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VACUUM ULTRAVIOLET PHOTOABSORPTION SPECTRA OF NITRILE ICES FOR THEIR IDENTIFICATION ON PLUTO

B. Sivaraman[1], S. Pavithraa[1], J.-I. Lo[2], B. N. Raja Sekhar[3], H. Hill[4], B.-M. Cheng[2], and N. J. Mason[5]
[1] Atomic Molecular and Optical Physics Division, Physical Research Laboratory, Ahmedabad, 380 009, India; bhala@prl.res.in
[2] National Synchrotron Radiation Research Center, Hsinchu 30076, Taiwan
[3] Atomic and Molecular Physics Division, BARC at RRCAT, Indore, 452 013, India
[4] International Space University, F-67400 Illkirch, France
[5] Department of Physical Sciences, The Open University, Milton Keynes, MK7 6AA, UK
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ABSTRACT

Icy bodies, such as Pluto, are known to harbor simple and complex molecules. The recent *New Horizons* flyby of Pluto has revealed a complex surface composed of bright and dark ice surfaces, indicating a rich chemistry based on nitrogen (N_2), methane (CH_4), and carbon monoxide (CO). Nitrile (CN) containing molecules such as acetonitrile (CH_3CN), propionitrile (CH_3CH_2CN), butyronitrile ($CH_3CH_2CH_2CN$), and isobutyronitrile ($(CH_3)_2CHCN$) are some of the nitrile molecules that are known to be synthesized by radiative processing of such simple ices. Through the provision of a spectral atlas for such compounds we propose that such nitriles may be identified from the ALICE payload on board *New Horizons*.

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

1. INTRODUCTION

After its near decadal journey *New Horizons* is now sending unprecedented images of Pluto's icy surface back to Earth. It is now necessary to evaluate and analyze these images and identify the molecules that are present in Pluto's icy mantle. While the main components are expected to be N_2 (Kelsi & Stern 2015), CH_4, and CO, it is probable that these form the basis of a richer ice chemistry initiated by irradiation of the surface and particles present in the atmosphere. Recent ground-based observations reported by Lorenzi et al. (2016) suggest an uneven distribution of simple ices and complex molecules. ALICE, the UltraViolet (UV) Imaging spectrometer (Kusnierkiewicz et al. 2005) on board *New Horizons* operating at wavelengths in 46.5–188 nm (~26.6–6.6 eV) could identify more complex chemical species present in Pluto's ices, should their spectral signatures be known (Schindhelm et al. 2015).

Since the 1940s several nitrile containing molecules, such as CN, HCN, HNC, HC_3N, CH_2CHCN, CH_3NC, NH_2CN, NH_2CH_2CN, CH_3CH_2CN, HC_7N, HC_9N, HCCNC, H_2CN, NaCN, OCN^-, CH_2CCHCN, CH_3C_5N, and CNCHO, have been discovered in the interstellar medium and, quite recently, the branched nitrile molecule $(CH_3)_2CH_2CN$ was reported to be present (Belloche et al. 2014). Therefore, it is highly likely that nitrile bearing molecules could have also been incorporated onto Pluto during its formation in our solar system. Furthermore, radiation processing of the N_2 and CH_4 ices present on Pluto has been shown to provide pathways for the synthesis of CN containing molecules such as acrylonitrile (CH_2CHCN; Kim & Kaiser 2012; Yu-Jong et al. 2012; Christopher et al. 2014) within the icy mantle; indeed, there has already been an attempt to identify the presence of acrylonitrile from ground-based observations at near-infrared wavelengths (Olkin et al. 2007).

Thus, there is a high probability for the presence of nitriles within Pluto's surface ices (Christopher et al. 2014) and therefore it is important to identify the spectral fingerprints by which *New Horizons* can resolve the chemical composition of Pluto's icy surface. The objective of the current study is to present a VUV spectral atlas of some simple nitrile molecules such as CH_3CN, CH_3CH_2CN, $CH_3CH_2CH_2CN$, and $(CH_3)_2CHCN$ in the ice phase obtained by recording VUV spectra using synchrotron radiation. Wide ranges of temperatures are present across icy bodies of the solar system and beyond; by recording VUV photoabsorption spectra as a function of temperature we can understand the morphology of the ice, whether amorphous or crystalline upon warming the ices formed at lower temperatures, and the presence of homodimers or even higher order clusters in the ice that affect the chemical reactivity (Bhuin et al. 2014). Therefore temperature-dependant studies of such ices are important. From our results we propose observable wavelengths that may help to detect nitrile molecules in an icy body dominated by N_2, CO and CH_4 such as Pluto.

