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S. Pavithraa, J.I. Lo, R.K. Kushwaha, B.N. Raja Sekhar, B.M. Cheng, N.J. Mason, B. Sivaraman



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**Vacuum Ultraviolet Photoabsorption of Prime Ice Analogues of Pluto and Charon**

S Pavithra<sup>a,†</sup>, J -I Lo<sup>b</sup>, R K Kushwaha<sup>a</sup>, B N Raja Sekhar<sup>c</sup>, B -M Cheng<sup>b</sup>, N J Mason<sup>d</sup> and B Sivaraman<sup>a,\*</sup>

<sup>a</sup> *Physical Research Laboratory, Ahmedabad, 380 009, India. († Presently at National Chiao Tung University, Taiwan).*

<sup>b</sup> *National Synchrotron Radiation Research Center, Hsinchu, 30076, Taiwan.*

<sup>c</sup> *Atomic and Molecular Physics Division, BARC at RRCAT, Indore, 452 013, India.*

<sup>d</sup> *Department of Physical Sciences, The Open University, Milton Keynes, MK7 6AA, UK.*

\* *Corresponding author: bhala@prl.res.in*

**Abstract**

Here we present the first Vacuum UltraViolet (VUV) photoabsorption spectra of ice analogues of Pluto and Charon ice mixtures. For Pluto the ice analogue is an icy mixture containing nitrogen (N<sub>2</sub>), carbon monoxide (CO), methane (CH<sub>4</sub>) and water (H<sub>2</sub>O) prepared with a 100:1:1:3 ratio, respectively. Photoabsorption of icy mixtures with and without H<sub>2</sub>O were recorded and no significant changes in the spectra due to presence of H<sub>2</sub>O were observed. For Charon a VUV photoabsorption spectra of an ice analogue containing ammonia (NH<sub>3</sub>) and H<sub>2</sub>O prepared with a 1:1 ratio was recorded, a spectrum of ammonium hydroxide (NH<sub>4</sub>OH) was also recorded. These spectra may help to interpret the P-Alice data from *New Horizons*.

*Key words:* astrochemistry – methods: laboratory: solid state – techniques: spectroscopic

## Introduction

New Horizons being the first dedicated mission to explore the Pluto and its moons has been returning data from the on board scientific payloads since July 2015. Well before the New Horizons encounter it was widely known that the chemical compositions of both Pluto and Charon were dominated by the presence of simple ices such as  $N_2/CH_4/CO$  [1] and  $NH_4OH$  [2]. A recent report also indicates compositional diversity of molecular ices on Pluto's surface [3]. The flyby of New Horizons, revealed water to be a component of icy Pluto and pure ammonia exists within Charon system.

The LEISA instrument also found ammonia ( $NH_3$ ) and crystalline water ( $H_2O$ ) ices [4-5] to be present on the surface of Charon with the mixture of these ices causing the geological features and activities on Charon's surface [6]. In addition, the spectra of these ices were measured using the Ultraviolet Imaging Spectrograph, P-Alice, from 50 – 180 nm region [7]. In order to determine the morphology and composition of these ices from P-Alice data it is necessary to record laboratory spectra under appropriate simulation conditions [8]. In a recent article, Sivaraman et al [9] had reported the detectable wavelength for nitriles. In this short communication we report the first VUV (110 – 180 nm) photoabsorption spectra of ice analogues of both Pluto and Charon. Such experimental spectral signature can also be used for other distant icy bodies such as Eris and Makemake.

## Experiment

The present experiments were carried out at National Synchrotron Radiation Research Centre (NSRRC) in Taiwan. A detailed description of the experimental setup was provided in an earlier publication [10-11]. In brief, the incident vacuum ultraviolet light from beamline BL03 was dispersed with a 6 m Cylindrical Grating Monochromator (CGM) and passed through a gold mesh with transmission about 90 %; the photocurrent was detected with an electrometer (Keithley 6512) to monitor and to normalize the beam [11]. To measure an absorption spectrum, a spectrum ( $I_0$ ) was recorded both before deposition of the ice mixtures. Subsequently, the gaseous samples were conducted into the Ultra High Vacuum (UHV) chamber and were deposited on a Lithium Fluoride (LiF) substrate attached to a cold head of a rotary cryostat (APD HC-DE204S) maintained at 10 K (*Figure 1*). Another spectrum ( $I$ ) was recorded after deposition of the ice mixtures; by this means, the absorption spectrum was derived based on Beer–Lambert's law. The spectra of pure ices were recorded at 0.2-0.5 nm and 1.0 nm step sizes [8] whereas the spectra of ice mixtures were recorded at 1 nm to match the step size of P-Alice.

