Vacuum ultraviolet photoabsorption spectra of an in-situ synthesized peptide precursor: hydroxylamine on a cold astrochemical dust analogue

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Abstract. The recent discovery of hydroxylamine (NH$_2$OH) molecule in the interstellar medium emphasizes the need to study the molecule in laboratory astrochemical ice analogues. Here, we present the first vacuum ultraviolet photoabsorption spectrum of hydroxylamine ice synthesized in-situ in an ammonia–oxygen (6:1) ice mixture irradiated by $\sim 10$ eV photons from synchrotron radiation source. The appearance of a new band between the 180–240 nm, with a band centered at $\sim 207$ nm, is assigned to the characteristic absorption of hydroxylamine molecule in the ice phase. This band maybe used in ammonia dominated, oxygen bearing, icy surfaces for the identification of hydroxylamine.

1 Introduction

Since the detection of ammonia (NH$_3$) in the Interstellar Medium (ISM) in the 1960’s [1], –NH$_2$ and –NH bearing molecules are expected to be present in the ISM. Similarly, in the outer Solar System, NH$_3$ is a surface ice component in several icy bodies, including comets [2]. The recent discovery of ammoniated salts on a comet [3] has revealed the extent of chemistry involving NH$_3$. Further, the detections of a host of NH bearing molecules like formamide (NH$_2$CHO) [4], methanimine (CH$_2$NH) [5], methylamine (CH$_3$NH$_2$) [6, 7] and cyanamide (NH$_2$CN) [8] as well as the imidogen (NH) [9] and amino radicals (NH$_2$) [10] has revealed the rich chemistry of amides and amines in the ISM.

Identification of acetamide (CH$_3$CONH$_2$) [11], ketenimine (CH$_2$C=NH) [12], amino acetonitrile (NCCH$_2$NH$_2$) [13], carbodiimide (HN$\equiv$CNH) [14] and ethanimine (CH$_2$CHNH)$_2$ [15], N-methylformamide (CH$_3$NHCHO) and even urea ((NH$_2$)$_2$CO) [16–18] has led to an increased number of observational campaigns to unambiguously identify amino acids. Search for the presence of amino acids, the building blocks of proteins, are central to understanding the origin of life in astro-biological point of view. Glycine (NH$_2$CH$_2$COOH), the simplest amino acid has been searched for since the 1980s [2, 19] (and references therein) and even though several detections were reported, of them have been confirmed and the unambiguous detection of glycine is still awaited. But glycine was found in the comets 67P and 82P [20, 21].

The finding of such diverse molecular derivatives of NH$_3$ supports the argument, derived from laboratory analogue experiments, for the likely presence of peptide precursors such as hydroxylamine (NH$_2$OH) on the cold dust in the ISM and radiation processed surface ices in the Solar System. Indeed, laboratory simulation of NH$_3$ bearing ices, in ice mixtures with oxygen (O$_2$) [22] (and references therein) have revealed the mechanism involved in the synthesis of NH$_2$OH, which is the most commonly synthesized molecule in NH$_3$–O$_2$ ice mixture on a dust surface even at higher temperatures ($\sim 200$ K). As predicted by the laboratory analogue the first detection of NH$_2$OH in NH$_3$ dominated and O$_2$ bearing regions of the ISM, has very recently been reported [23] in quiescent molecular cloud in the Galactic Center. However, Rivilla et al. stressed the need for more laboratory analogue experiments to understand
the formation mechanisms of NH$_2$OH in the ice versus gas phase.

Furthermore, the spectral signatures required to make an unambiguous identification of NH$_2$OH are also lacking, especially to support space-based observations in the Vacuum Ultra Violet (VUV) region. Here we report the first VUV photoabsorption spectrum of solid NH$_2$OH, synthesized in-situ in an NH$_3$–O$_2$ ice mixture, which will both aid our search for these molecules in icy mantles and aid our understanding on the physico-chemical nature of NH$_2$OH molecule. NH$_2$OH is a possible precursor for formation of amino acids, therefore, our understanding of NH$_2$OH molecule in the ice phase will have implications in the complex biomolecules synthesis on cold ISM dust.