2. EXPERIMENTAL METHOD

We have carried out a series of experiments to measure VUV spectra of nitrile molecules in the ice phase at the National Synchrotron Radiation Research Centre, NSRRC, in Taiwan. A detailed discussion of the experimental setup, liquid sample preparation, and spectra acquisition has been presented in an earlier publication (Hsiao-Chi et al. 2005; Kuo et al. 2007; Lu et al. 2008). In summary, the incident VUV light from beamline BL03 dispersed with a monochromator (cylindrical grating, 6 m) and passed through a gold mesh with transmission about 90%; to monitor and to normalize the beam, the photocurrent of the gold mesh was detected with an electrometer (Keithley 6512). Nitrile molecules were deposited onto a LiF window maintained at 10 K using a refrigerator system (APD HC-DE204S); therefore, we measured the absorption spectra in the VUV region to the limit of transmission of optical components, about 106 nm. For the absorption measurements, the VUV light from the synchrotron was perpendicularly intersected to the solid samples with the transmitted light incident upon a glass window coated with sodium salicylate, which converts incident UV light to visible

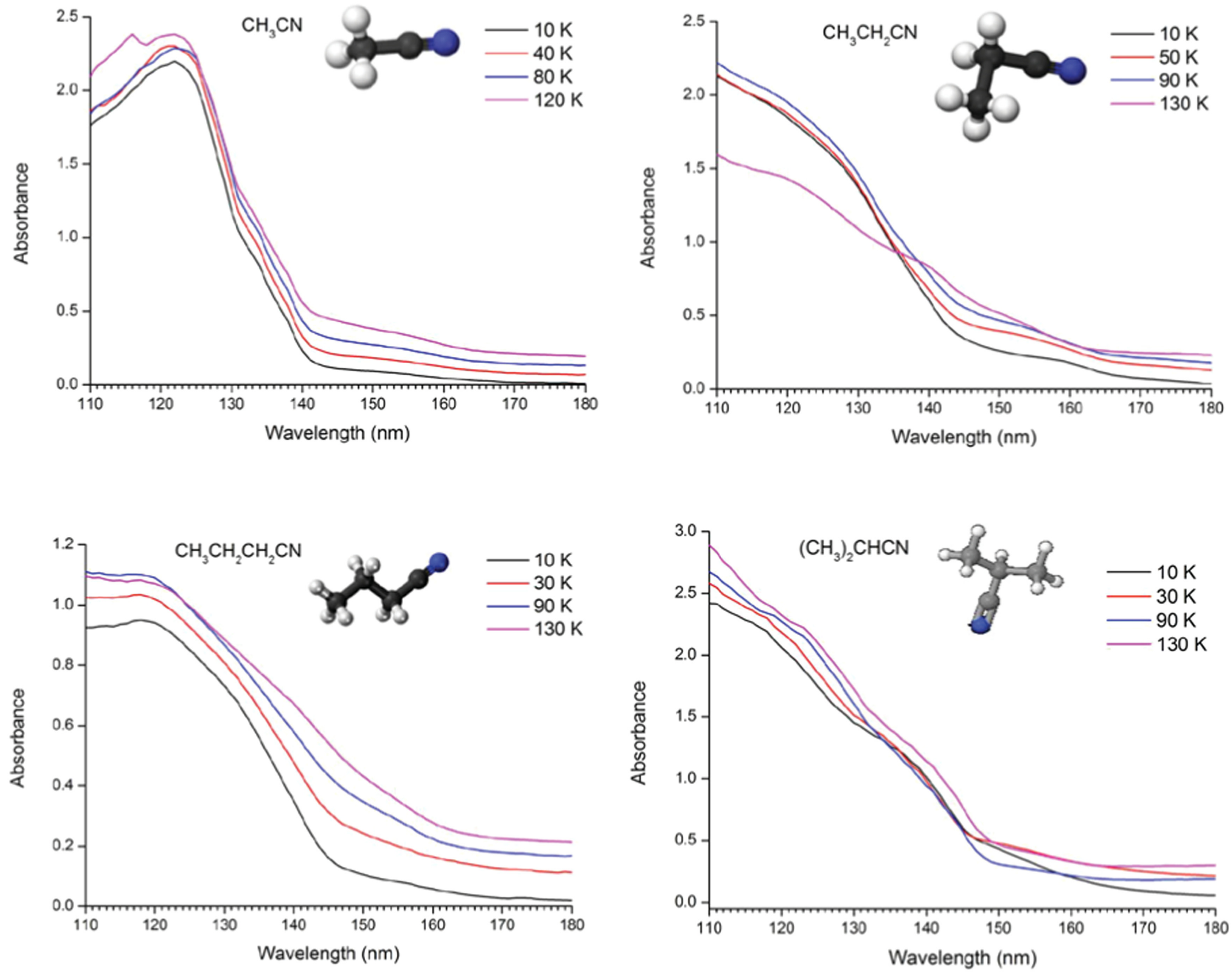

Figure 1. VUV photoabsorption spectra of acetonitrile, propionitrile, butyronitrile, and isobutyronitrile ices as a function of temperature. Note that baselines are displaced to show spectra at different temperatures.

light and was measured with a photomultiplier tube (Hamamatsu R943-02) in a photon-counting mode.

