RAMAN SHOP: EXPLORING THE CARBON MONOXIDE-NITROGEN-METHANE TERNARY SYSTEM OF SPUTNIK PLANITIA VIA RAMAN SPECTROSCOPY.

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Introduction: On 14 July 2015, New Horizons completed its primary mission when it flew by Pluto at a distance of 12,000 km from the surface [1]. Data sent back to Earth presented a planetary surface not wholly dead; Sputnik Planitia, the left lobe of Tombaugh Regio, displays ongoing convective processes with an average turnover rate of about 500,000 years [2]. Most likely formed by a >150 km ancestral Kuiper Belt impactor, this oval-shaped structural depression is measured to be approximately 1300 km x 900 km in size [3]. The impact basin covers roughly 5% of Pluto's surface and is characterized by polygonal convective cells surrounded by geologically diverse terrain [4]. This area of convection is composed predominantly of N_2 ice with smaller quantities of CO and CH_4 ices.

It is this N_2-rich ice that we are most interested in describing by means of Raman spectroscopy. Pure N_2 freezes at 63.15 K and shifts from its hexagonal β-phase to a cubic α-phase at 35 K [5]. CO is fully miscible, in N_2 and encounters its phase transition at 61 K. The addition of CO to N_2 increases the temperature at which the α-β transition occurs, making it possible for the process to take place on and below Pluto's ~40 K surface. That being said, it is of particular interest to find how the CO-N_2 system is perturbed when CH_4 is introduced. The exploration of this ternary system may provide insight into whether the occurrence of the α-β transition is plausible within the Sputnik Planitia region.

Analysis: Raman scattering provides a means of detecting phase transitions by displaying a downshift in frequency when the transition occurs. Each of the three components used in the mixture exhibit a prominent peak in a given region of the spectrum, as shown in figure 1.

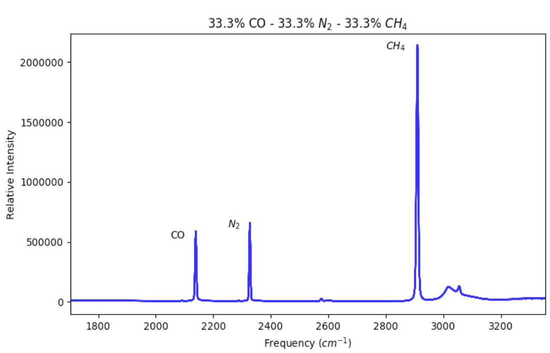

Figure 1: Spectrum of equal mixing at 45 K. Each prominent peak is described with the corresponding molecule. As the temperature is decreased the peak shifts downward.

By using a Guassian fit we are better able to track the movements of the peaks as they shift in wavenumber. In the case of the CH_4 peak, we implemented a double Gaussian fit as it displays a double peak feature as the temperature is lowered. This is caused by the solubility limit, and indicates that CH_4 is crystallizing out of the liquid. When the CH_4 is dissolved in the mixture, it peaks predominantly near 2912 cm^{-1}. As the solubility limit is reached, a second peak forms at 2905 cm^{-1}, which is the region of the spectrum where pure CH_4's most prominent peak appears.

Figure 2 shows how the peaks shift in frequency as a function of temperature. The double peak feature is displayed in the temperature-frequency diagram as a split in the max peaks where the feature begins to occur.

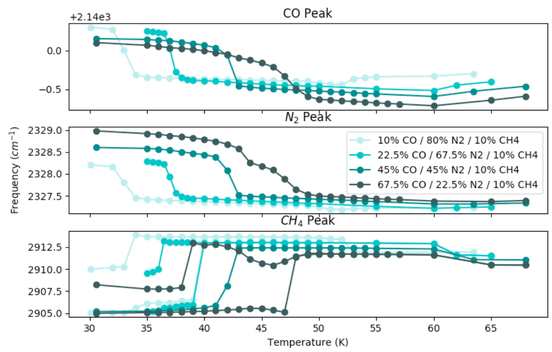

Figure 2: Temperature-Frequency Diagram of CO-N_2-CH_4. Each point represents a measurement taken at a specific temperature and the resulting shift in frequency.

While the N_2 and CO peaks mostly agree with one another, the CH_4 peak tells a different story. CH_4 has a strong Raman feature, and quickly overshadows the peaks formed by N_2 and CO, even when it is only 10% of the overall solution. This indicates that it may have the ability to display more subtle changes occurring in the system.

Results: A multitude of spectra were collected first as a binary sequence of CO-N_2 and then as a ternary system by adding 10% CH_4 to the CO-N_2 mixtures. Previous research has shown that the combination of CO and N_2 raises the temperature at which the solid-solid α-β phase transition occurs in N_2 alone. The elevation in temperature implies that a phase transition should be apparent in the remotely sensed New Horizons data, and yet, it is not. Figure 3 demonstrates that inserting CH_4 into the system depresses the temperature at which the transition from β to α occurs, indicating that the convective cells of Sputnik Planitia may not actually be at appropriate temperatures for solid phase transitions to take place.

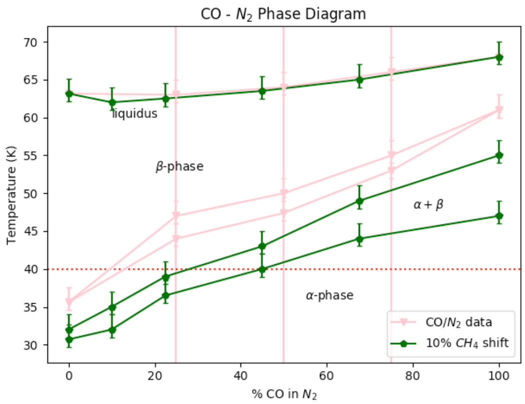

Figure 3: Phase diagram of the apparent shift caused by the addition of CH_4 into the CO-N_2 system. Measurements indicate that the introduction of CH_4 into the system causes a depression of when the solid-solid transition occurs. The red dotted line represents the average temperature of Pluto's surface.

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