The molecules forming the ice film were premixed with required ratio before being let into the UHV chamber and deposited on a LiF substrate attached to a cold head maintained at a temperature of 10 K. The Pluto mixture was also mixed with water in the ratio  $N_2:CO:CH_4:H_2O = 100:1:1:3$  to explore the effect of water in the VUV spectra of the surface of Pluto. Such a mixture is an analogue of certain regions of Pluto's icy surface due to molecular compositional diversity across different regions in Pluto. In order to mimic the ice layers on Charon  $NH_3$  (99% pure) and  $H_2O$  molecules were mixed in gas phase in the ratio 1:1 and then allowed to condense onto the LiF substrate at 10 K. A spectrum of an  $NH_4OH$  ice was also recorded to compare with observational data on the surface ices of Charon. Due to the lack of ice thicknesses values for those ice mixtures used in these experiments we are unable to present the cross section values for those spectra recorded.

## Results and Discussions

### Pluto ice analogue

$N_2$ , CO and  $CH_4$  were mixed in the ratio 100:1:1 in order to mimic Pluto's chemical composition and the gas mixture was deposited on the LiF substrate maintained at 10 K to form an ice layer of a few nanometres thickness. Spectra were recorded at 10 K after deposition and after warming the ice to 30 K (*Figure 2*).  $H_2O$  molecules were added to the pre-existing mixture ( $N_2:CO:CH_4$ ): $H_2O$  in the ratio (100:1:1):3 and was made to condense on the LiF substrate at 10 K with subsequent recording of spectra at 10 K and at 30 K.

The spectrum recorded at 10 K for the  $N_2:CO:CH_4$  mixture was found to have three distinct sections; absorption at 110 – 130 nm, 130 – 160 nm and 160 – 180 nm. When comparing the pure  $N_2$ ,  $CH_4$  and CO (Table 1) in all these three distinct regions we could clearly observe the contribution from  $CH_4$  and CO absorption the region 110 – 130 nm. However, the cross section for  $N_2$  [12] is much lower than the  $CH_4$  and CO so the peaks corresponding to  $N_2$  are not clearly seen in this region. The next region 130 – 160 nm has peaks corresponding to CO whereas  $CH_4$  and  $N_2$  are not evident as they do not have significant absorption in this region. However, the last part of the spectrum, 160 – 180 nm, showing continuous absorption is very interesting as the primary molecules used in this experiment do not have significant absorption in this region. Absorption in this region therefore could be from the interaction of  $N_2$ ,  $CH_4$  and CO molecules at 10 K.

The spectrum recorded after warming the ice mixture to 30 K revealed two distinct regions; 110 – 130 nm and 130 – 160 nm but the third absorption region, 160 – 180 nm, observed at 10 K was found to be absent at 30 K (*Figure 2*). At 30 K, absorption between 110 – 130 nm was from both  $CH_4$  and CO but absorption

between 130 and 160 nm is only from CO as CH<sub>4</sub> does not have any significant absorption in this region. Absence of further absorption extending to 180 nm at 30 K might be due to the N<sub>2</sub> matrix subliming off at 30 K leaving behind CH<sub>4</sub> and CO. These suggest the absorption in the 160 – 180 nm at 10 K could be due to the interaction of CH<sub>4</sub>, CO with the N<sub>2</sub> molecules.