2 Experimental methodology

The present experiments were carried out in an end station attached to the high flux beam line BL03A1 of the storage ring (1.5 GeV) at the National Synchrotron Radiation Research Centre, NSRRC, in Taiwan. The end station is an ultrahigh vacuum chamber, pressure at $10^{-9}$ mbar, that houses the tip of a cold head that reaches temperatures as low as 3 K. VUV transparent windows made of Lithium Fluoride (LiF) were used as the cold dust analogue on which to form molecular ices. The details of experimental setup used at the end station have been discussed earlier [24, 25].

The spectrum recorded after the LiF substrate was cooled to 3 K, and before sample deposition, was taken as $I_0$. After recording $I_0$, premixed gaseous samples of pure NH$_3$ and O$_2$ (6:1 ratio) were deposited, at $5 \times 10^{-8}$ mbar for 390 s, approximately 20 monolayers, onto a LiF window maintained at 3 K. The spectra recorded post deposition were taken as $I$. Using the Beer–Lambert law VUV photoabsorption spectra of the molecular ices were derived. The photoabsorption spectrum obtained at 3 K, after deposition, was then used as a reference spectrum. The NH$_3$:O$_2$ ice mixture held at 3 K was then irradiated at $\sim 10 \text{ eV}$ (123.9 nm) for 3 h and the spectrum was recorded once more. The sample was then warmed (at the rate of 5 K min$^{-1}$) to higher temperatures until full sublimation of the irradiated ice, with spectra being recorded at regular temperature intervals.

3 Results and discussion

Spectra recorded after depositing the desired ratio of NH$_3$:O$_2$ mixture at on to the LiF substrate held at 3 K, showed characteristic bands corresponding to NH$_3$ at $\sim 170$ nm with an absorption edge around 200 nm [25, 26]. The other peak observed at $\sim 140$ nm is assigned to the oxygen molecule in the NH$_3$ ice before irradiation. No absorption bands were observed beyond 200 nm in the absorption spectrum after deposition and before irradiation. Upon irradiating the ice using quasi monoenergetic ($\sim 10 \text{ eV}$) photons for three hours and recording a spectrum at the end of irradiation the intensity of the characteristic NH$_3$ band at 170 nm reduced (Fig. 1), whilst the intensity of the 140 nm band remained broadly the same. The appearance of a new absorption band beyond 200 nm (Fig. 1) is a clear indication of a new molecule being formed during irradiation.

The temperature dependent spectra of the irradiated ice can reveal the chemical nature of the observed new band beyond 200 nm, as most of the NH$_3$:O$_2$ left over from irradiation sublimes while warming the ice: less than 35 K for O$_2$ ice and less than 85 K for NH$_3$ ice. So the spectral signatures observed beyond the sublimation temperatures of these molecules we started with are clear signatures of the irradiated products. Hence, temperature dependent spectra of the ice post-irradiation, in comparison with studies carried out in similar ices probed using Infrared (IR) spectroscopy [22], can be used when assigning the new peaks. By warming the ice to higher temperatures at the rate of 5 K min$^{-1}$ and recording spectra at different temperatures we could observe the spectrum is unaltered until 130 K, with the two prominent bands centered at 140 nm and 207 nm remaining unchanged (Fig. 2).

However, by further increasing the temperature to 150 K, the spectral signatures at 140 nm and 207 nm band were observed to more prominent, and at 160 K the 140 nm band was absent whilst the 207 nm band remained and a band centered at $\sim 127$ nm was also observed (Fig. 2). The 207 nm band remained in the spectra until 220 K, suggesting another molecule (among the products obtained from irradiation) to be responsible for this absorption at these wavelengths. This suggests that the molecule synthesized by irradiation was sublimating at these higher temperatures and also the irradiation products must be molecules containing N, O and H atoms, free of C atoms, as we do...
molecules such as H₂O to 150 K. Though the sublimation temperature for some of the molecules, listed above, lies less than or equal to vary and also the sublimation temperatures of most molecules are reported [22]. Spectra are stacked for clarity.

