NEAR-INFRARED REFLECTANCE OF THOLINS IN METHANE ICE: PRELIMINARY RESULTS AND IMPLICATIONS FOR INTERPRETATION OF NEW HORIZON'S LEISA DATA.
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Introduction and objectives: Tholins are considered to be the main darkening component of the surface of Pluto. They may form by chemical alteration of the surface ices exposed to the galactic cosmic rays, the dominant ionizing radiation at Pluto's surface [1]. They may also be precipitates from UV radiolysis of CH_4/N_2 in Pluto's tenuous atmosphere. Their proportion at the surface may vary according to the seasons, increasing toward perihelion while surface ices transform to vapor that densifies the atmosphere, then decreasing while the atmosphere condenses and rejuvenates the surface [2]. Tholins of Titan composition adequately fits Pluto's spectrum in the near-infrared [3]. It has also been observed that vibrational absorptions of methane ice dominate the 1.2 to 2.5 µm spectral region of the OSIRIS Pluto's surface spectra [4], in spite of CH_4 perhaps being less abundant than N_2 ice. Such considerations make understanding the spectral signature of tholin-methane mixtures necessary, especially in the wavelength range of the LEISA hyperspectral sensor onboard New Horizons, 1.25-2.5 µm. In order to obtain useful data, a preliminary, feasibility experiment of laboratory spectral measurement of tholin-methane ice mix was conducted at varying temperatures, allowing reconstruction of the spectral behaviour of the mix while methane gas liquifies and solidifies during temperature decrease, then melts and evaporates when temperature rises.

Description of experiment: Tholins of Titan composition (10% CH_4, 90% N_2) synthesized at NASA Ames [5] were placed on a spectralon in a Petri dish and inserted in the Andromeda chamber [6] built at the Keck Laboratory of the Arkansas Center for Space and Planetary Sciences. The chamber was filled with a N_2 atmosphere, and cooled by liquid N_2 flow in a solenoid surrounding the chamber. Temperature was monitored using 8 thermocouples, including 1 in the Petri dish. At 92K in the Petri dish, CH_4 was poured in a condenser located in the chamber above the Petri dish, and flowed to the Petri dish. Temperature was decreased to 87.4K, then increased, attaining 240K at the end of the experiment. NIR infrared spectra where measured continuously in the range 1-2.5 µm with an optical fiber ending on one side vertically above the Petri dish and below the condenser, and connected on the other side to a FTIR spectrometer. Each spectrum was averaged from 450 measurements (~10 minutes) and the total length of the experiment was 5h09'. The proportion of tholin vs. spectralon below the beam was estimated to ~20% at the beginning of the experiment, and was still ~15% at the end of the experiment. It could not be monitored during the experiment.

As a feasibility study, all the requirements to reproduce the conditions at the surface of Pluto were not matched. For instance, temperature was decreased enough to freeze methane, but is still too high to match the true surface temperature conditions (~40K). No attempt was made to comply with the atmospheric pressure of Pluto, a minor issue because the atmosphere used in the experiment is composed of pure N_2, which is chemically non reactive and does not have any absorption feature in the considered spectral and temperature range.

Results: A selection of the obtained spectra is provided on Figure 1. Noise is mainly attributed to the 15 m optical fiber length required to connect the chamber to the spectrometer.

Spectrum #1 – Cooling – Tholin without methane (121 to 103K). All the observed absorptions are also observed at ambient temperature on the same sample: 1.54, 1.69, 1.74, 1.92 and 1.99 µm.

Spectrum #2 – Cooling – Tholin in methane slush (91K to 88.5K). The spectrum is strongly dominated by CH_4 absorptions [7] at 1.33, 1.36, 1.41, 1.67, 1.72, 1.79, 1.85, 1.93, 2.2 µm and perhaps 2.32 µm. The presence of tholins is inferred from the 1.54 and 1.99 µm broad absorptions, which contrast with a flat to convex-shaped signature of CH_4 in these spectral zones. No new absorption band is observed.

Spectrum #3 – Cooling – Tholin in frozen methane (87.7K-87.4K). The spectrum is very similar to the previous spectrum, with deeper methane bands and a slightly lower overall reflectance.

Spectrum #4 – Warming – 97K to 108.5K. CH_4 is in the liquid field. The overall reflectance is below #2 in spite of a higher temperature, perhaps because the proportion of methane ice still present is higher than in #2.

Spectrum #5 – Warming – Tholin while evaporating methane (109K to 123K). After passing the boiling point (109-111K at atlmospheric pressure), the overall reflectance increases with decreasing temperature, both methane and tholin absorptions are similar to the absorptions observed at lower temperature.

Spectrum #6 – Warming – Tholin by the end of methane evaporation (138K to 149.5K). Most methane bands are still observed but are strongly attenuated. The overall reflectance level is back to that of Spectrum #1.

Spectrum #7 – End of experiment (194K to 190.5K). This spectrum is intermediate between spectra #6 and spectrum #1, before pouring methane.