The spectrum recorded after adding H<sub>2</sub>O molecules to the gas mixture and then depositing the refined mixture at 10 K was found to be similar to that recorded without the H<sub>2</sub>O molecules. No significant changes in the spectrum were seen throughout the spectrum. This could be due to the H<sub>2</sub>O absorption falling well within the 110 – 130 nm / 130 - 165 nm regions, which is already present in the absorption spectrum of the ice mixture without H<sub>2</sub>O. The spectrum at 30 K for the mixture with H<sub>2</sub>O was similar to the spectrum recorded without H<sub>2</sub>O. This clearly shows even warming up the ice has no significant H<sub>2</sub>O effect in the photoabsorption spectrum recorded at 30 K. Temperature on Pluto surface is slightly warmer than those results presented in the experimental data. By increasing the temperature further, in experiments, molecular ice mixture was found to desorb. Therefore, spectra up to 30 K were presented for Pluto ice mixture.

### Charon ice analogue

In order to experimentally simulate the conditions on Charon's surface (temperature ranges from 50 – 60 K), H<sub>2</sub>O and NH<sub>3</sub> ices were studied in layered and mixed deposits on a LiF substrate cooled to 10 K with a 1:1 ratio. *Figure 3* presents a comparison of the VUV photoabsorption spectra of these layered and mixed ices with that of the pure H<sub>2</sub>O and NH<sub>3</sub> ices. Pure NH<sub>3</sub> ice has a broad absorption band from 110 – 200 nm with maximum absorptions at 125 and 178 nm. Pure H<sub>2</sub>O ice has a broad band extending till 160 nm with the maximum absorption at 145 nm. Photoabsorption spectrum of layered ices NH<sub>3</sub> below H<sub>2</sub>O has a band from 110 - 200 nm with three absorptions peaks at 125 nm, 145 nm and 178 nm. However, in the mixed H<sub>2</sub>O and NH<sub>3</sub> ices there are only two distinct maximum absorptions at 125 and 180 nm as this could be due to the different in the absorption cross section between these two molecules.

On the surface of icy satellites like Charon, rich in H<sub>2</sub>O and NH<sub>3</sub>, the presence of NH<sub>4</sub>OH is inevitable [13]. It is evident from *Figure 4* that the characteristic absorption of NH<sub>4</sub>OH closely resembles that of NH<sub>3</sub> – H<sub>2</sub>O ice mixtures except for the tail which extends up to 190 nm. NH<sub>4</sub>OH ice has a maximum absorption band centered at 120 nm and 145 nm followed by another absorption band centered at 172 nm, where these two peaks arise from the OH and NH absorptions, respectively, in the NH<sub>4</sub>OH molecule. Spectra recorded by warming up the NH<sub>4</sub>OH ice up to 130 K did not show any significant change and beyond 130 K the ice

was found to sublime (Figure 4a).

Unlike the Pluto ice mixtures where sublimation of molecules were observed at very low temperatures, Charon ice mixtures were warmed up to 150 K due to the larger concentration of H<sub>2</sub>O governing the ice mixture sublimation. From spectra (Figure 4b) acquired at various temperatures during the warm-up process the matrix effect was clearly seen for the layered ice deposit NH<sub>3</sub> below H<sub>2</sub>O. Due to a phase change in NH<sub>3</sub> ices [14-15] the spectral band in the 160 -180 nm region was found to significantly shift in the absorption peak for the spectra recorded at 80 K. For these ice mixtures such change in peak position was not observed though infrared spectral studies using a similar mixture report phase change to take place in the NH<sub>3</sub>-H<sub>2</sub>O ice mixture. The 145 nm peak that corresponds to H<sub>2</sub>O appears in the ice mixture at 150 K is due to the sublimation of NH<sub>3</sub> molecules. The rest of the peaks corresponding to NH<sub>3</sub> show that the molecule is still trapped in the H<sub>2</sub>O matrix.