Nitrile molecules CH$_3$CN, CH$_3$CH$_2$CN, CH$_3$CH$_2$CH$_2$CN, and (CH$_3$)$_2$CHCN of high purity 99.8%, 99%, 99%, and 99.6%, respectively, were used to form pure nitrile ices on a VUV transmitting LiF substrate at 10 K. Upon deposition a spectrum was recorded at 10 K, the sample was then heated, and spectra were recorded in intervals of 10 K or 20 K depending on the spectral signatures obtained.

3. RESULTS

3.1. Acetonitrile

A VUV spectrum was measured for CH$_3$CN ice in the wavelength range 110–190 nm (11.3–6.5 eV) (Figure 1). CH$_3$CN was found to absorb up to 170 nm with a strong feature around 123 nm and two smaller absorption peaks at 134 and 138 nm. A second absorption peak was observed at about 151 nm in the 140–170 nm (8.8–7.3 eV) range.

Upon warming the ice to higher temperatures, all the spectral signatures observed at 10 K were found to be present up to 120 K (Figure 1) where a phase change in the CH$_3$CN ice has been reported (Bhuin et al. 2015).

3.2. Propionitrile

A VUV spectrum of CH$_3$CH$_2$CN was found to have strong absorption between 110 and 145 nm (11.3–8.5 eV) and another absorption band with a peak centered at 159 nm was observed in the region 145–180 nm (Figure 1). No significant changes in the absorption spectra were observed in spectra recorded up to 130 K. However, above 130 K the spectrum was found to undergo significant changes in its absorption between the 110 and 135 nm region with a new peak appearing at 140 nm and extending to the second absorption band, which was also shortened, by nearly 20 nm (Figure 1).

3.3. Butyronitrile and Isobutyronitrile

VUV spectra of CH$_3$CH$_2$CH$_2$CN and (CH$_3$)$_2$CHCN were recorded between 110 and 145 nm (11.3–8.5 eV). CH$_3$CH$_2$CH$_2$CN showed one broad absorption band with a peak at 119 nm and with a shoulder at 132 nm (Figure 1). A second absorption band was observed in the region

145–170 nm. Upon warming the ice to 30 K no changes in the spectral shape were observed. However, a spectrum recorded by warming the ice to 90 K was found to show a slight intensity change in the absorption between 145 and 170 nm with a peak intensifying at 155 nm while at the same time no absorption beyond 165 nm was observed. Upon further heating to 130 K the spectrum was found to be similar to the spectrum recorded at 90 K with the 132 nm peak observed in the 10 K spectrum shifted to about 140 nm (Figure 1).

The $(CH_3)_2CHCN$ spectrum recorded at 10 K was found to show strong absorption in the 110–146 nm region with two strong peaks centered around 120 and 139 nm (Figure 1). Beyond this, spectra showed an extended absorption up until 170 nm. After warming the ice to 30 K, the spectrum recorded was found to be similar to the spectrum recorded at 10 K. Further heating to 50 K revealed differences in the 145 nm to higher wavelength region where absorption was found up to 160 nm (Figure 1). The intensity of the 139 nm peak fell when warming the ice from 30 to 50 K. On further heating to 150 K revealed spectra similar to those recorded at 50 K.

4. DISCUSSION AND IMPLICATIONS

In the case of CH_3CN no change in the spectral shape was found even when the ice was annealed to the phase change temperature around 120 K, whereas for CH_3CH_2CN the spectrum recorded at 130 K was observed to be very different to that obtained at 10 K. This change in the spectral signature could be due to the phase change occurring at these higher temperatures in CH_3CH_2CN ices as revealed by the infrared spectral observations (Marla et al. 2010). However, for $CH_3CH_2CH_2CN$ ices the spectrum recorded at 130 K showed changes in the absorbance and peak position which could be an indication of the phase change that occurs in $CH_3CH_2CH_2CN$ ices as reported by the infrared spectral studies at similar conditions. This phase change from amorphous to crystalline could be expected in the $(CH_3)_2CHCN$ ice sample but from the VUV photoabsorption spectra recorded for $(CH_3)_2CHCN$ we are unable to observe such phase change and the temperature at which it occurs. From our previous results for other molecules we understand that for the case of $(CH_3)_2CHCN$ we have to rely on the infrared spectra of this molecule in order to observe the morphology changes that occur by warming the ice deposited at 10 K.

