

**SPECTRAL CHARACTERISTICS OF CARBON MONOXIDE IN NITROGEN AND METHANE MIXTURES IN SIMULATED PLUTO CONDITIONS.** C. J. Ahrens<sup>1</sup>, V. F. Chevrier<sup>1</sup>. <sup>1</sup>Arkansas Center for Space and Planetary Science, University of Arkansas, Fayetteville, AR 72701, (ca006@email.uark.edu).

**Introduction:** Preliminary compositional mapping from the New Horizons fly-by has provided details to the differing spectral regions on Pluto. These regions correspond to different ratios and potentially various phases of the three main compounds: nitrogen (N<sub>2</sub>), methane (CH<sub>4</sub>), and carbon monoxide (CO) [1, 2]. Differing ice abundances and interactions thereof play many roles in the development of mineralogical structure, different localized sublimation, and geological processes [2-4]. Some areas of Pluto have been observed to have sharp boundaries between various ices [5].

Pluto's surface temperatures range from 33 K – 55 K with a surface pressure of approximately 10-25 microbar [6-7]. The New Horizons Linear Etalon Imaging Spectral Array (LEISA) data consists of the observational wavelength range 1.25 μm – 2.5 μm [8]. Spectral data under Plutonian conditions would be ideal to compare with LEISA data and for extending theoretical modeling of seasonal effects with ices and gases.

N<sub>2</sub> and CH<sub>4</sub> form a solid solution at Plutonian conditions due to both being nonpolar compounds and thus exhibiting partial miscibility [9].

CH<sub>4</sub> 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 [5, 10].

CH<sub>4</sub>-CO mixture, however, has a lack of literature and experimental data at Pluto's low temperature and pressure conditions.

CO-N<sub>2</sub> mixtures also pose an interesting question to phase changes and behavior at low temperatures and pressures, as previous studies were mainly theoretical at low Plutonian conditions [11].

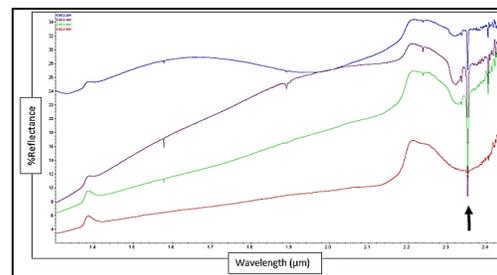
**Experimental Approach:** The Pluto simulation chamber at the W.M. Keck Laboratory for Space Simulations at the University of Arkansas is 1.31 m. in length and 0.56 m. in diameter (Figure 1) [12]. This stainless-steel vacuum chamber includes FTIR capabilities and a camera system for visual confirmation of the ice production and phase behavior.

The experimental protocol for this task is as follows: CO is mixed in ratio with a second constituent (CH<sub>4</sub> or N<sub>2</sub>) within a pre-mixing chamber connected to the simulation chamber. Then the mixture is flow-controlled injected into the cryo-vacuum pre-chilled

simulation chamber at a temperature of 10 K and 10 microbar and condenses onto the vertical coldhead where recording from the FTIR and camera begin recording. The mixture is then heated by 10 K increments, which helps determine the temperature point of any recorded changes detected by spectroscopy or optical instruments (Figure 1).

FTIR spectra is acquired using a Thermo Nicolet 6700 Spectrometer with a TEC InGaAs detector at a resolution of 2 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, band areas, and change of scattering effects (for potential amorphous phases) can be analyzed using this software for ice structure behavior.

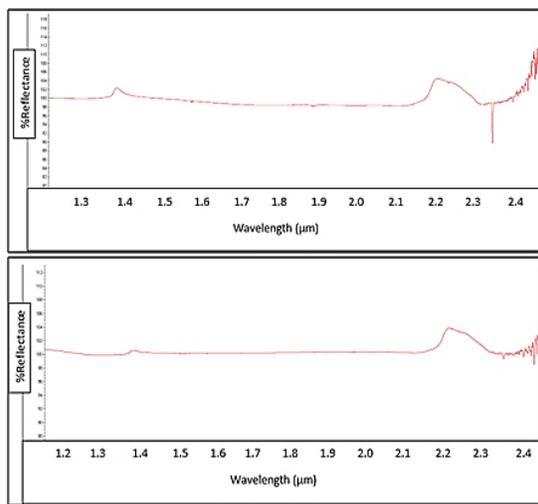


**Figure 1:** Example of 20% CO in N<sub>2</sub> from 20 K to 50 K, with 20 K at top. Arrow points to CO signature at 2.35 μm.