### Conclusion and Implications

VUV photoabsorption spectra of the dominant ices on Pluto and Charon were recorded over a range of temperatures. When found in mixtures, interaction between the molecules N<sub>2</sub>, CH<sub>4</sub> and CO were found to contribute to an additional absorption beyond 160 nm until 180 nm which is transparent in the respective pure ices. Addition of H<sub>2</sub>O molecules did not affect the spectra recorded for the prime ice composition of Pluto. By simulating Charon's chemical composition using NH<sub>3</sub>, H<sub>2</sub>O mixtures and NH<sub>4</sub>OH molecules we could clearly observe typical absorption bands that will allow us to know whether NH<sub>3</sub> exist as a mixture with H<sub>2</sub>O or as a layer below H<sub>2</sub>O. The difference in absorption limit for NH<sub>3</sub>-H<sub>2</sub>O mixture/layered deposit and NH<sub>4</sub>OH ice may be used to differentiate between the mixtures and NH<sub>4</sub>OH. The lack of UV absorbing atmosphere over Charon makes it easier to compare the results presented. Future laboratory simulation experiments will focus on the changes in the photoabsorption spectra due to irradiation of such mixtures that are studied at conditions commensurate to Pluto and Charon.

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**Figure caption**

**Figure 1:** Schematic of the Experimental Facility housed at NSRRC, Taiwan to record VUV spectra of Pluto and Charon ice analogues.

**Figure 2:** VUV Photoabsorption spectra of Pluto ice mixtures at 10 K and warmed to 30 K.

**Figure 3:** VUV Photoabsorption spectra of Charon ice mixtures at 10 K mixed and layered deposits, compared with the pure astrochemical ices of  $\text{NH}_3$  and  $\text{H}_2\text{O}$  at 10 K, and a product of ammonia and water:  $\text{NH}_4\text{OH}$ .

**Figure 4:** Temperature dependent VUV photoabsorption spectra of Charon ice analogue, **(a)**  $\text{NH}_4\text{OH}$ , **(b)**  $\text{NH}_3\text{-H}_2\text{O}$  mixture and layer.



**Table1:** Peak positions observed in the photoabsorption of pure ices  $N_2$ , CO,  $CH_4$ ,  $H_2O$  [8] and the Pluto ice mixtures with and without  $H_2O$ . The spectral scan steps for ice mixtures were 1 nm.

$N_2$ (nm)	CO (nm)	$CH_4$ (nm)	Pluto mixture (nm)	Pluto mixture with water (nm)
111.5	130.5	110 - 133	121	121
113.1	132.6	$H_2O$ (nm)	123	123
114.9	135	110 - 160	130	130
116.7	137.2		133	133
118.5	139.7		137	137
120.3	142.2		140	140
122.2	145.3		142	142
123	148.5		145	145
124.5	152.8		148	148
125.2	156.2		152	152
126.8			155	155
127.5				
129.2				
130				
131.8				
132.8				
134.2				
135.6				
137.2				
138.6				
142				
145.5				