After the end of the experiment, a new tholin spectrum was taken out of the Andromeda chamber and compared to a spectrum taken immediately after synthesis. The two spectra are almost similar, apart from a general steeper slope. The tholins have not significantly reacted with methane during the experiment.

Conclusion: (1) Tholin reactivity in CH_4 is very low to null. (2) Whatever its phase, CH_4 dominates the spectral signature of the tholin-methane mix for the studied proportions of tholin and methane. Nevertheless, evidence of tholins is constant through bands located at 1.54 and 1.99 µm, regions where the methane signature is flat or convex-shaped. this result is encouraging for the detection of small proportions of tholins in CH_4 ice by LEISA at the surface of Pluto, even in the presence seasonal configuration where Pluto moves away from its perihelion.

Future works: Further experiments will be conducted at lower temperature and pressure in a new chamber in which tholins will be synthesized and their spectra measured in situ. Temperature will be varied more slowly in order to make sure that CH4 has enough time to equilibrate with its stability field. Experiments of tholins with CH_4/N_2 ice mixtures will also be performed to simulate an icy composition closer to Pluto's surface.

References: [1] Johnson, R. E. (1989) *Geophys. Res. Lett.*, *16*, 1233–1236. [2] Hansen, C. J., and Paige, D. A. (1996) *Icarus*, *120*, 247–265. [3] Olkin, C. B. et al. (2007) *Astron. J.*, *133*, 420–431. [4] Grundy, W. M., and Buie, M. W. (2001) *Icarus*, *153*, 248–263. [5] Nna-Mvondo, D., et al. (2013) *Planet. Space Sci.*, *85*, 279–288. [6] Wasiak et al. (2013) *Adv. Space Res.*, *51*, 1213–1220. [7] Clark, R. N., et al. (2009) *J. Geophys. Res.*, *114*, E03001.

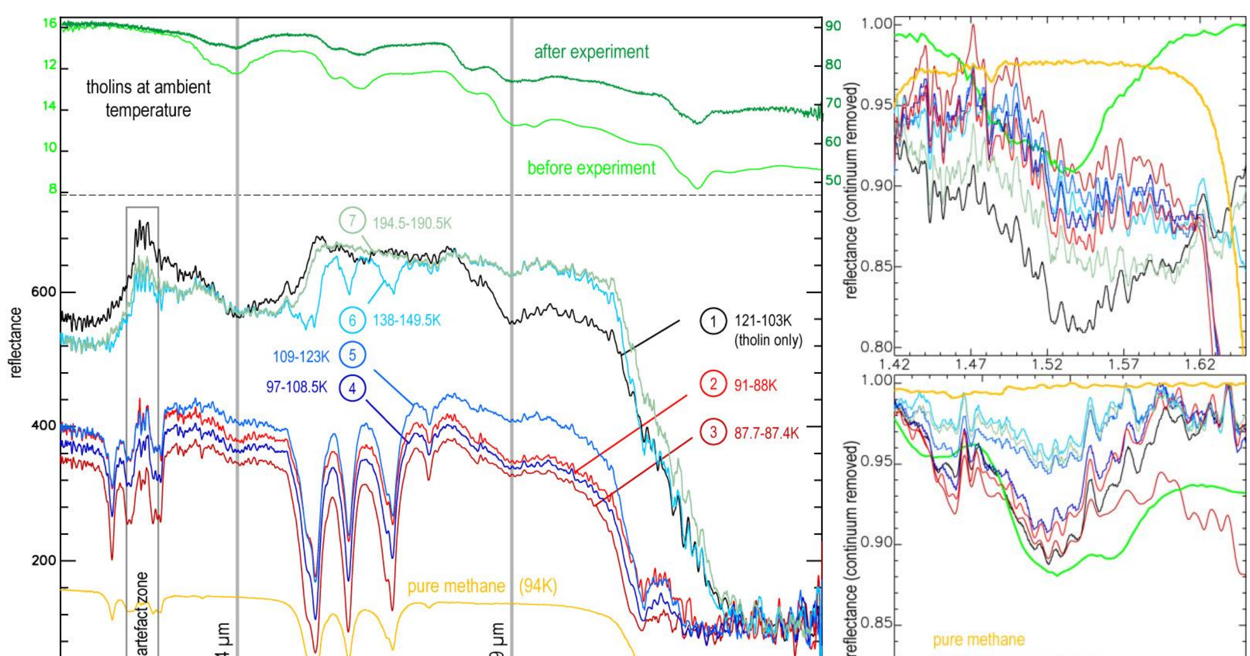

Figure 1. Left: Summary of the tholin-methane mix experiment and comparison with the tholin spectrum after synthesis and after experiment and with a spectrum of pure methane (methane spectrum multiplied by 5 vertically). Right: Zoom on the two persistent tholin absorptions, continuum removed. The tholin absorptions at 1.54 and 1.99 µm are observed throughout the experiment.