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# A possible answer to the mysterious non-detection of hydroxylamine in space: the thermal desorption mechanism

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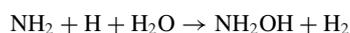
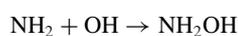
## ABSTRACT

The presence of  $\text{NH}_2\text{OH}$ , one of the main precursors in the formation of amino-acids, on dust grain mantles, may be the most obvious elucidation for the creation of large pre-biotic molecules in the interstellar medium. However, while many laboratory experimental studies, to simulate the icy grain chemistry in space, found that  $\text{NH}_2\text{OH}$  molecules may be easily formed in solid phase with high abundances and then they should desorb, through a temperature-induced desorption into the gas phase, with the same high abundances; all the spatial observations conclude that  $\text{NH}_2\text{OH}$  is not detected in gas phase within any of the explored astronomical sources. Such inconsistencies between laboratory experiment simulations and spatial observations lead our investigations towards this experimental study to see if there is any chemical transformation of  $\text{NH}_2\text{OH}$ , occurring in the solid phase before the desorption processes of  $\text{NH}_2\text{OH}$  from the mantle of interstellar icy grains. Our experimental results show that the heating of  $\text{NH}_2\text{OH}-\text{H}_2\text{O}$  ices lead to a decomposition of  $\text{NH}_2\text{OH}$  into  $\text{HNO}$ ,  $\text{NH}_3$  and  $\text{O}_2$ , even before reaching its desorption temperature. We show through this work that the  $\text{NH}_2\text{OH}$  non-detection from previous examined astronomical sources could mainly due to its high reactivity in solid phase on the icy interstellar grains.

**Key words:** astrochemistry – methods: laboratory – techniques: spectroscopic – ISM: clouds – ISM: molecules.

## 1 INTRODUCTION

Although various complex molecules have already been identified in space, a simple species constantly considered as the main precursor of amino acids,  $\text{NH}_2\text{OH}$  is still not detected. To solve this mystery many laboratory investigation have focused their theoretical as well as experimental investigations into the formation of  $\text{NH}_2\text{OH}$  under extreme conditions similar to those found in the interstellar medium. From an experimental point of view, most of the studies have been devoted into the synthesis processes of hydroxylamine in solid phase at cryogenic temperatures. Nishi, Shinohara and Okuyama (1984) found that the UV irradiation of ammonia containing ices may be one of the efficient reaction pathways to produce hydroxylamine through radical recombination involving,  $\text{NH}_2$ ,  $\text{H}$ ,  $\text{OH}$  and  $\text{H}_2\text{O}$ :



Using electron irradiations of ammonia–water ices between 10 and 50 K, Zheng & Kaiser (2010) investigated the  $\text{NH}_2\text{OH}$  for-

mation, where the synthesis of molecular hydroxylamine has been accompanied by many secondary reaction products such as  $\text{H}_2$ ,  $\text{H}_2\text{O}_2$  and  $\text{N}_2\text{H}_4$ . A few years ago Strazzulla’s group (Strazzulla & Palumbo 1998) proposed such similar studies, suggesting that the irradiated  $\text{NH}_3-\text{H}_2\text{O}-\text{CH}_4$  mixture on Saturnian satellite surfaces can be partially converted into pre-biotic molecules. In recent years various experiments involving atom or radical bombardment of interstellar ice analogues have been proposed to justify the formation of complex organic molecules in space. Within this context, Congiu et al. (2012) illustrated that the  $\text{NH}_2\text{OH}$  formation on interstellar ices analogues might arise from successive hydrogenation of solid nitric oxide at 10 K, while He et al. (2015) reported another hydroxylamine synthesis method on an amorphous silicate surface through the oxidation of ammonia at 70 K.

Concurrently with these experimental studies, many theoretical investigations have been devoted to diverse mechanisms of reactions leading to the formation of  $\text{NH}_2\text{OH}$  as an intermediate or a final reaction product. The radical recombination  $\text{NH}_2 + \text{OH}$  reaction has been theoretically investigated on the lowest singlet and triplet surfaces by Mousavipour et al. (Mousavipour et al. 2009, 2014). They underline the formation of two hydroxylamine isomers  $\text{NH}_2\text{OH}$  and  $\text{NH}_3\text{O}$  which may decompose into small fragments such as  $\text{HON} + \text{H}_2$ ,  $\text{HNO} + \text{H}_2$  and  $\text{NH}_3 + \text{O}$ . Similar study has been also proposed

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by Wang et al. (2004) by investigating the branching product for  $O + NH_3$  reaction which was found to be occurring through an insertion mechanism leading to a long-lived chemically activated  $NH_2OH$  as intermediate before it dissociated into  $NH_2$  and  $OH$ .