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Figure 1

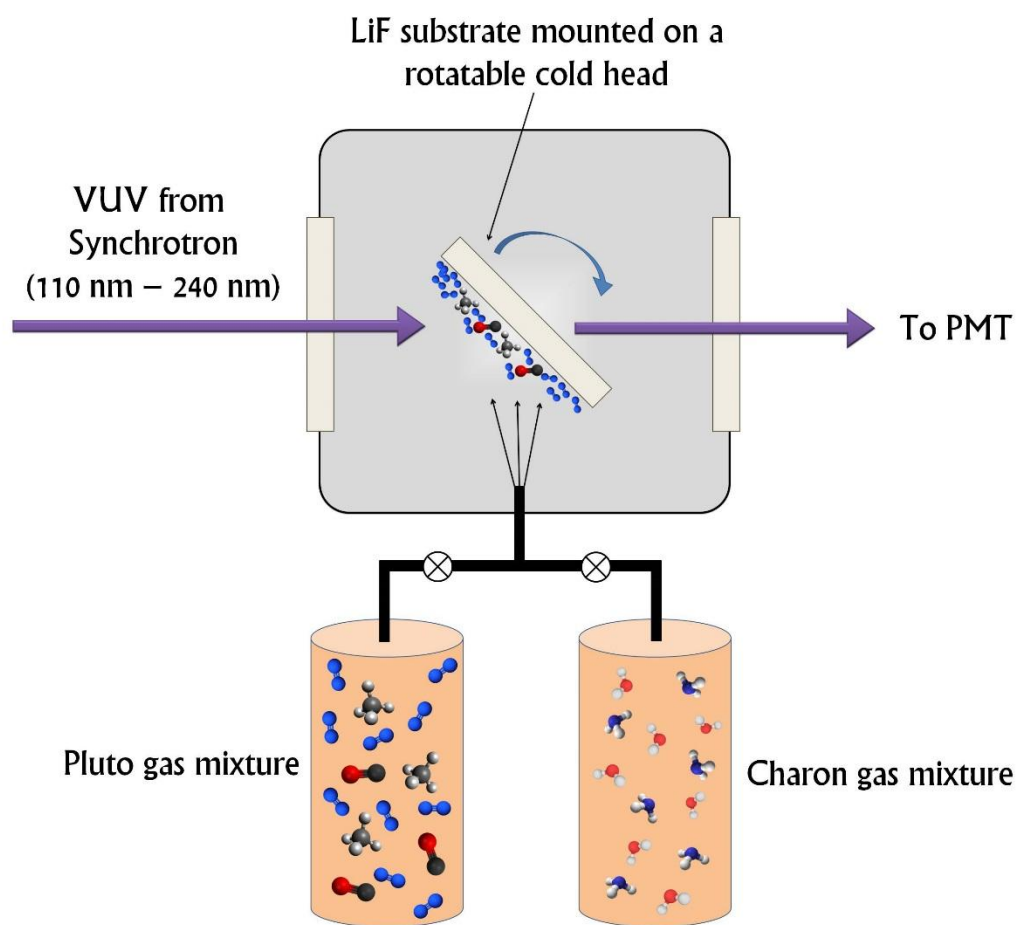


Figure 2

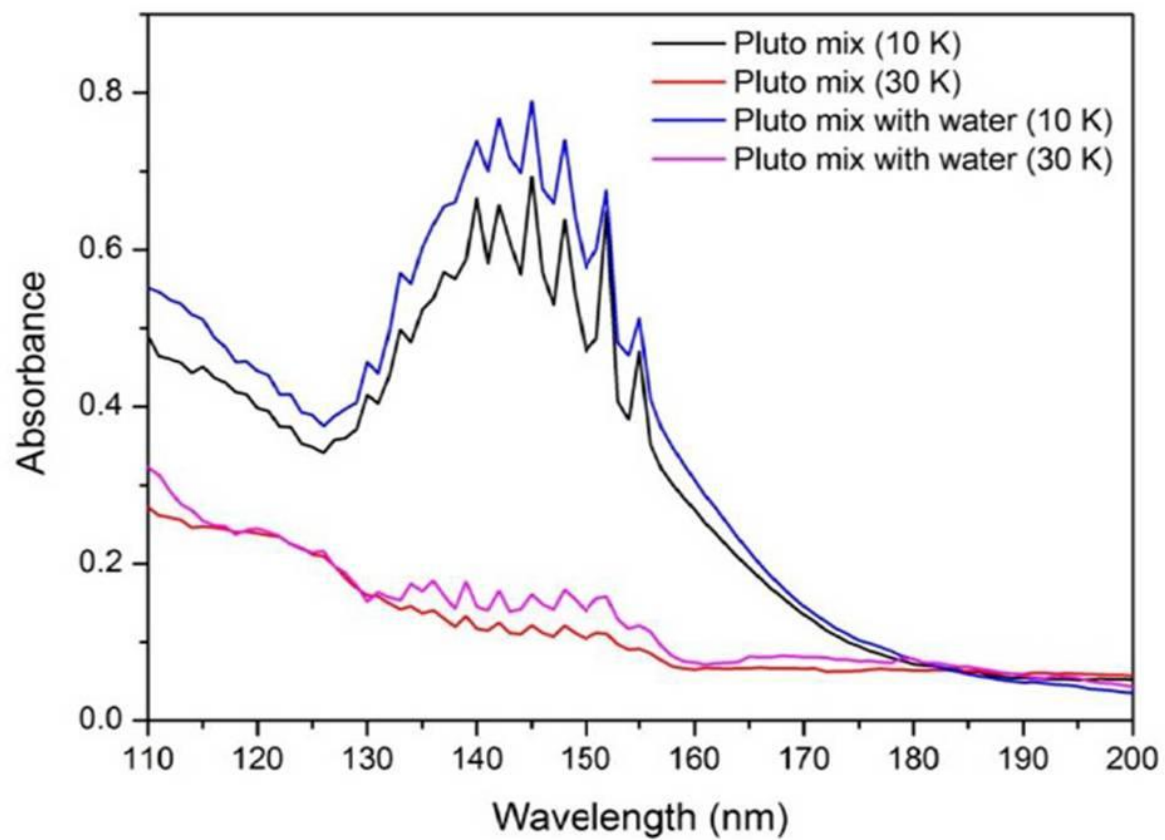


Figure 3

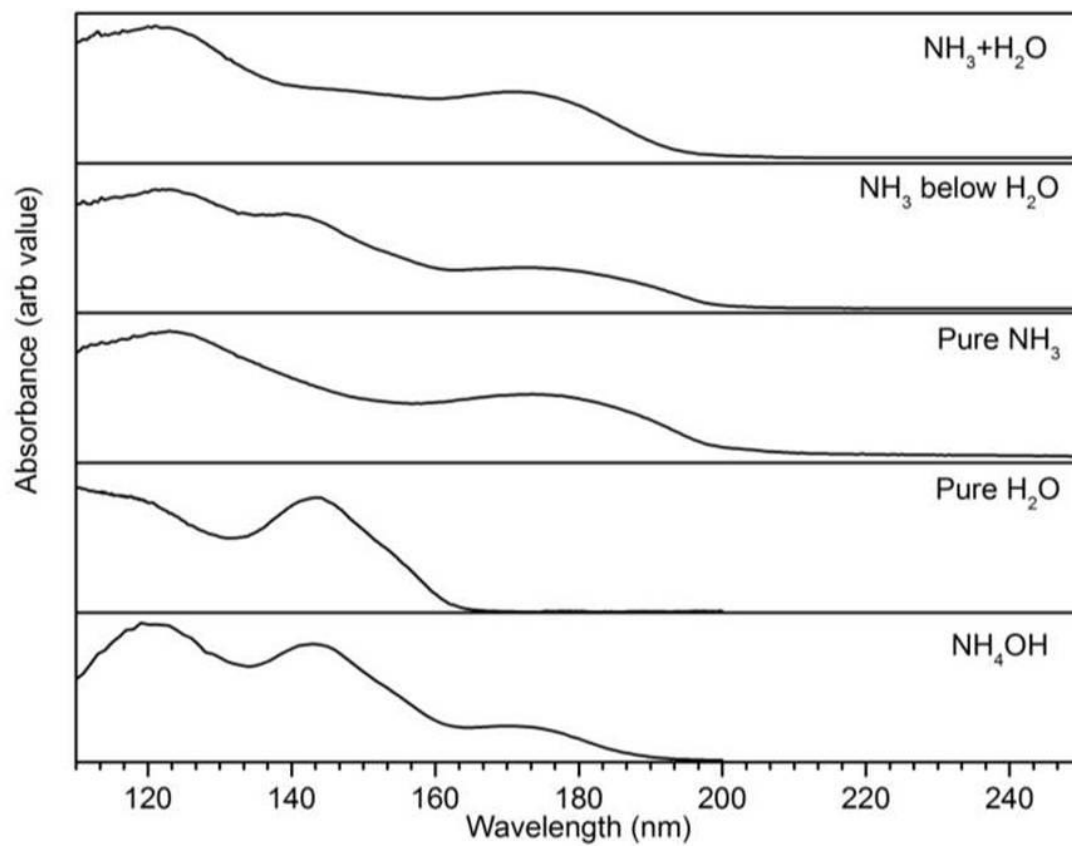