From the temperature-dependent spectra obtained, we could clearly observe that all four nitrile molecules studied had a strong absorption band between 110 and 145 nm (Figure 1) followed by a relatively less intense band from nearly 145 nm to approximately 175 nm (Figure 2). These spectral characteristics may be used to identify nitriles in the surface ice of Pluto.

VUV spectra for the Pluto dominant molecules, N_2, CH_4 are well known. Methane ice spectra show no absorption above 136 nm (Mason et al. 2006) while VUV absorption in nitrogen ices may vary in the 120–150 nm region but most spectra beyond 145 nm report no significant absorption. CO ice shows a discrete feature at 150–160 nm but nothing beyond (Cruz-Diaz et al. 2014). However, for the four nitrile molecules studied here there is a second absorption band starting around 145 nm and extending up to nearly 175 nm (Figure 2). Therefore the presence of continuous absorption in any ice spectra recorded from Pluto's surface between 150 and 175 nm could be an indicator on the presence of nitriles.

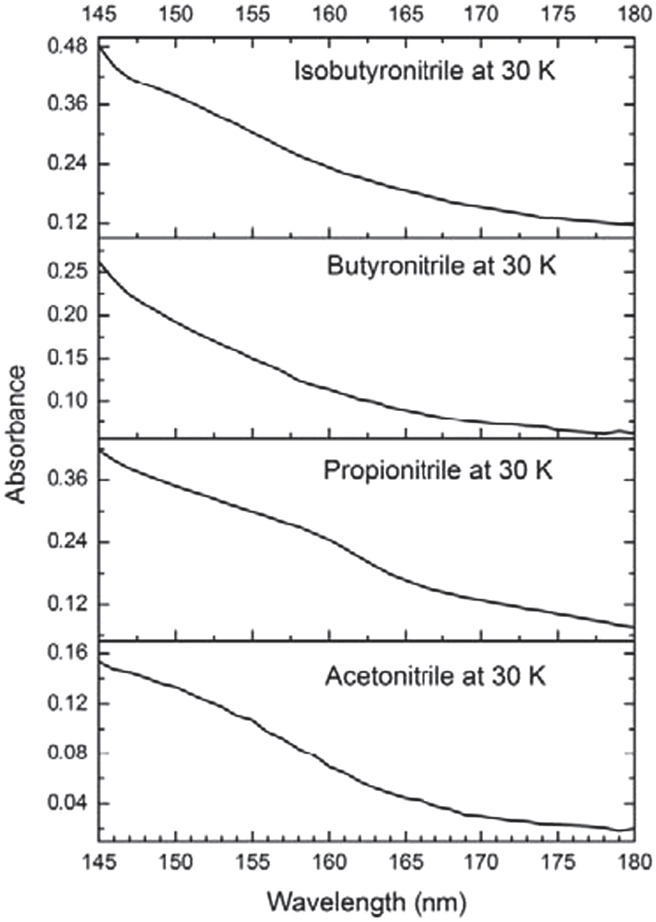

Figure 2. VUV photoabsorption spectra, in the 145–180 nm region, for all the four nitriles studied are compared to show the similarity in absorption beyond 150 nm.

Water ice has been observed on Charon (Brown & Calvin 2000) and is present on other Kuiper Belt objects (Michael et al. 2000; Jewitt & Luu 2004) too. With the recent report of water ice on Pluto (Grundy et al. 2016), its effect in the photoabsorption spectrum of Pluto should not be ignored. Similarly the formation of oxygen ice by radiolysis should be considered. However, any water absorption band would only extend to 161 nm and for oxygen absorption the band would only extend up to 190 nm (Mason et al. 2006; Lu et al. 2008).

Hence an absorption band between 150 and 175 nm could be a good indication of the presence of nitrile molecules within the surface ice of Pluto even in the presence of water and oxygen. Sputtering and/or desorption from such an ice surface will lead to the release of nitriles and/or their fragmentation products into the atmosphere of Pluto where they may be observed and correlated with the ice spectra. The signatures of these processes are subject to current studies. However, since pure nitrile ices were studied, there could be some matrix effects that are unaccounted for on Pluto because of either ice matrix effects or matrix effects caused by the presence of other complex organics.

5. CONCLUSION

The first VUV photoabsorption spectra of nitrile bearing molecules such as aceto, propio, butyro, and iso-butyronitrile molecules are reported for ices prepared at 10 K and at higher temperatures. The spectral signatures of all the nitrile ices were found to be similar in the 110–145 nm region with subtle changes in the absorption intensity due to morphology changes (amorphous to crystalline) upon warming the ice to higher temperatures. Comparison of the nitrile spectra with the spectra of several of the simpler and dominant molecules on Pluto (N_2, CH_4, and CO) and other possible trace species such as water and oxygen, suggest that the detection of continuous absorption in the 150–175 nm region may be a good indicator for the detection of nitrile molecules in the surface ice of Pluto.

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