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Vacuum Ultraviolet Photoabsorption of Prime Ice Analogues of Pluto and Charon

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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 (N₂), carbon monoxide (CO), methane (CH₄) and water (H₂O) prepared with a 100:1:1:3 ratio, respectively. Photoabsorption of icy mixtures with and without H₂O were recorded and no significant changes in the spectra due to presence of H₂O were observed. For Charon a VUV photoabsorption spectra of an ice analogue containing ammonia (NH₃) and H₂O prepared with a 1:1 ratio was recorded, a spectrum of ammonium hydroxide (NH₄OH) 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 $\text{N}_2/\text{CH}_4/\text{CO}$ [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 $\text{N}_2:\text{CO}:\text{CH}_4:\text{H}_2\text{O} = 100:1:1:3$ 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 ($\text{N}_2:\text{CO}:\text{CH}_4$): 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 $\text{N}_2:\text{CO}:\text{CH}_4$ 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 CH₄ 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 N₂ matrix subliming off at 30 K leaving behind CH₄ and CO. These suggest the absorption in the 160 – 180 nm at 10 K could be due to the interaction of CH₄, CO with the N₂ molecules.

The spectrum recorded after adding H₂O molecules to the gas mixture and then depositing the refined mixture at 10 K was found to be similar to that recorded without the H₂O molecules. No significant changes in the spectrum were seen throughout the spectrum. This could be due to the H₂O 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 H₂O. The spectrum at 30 K for the mixture with H₂O was similar to the spectrum recorded without H₂O. This clearly shows even warming up the ice has no significant H₂O 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), H₂O and NH₃ 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 H₂O and NH₃ ices. Pure NH₃ ice has a broad absorption band from 110 – 200 nm with maximum absorptions at 125 and 178 nm. Pure H₂O ice has a broad band extending till 160 nm with the maximum absorption at 145 nm. Photoabsorption spectrum of layered ices NH₃ below H₂O has a band from 110 - 200 nm with three absorptions peaks at 125 nm, 145 nm and 178 nm. However, in the mixed H₂O and NH₃ 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 H₂O and NH₃, the presence of NH₄OH is inevitable [13]. It is evident from *Figure 4* that the characteristic absorption of NH₄OH closely resembles that of NH₃ – H₂O ice mixtures except for the tail which extends up to 190 nm. NH₄OH 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 NH₄OH molecule. Spectra recorded by warming up the NH₄OH 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 H₂O 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 NH₃ below H₂O. Due to a phase change in NH₃ 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 NH₃-H₂O ice mixture. The 145 nm peak that corresponds to H₂O appears in the ice mixture at 150 K is due to the sublimation of NH₃ molecules. The rest of the peaks corresponding to NH₃ show that the molecule is still trapped in the H₂O 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 N₂, CH₄ 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 H₂O molecules did not affect the spectra recorded for the prime ice composition of Pluto. By simulating Charon's chemical composition using NH₃, H₂O mixtures and NH₄OH molecules we could clearly observe typical absorption bands that will allow us to know whether NH₃ exist as a mixture with H₂O or as a layer below H₂O. The difference in absorption limit for NH₃-H₂O mixture/layered deposit and NH₄OH ice may be used to differentiate between the mixtures and NH₄OH. 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 NH_3 and H_2O at 10 K, and a product of ammonia and water: NH_4OH .

Figure 4: Temperature dependent VUV photoabsorption spectra of Charon ice analogue, **(a)** NH_4OH , **(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 N_2 , CO , CH_4 , with and without H_2O .
- No significant change in the Pluto spectra due to presence of H_2O .
- Charon ice analogue is an icy mixture of NH_3 and H_2O .
- These spectra may help to interpret the P-Alice data from *New Horizons*.