At the end of the irradiation period the significant reduction observed in the 170 nm band indicates the loss of NH₃ from the ice and a similar drop in intensity is expected for the 140 nm that was assigned to be from the absorption of oxygen molecule before irradiation. However, the 140 nm band remained prominent even after irradiation, suggesting the appearance of another molecule with strong absorption at 140 nm. Though oxygen molecules are dissociated releasing O atoms for reactions these can further combine with molecular oxygen synthesizing ozone, but the characteristic Hartley (240–280 nm) absorption for ozone was absent, suggesting insufficient O atoms for synthesizing ozone in sufficient concentrations to be measured. Nevertheless, ozone absorption in the VUV wavelength region has a band at 140 nm [27] even though the Hartley band was absent at higher temperatures, greater than or equal to 60 K. However, the presence of the band centered at 140 nm until 150 K without any significant change in intensity rules out the role of ozone molecule being responsible for this absorption because of its lower sublimation temperature [27].

Temperature dependent spectra revealed the 140 nm band to be prominent until 150 K but it was absent in the spectrum recorded at 160 K. Therefore, based on the nature of the irradiated ice, characteristic absorption at 140 nm [28] and sublimation temperature, we conclude H₂O to be one of the major molecular component contributing to the photoabsorption spectra along with the NH₃OH up until 160 K, beyond which the spectrum recorded corresponds to the NH₃OH molecular ice left over from irradiation. The gas phase spectrum of NH₃OH [29] shows strong absorption at lower wavelengths (below 160 nm) and a continuous absorption, with peak around 182 nm, until 220 nm. Whereas the VUV photoabsorption of solid phase NH₃OH shows strong absorption in the 180–240 nm with a peak around ~207 nm.

The broad absorption band of NH₃OH was compared, in Fig. 3, with a similar band observed from the in-situ synthesis of carbonic acid (H₂CO₃) molecule [30]. Both of these molecules were observed to have absorption bands lying close to one another at higher wavelengths. In fact, there is ~7 nm shift in the band centers which is very useful for identifying these molecules. In addition, NH₃OH and H₂CO₃ molecules that are synthesized in-situ, from VUV photon irradiation, originate from different ice mixtures; NH₃:O₂ and H₂O:CO₂, respectively. Therefore, the abundance of reactant molecules, such as NH₃/O₂/H₂O/CO₂, on the surfaces of icy satellites or other cold surface ice bearing planetary bodies, along with the observation of characteristic absorption bands will help us to identify the presence of such intermediate ammoniated species that are imperative for the complex molecules of life.

**Fig. 2** Temperature dependent VUV spectra of the irradiated ice warmed at the rate of 5 K min⁻¹. Spectra are stacked for clarity.

not involve any molecule containing C atoms in the ice mixture.

Upon irradiation of NH₃–O₂ ice, N/H/O atoms are formed for reaction with the molecules in the surrounding ice. Perhaps the excess amount of NH₃ used in this experiments, after reacting with the O (¹D) atoms, released from oxygen molecule dissociation, will readily form NH₂OH [22]. There are a number of other molecules such as OH, H₂O, H₂O₂, O₃, NO, NO₂, N₂O, N₂O₃ that may be to be co-synthesized in an irradiated NH₃–O₂ ice analogue [22]. However, the abundances of such synthesized molecules are reported [22] to vary and also the sublimation temperatures of most of the molecules, listed above, lies less than or equal to 150 K. Though the sublimation temperature for molecules such as H₂O₂ and NH₂OH are known to be greater than 150 K, their relative abundances reported, (NH₂OH/H₂O₂ = 10²) [22], indicates NH₂OH to be likely candidate left over on the substrate at temperatures greater than 150 K and contributing to the photoabsorption spectra at such higher temperatures. So the broad band observed at ~207 nm and the weak absorption at ~127 nm, in the spectra from 160 to 220 K, are assigned to the NH₂OH molecules (Fig. 2). In fact, the absorption band centered at ~207 nm was observed to be present in the irradiated ice at 3 K until sublimation at 220 K.
4 Conclusion

In-situ synthesized hydroxylamine in a mixture of NH$_3$–O$_2$ ices subjected to 10 eV photon irradiation was found to remain on the dust analogue until 220 K with characteristic spectral signatures at VUV wavelengths. The broad band observed with a peak center at ≈ 207 nm, corresponding to NH$_2$OH, remained unaltered from lower to higher temperatures, until sublimation of the ice. As this broad band appears away from the absorption of the reactant molecules (NH$_3$/O$_2$), as well as from the other abundant simple molecular ices such as H$_2$O/CO$_2$, this band can be used to detect the presence of NH$_2$OH on the icy surfaces in the Solar System.

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