Figure 4a

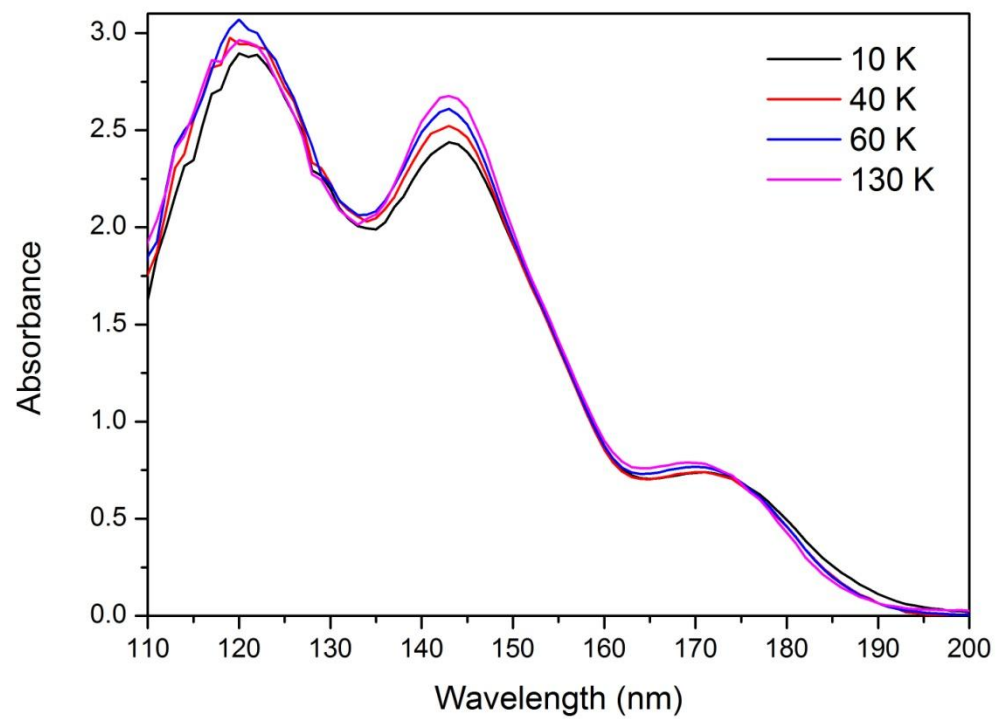
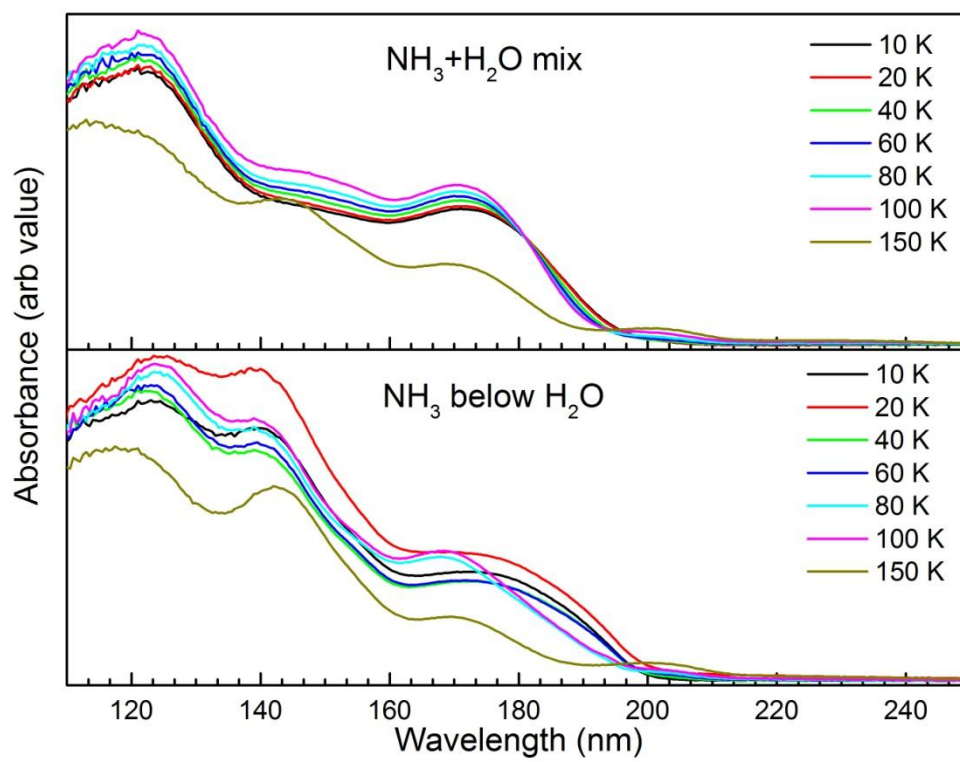
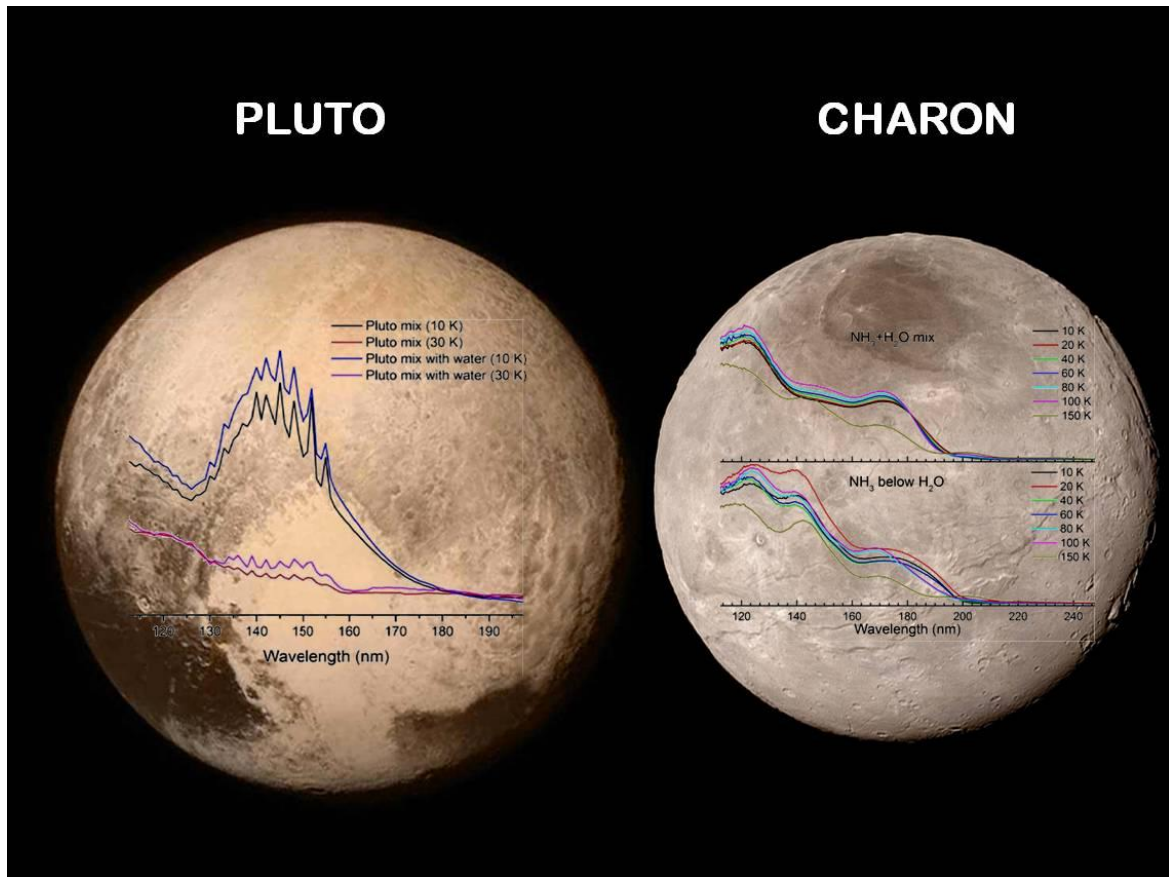


Figure 4b



## Graphical abstract





## Highlights:

- First VUV spectra of prime ice analogues of Pluto and Charon ice mixtures.
- Pluto ice analogue is an icy mixture of  $\text{N}_2$ ,  $\text{CO}$ ,  $\text{CH}_4$ , with and without  $\text{H}_2\text{O}$ .
- No significant change in the Pluto spectra due to presence of  $\text{H}_2\text{O}$ .
- Charon ice analogue is an icy mixture of  $\text{NH}_3$  and  $\text{H}_2\text{O}$ .
- These spectra may help to interpret the P-Alice data from *New Horizons*.