Grundy W.M. (2012) *Icarus*, *219*, 733-736. 4. Protopapa S. et al. (2015) *Icarus*, *253*, 179-188. 5. Hanley J. et al. (2016) *LPSC*, Abstract #2438. 6. Prokhvatilov A. and Yantsevich L. (1983) *Sov. J. Low Temp. Phys., vol. 9, p. 94-98 (1983). 9*, 94-98.