Introduction: In 2015, the New Horizons spacecraft fly-by unveiled Pluto’s volatile surface ices to be predominantly methane (CH₄), nitrogen (N₂), and carbon monoxide (CO) [1-3]. However, the development of physical and mineralogical models requires new laboratory data for interpreting these spectral observations from New Horizons, mainly from the Linear Etalon Imaging Spectral Array (LEISA) data, which consists of the near-infrared (near-IR) wavelength range 1.25 µm – 2.5 µm [4]. Therefore, spectral data acquired under experimental Plutonian conditions would be ideal to compare with LEISA data and for extending theoretical modeling of mineralogical effects on ices.

Pluto’s surface temperatures range from 33 K – 55 K (though can be < 33 K in certain seasons or cold-trap settings) with a surface pressure of approximately 14 – 25 µbar [5-6]. This temperature range gives rise to potential α-β phase changes in N₂, CH₄, and CO. CH₄-N₂ mixtures, according to [7], show specific phase transitions within Pluto’s temperature range. N₂ α-β transition occurs at ~35 K at 2.149 µm, whereas CH₄ α-β transition occurs at ~21 K, mainly noticeable in the pure CH₄ ice samples. In the N₂-CO mixtures, according to [8], CO (at the 2.358 µm) α-β transitions occur on a “lens” curve, depending on the molar ratio of CO in the mixture (e.g., CO < 50 mol%, phase change occurs at ~40 K, CO > 50 mol%, phase change occurs at 50 K). Ice molar ratio abundances and interactions within this temperature range therefore play various roles in the development of mineralogical structures, different localized sublimation behavior, and geological or rheological processes [3, 9-10].

However, spectral characteristics in the ternary system N₂-CH₄-CO remain poorly studied. CH₄ in N₂ is particularly of interest due to the observed presence of two phases: one highly diluted in solid beta-nitrogen and another that is still unknown, but hypothesized to be a segregated layer in patches or intimate with the diluted phase [11-12]. Some CH₄ spectral signatures also seem to only be observed when mixtures with N₂ [12]. The behavior of CO has a lack of literature and experimental data at these extremely low temperatures, mainly only having an α-β transition at ~45 ± 5 K when in binary mixture with N₂ [8].

Experimental Setup: The Pluto simulation chamber at the W.M. Keck Laboratory for Space and Planetary Simulations at the University of Arkansas is 1.31 m in length and 0.56 m in diameter [13]. The experimental protocol for this task is as follows: the gas constituents are mixed in a set molar ratio within a pre-mixing chamber connected to the simulation chamber. Then the mixture is injected into the cryo-vacuum pre-chilled simulation chamber at a temperature of 10 K and 14 µbar, and condenses onto the vertical coldhead where recording from the FTIR and camera begins. The mixture is then heated by 10 K increments, which helps determine the temperature gradient of phase transition detected by spectroscopy or optical instruments. FTIR spectra are acquired using a Thermo Nicolet 6700 Spectrometer with a TEC InGaAs detector at a resolution of 2 cm⁻¹ and 450 second intervals. Long acquisition times allows a higher resolution to identify and separate more complex intimate mixtures. The spectra are collected using the OMNIC software. Peak changes, shifts, and band areas are analyzed using this software.

Spectral Results: The first set of experiments were compared at 10 K with a variation of ternary mixtures (Fig. 1). The mixtures are as follows: a) 90 mol% CH₄ : 5 mol% N₂ : 5 mol% CO; b) 50 mol% CH₄ : 40 mol% N₂ : 10 mol% CO; c) 10 mol% CH₄ : 50 mol% N₂ : 40 mol% CO. At 10 K, all constituents are in the α phases. The CH₄ 1.485 µm band is present when the CH₄ molar ratio is > 50 mol%. This particular band is only observed in mixture with CH₄-N₂, though an increase in CO concentration may mask this band. The N₂ 2.149 µm band is not present, which is expected from previous results of the α-N₂ band not appearing until > 35 K [10]. The 2.358 µm CO band produces a double-mode appearance when the molar ratio of CO increases.

Figure 1: Near-IR spectra (1 – 2.4 µm) of three different ternary mixtures at 10 K. Spectra has been offset for clarity. Green indicates certain CH₄ bands (1.485, 1.85, 2.33 µm), red indicates N₂, blue is CO.
The second set of experiments were compared at 40 K with a variation of ternary mixtures (Fig. 2), the same mixtures as those from Fig. 1. At 40 K, N₂ and CH₄ are in their respective β-phases, while CO is at the α-β transition. The CH₄ 1.485 μm band is again present when the CH₄ molar ratio is > 50 mol%. It seems that an increase in CO again “masks” this CH₄ band. The N₂ 2.149 μm band is now present at temperatures > 35 K. This N₂ band narrows in depth when the N₂ molar ratio increases. The 2.358 μm CO band produces a double-mode appearance when the molar ratio of CO increases, similar to the spectra at 10 K.

The third set of experiments were compared at 40 K with a variation of ternary mixtures, specifically with a focus on the change of the CO spectral band with respect to CH₄ and N₂ (Fig. 3). The mixtures are as follows: a) 5 mol% CH₄ : 5 mol% N₂ : 90 mol% CO; b) 20 mol% CH₄ : 20 mol% N₂ : 60 mol% CO; c) 90 mol% CH₄ : 5 mol% N₂ : 5 mol% CO; d) 5 mol% CH₄ : 90 mol% N₂ : 5 mol% CO. Again at 40 K, these constituents should remain in the β-phases. The CH₄ 1.485 μm band is not present except for the 90 mol% CH₄ ternary mixture. The N₂ 2.149 μm band is present mainly at molar ratios < 20 mol%, though may be oversaturated when N₂ concentration increases. The 2.358 μm CO band produces a double-mode appearance when the molar ratio of CO at the 60 mol% ternary mixture, though may become oversaturated with > 90 mol% concentration, or masked by the increase in N₂ or CH₄.

**Figure 2:** Near-IR spectra (1 – 2.4 μm) of three different ternary mixtures at 40 K. Spectra has been offset for clarity. Green indicates certain CH₄ bands, red indicates N₂, blue is CO.

**Figure 3:** Near-IR spectra (1 – 2.4 μm) of four different ternary mixtures at 40 K. Spectra has been offset for clarity. Green indicates certain CH₄ bands, red indicates N₂, blue is CO.

**Conclusions:** Ternary mixtures show the phase transitions using the near-IR FTIR instrumentation, allowing for further investigation to other potential phase transitions. CO shows a potential influence of phase characteristics depending on the molar concentration of N₂ and CH₄. CO also poses an interesting objective toward understanding the spectral behavior of the double-mode with increased CO concentrations and possibly temperature-dependent. The concentration of N₂ and CO show potential oversaturation of their respective absorption bands.

This observed behavior could influence the evolution of certain mineralogical and climatic aspects of Pluto, such as boundary layers and glaciation.

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**References:**