**Results:** With the CO-N<sub>2</sub> mixtures, lower concentrations of CO were found to have an unidentified spectral and mechanical behavior below 30 K. The ice characteristic at concentrations below 30% CO, and at temperatures below 35 K showed a possible glass-like microcrystalline structure (Figure 2) [13]. This phase was verified with FTIR to show strong signals of CO at 2.35 μm with scattering effects. These effects would disappear once temperatures reached 35 K. This strong CO signature would be minimal or undetected above 30% CO concentration (Figure 3).

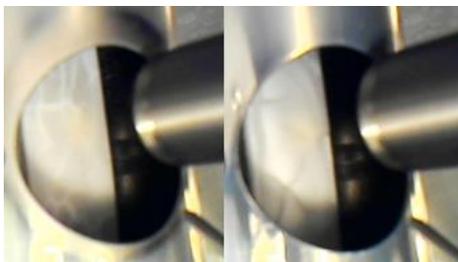


**Figure 2:** Visual example inside the Pluto simulation chamber of 5% carbon monoxide, 95% nitrogen at 10 K and 14 microbar pressure. FTIR probe on right.



**Figure 3:** 5% CO in N<sub>2</sub> at 20 K (Top). 90% CO in N<sub>2</sub> at 20 K (Bottom).

With the CO-CH<sub>4</sub> mixtures, we analyzed a rapid condensation of crystal growth (< 30 seconds) versus slower condensation of the mixture (> 60 seconds) with 80% CO in CH<sub>4</sub>. The sublimation process at ~50 K, as evidenced by our optical equipment, differed by displaying a smoother surface (rapid condensation) versus a variegated surface (slower condensation) (Figure 4).



**Figure 4:** Visual examples inside the simulation chamber of ice mixtures condensing onto the cold head

at 40K. (Left) Rapid condensation. (Right) Slower condensation.

**Discussions:** The CO-CH<sub>4</sub> mixture had observable changes different than that of CO-N<sub>2</sub>. During the CO-CH<sub>4</sub> mixtures, pressures and temperatures spike rapidly from 13 microbar to > 200 microbar within 120 seconds, taking another < 180 seconds to equilibrate back to < 25 microbar. This transition region may suggest the layering of the polar-nonpolar gas mixtures and eventual sublimation of one constituent (probably CO) before the other (CH<sub>4</sub>). In the CO-N<sub>2</sub> mixtures, lower ratios of CO to form a potential microcrystalline phase may also imply layering as well.

**Conclusions:** CO-N<sub>2</sub> mixtures reveals a potential new microcrystalline phase < 35 K at lower ratios of CO as detected visually and spectrally. This observed behavior could influence the evolution of certain mineralogical aspects of Pluto, such as boundary layers and glaciation [4-5]. CO-CH<sub>4</sub> mixtures separation of the polar-nonpolar volatiles to produce a variegated sample surface during the sublimation process.

Additional information for interpretation and seasonal perspectives must be obtained by laboratory simulations to help confirm theoretical models and extend current phase diagrams to low temperatures and pressures. In understanding the behavior and structure of these CO-CH<sub>4</sub> and CO-N<sub>2</sub> mixtures, we can hypothesize the stability of phases and structures of macro-scale geology.

**References:** [1] Stern, S. et al. (2015), AAS DPS 47, Abstract 100.01. [2] Kim, Y., Kaiser, R. (2012) The Astrophysical Journal, 758:37, 1-6. [3] Schmitt, B. et al. (2017) Icarus, 287, 229-260. [4] Moore, J. et al. (2016) Science, 351:6279, 1284-1293. [5] Schmitt, B. et al. (2016), LPSC XLVII, Abstract 2794. [6] Lorenzi, V. et al. (2015), AAS DPS 47, Abstract 210.08 [7] Cruikshank, D., et al. (2015), Icarus, 246, 82-92. [8] Reuter D. C. et al. (2008) Space Science Reviews, 140, 129. [9] Trafton, L. (2015) Icarus, 246, 197-205. [10] Doute, S. et al. (1999) Icarus, 142:2, 421-444. [11] Angwin, M., Wasserman, J. (1966) Journal of Chem. Phys., 44:1, 417-418. [12] McMahon, Z. et al. (2016) LPSC XLVII, Abstract 1728. [13] Ahrens, C. et al. (2017) LPSC XLVIII, Abstract 1352.