Even though all those laboratory investigations suggest the efficiency of hydroxylamine formation under conditions similar to those found in the interstellar medium and some planetary atmospheres, till now the question of the presence of  $NH_2OH$  with relatively high abundance in space remains unresolved. And many explorations of hydroxylamine in several astronomical sources carried out by McGuire et al. (2015) and Pulliam, McGuire and Remijan (2012) result in a pure non-detection of this simple molecule. An obvious and possible explanation is that the  $NH_2OH$  abundances in different regions in space might be lower than estimated from laboratory studies. If all the laboratory experimental studies showed several reaction pathways to form  $NH_2OH$  in solid phase to simulate the icy grain chemistry and all the space observations conclude that  $NH_2OH$  is not detected, the chemical transformation of  $NH_2OH$  in solid phase during the desorption processes of  $NH_2OH$  containing interstellar grains could result in its very low abundance in space. Paradoxically, even though  $NH_2OH$  is a stable and commercially available molecule, all the laboratory investigations have focused on the formation of  $NH_2OH$  in ‘cold-solid-phase’ interstellar medium conditions but no experiments have ever been realized to simulate the desorption  $NH_2OH$  trapped in water ices to monitor the  $NH_2OH$  evolution during the solid–gas transitions and then to simulate the desorption of interstellar icy grain mantle containing water and hydroxylamine.

In this paper, we are investigating the evolution  $NH_2OH$  molecule via a thermal chemistry during the desorption of  $NH_2OH-H_2O$  ices in the temperature range of 10–200 K. This is the first study devoted to the formation and evolution of  $NH_2OH-H_2O$  ices at low temperature. Do  $NH_2OH$  molecules really desorb from  $NH_2OH-H_2O$  ices? Are there any thermal reactions transforming  $NH_2OH$  before its desorption? To answer those questions, we have explored such an experimental study to characterize  $NH_2OH$  stability between 10 and 200 K, by coupling infrared spectroscopic analysis and temperature-programmed desorption. Knowing that the  $NH_2OH$  desorption temperatures range from 160 to 190 K, we show, through this study, there is a competition between  $NH_2OH$  desorption into the gas phase and its chemical transformation in the solid sample occurring at relatively lower temperature and leading to the formation of  $HNO$ ,  $NH_3$  and  $O_2$ . This is the first infrared spectroscopic experimental study probing at different temperatures an ice formed directly by condensing  $NH_2OH$  molecules. From our experimental results, we prove that the chemical transformation of  $NH_2OH$  starts occurring in solid phase at 130 K, a temperature far lower than that of  $NH_2OH$  desorption and this may reduce considerably the abundance of  $NH_2OH$  molecules releasing in the gas phase. We also show that this  $NH_2OH$  chemical transformation is due mainly to the presence of high amount of  $H_2O$  aggregates. Finally, those results might be the primary explanation to the non-detectability of hydroxylamine in space.

## 2 EXPERIMENTAL SECTION

The experiments have been performed in ultrahigh vacuum chamber maintained at  $10^{-9}$  mbar. A closed-cycle helium cryogenerator was used (Sumitomo cryogenics F-70) connected to a rotary platform attached in the vacuum chamber holding highly polished, Rh-plated copper mirror at low temperatures. Using a programmable temperature controller (Lakeshore 336), the temperature of the mirror sam-

ple holder can be regulated in a wide range, between 3 K and room temperature. Infrared spectra were recorded in the transmission–reflection mode between 5000 and  $500\text{ cm}^{-1}$  using a Bruker Vertex 80v fourier transform infrared (FTIR) spectrometer equipped with KBr beam splitter and liquid  $N_2$  cooled HgCdTe detector. A resolution of  $0.5\text{ cm}^{-1}$  was used and 500 scans were recorded for each spectrum. Infrared spectra of bare mirror are recorded before the sample deposition and used as references in processing the sample spectra. Absorption spectra in the mid-infrared region were collected from the samples through a KBr window separating the interferometer vacuum ( $10^{-2}$  mbar) from the cryostatic cell ( $10^{-9}$  mbar). Hydroxylamine was produced by heating hydroxylamine phosphate  $(NH_2OH)_3H_3PO_4$  salt (Sigma-Aldrich) at temperatures lower than  $40^\circ\text{C}$  in a glass tube. Two methods have been adopted to create a solid  $NH_2OH$ .

(i) Solid samples were prepared using a direct condensation at 3 or 10 K of the thermal decomposition of  $(NH_2OH)_3H_3PO_4$  salt.

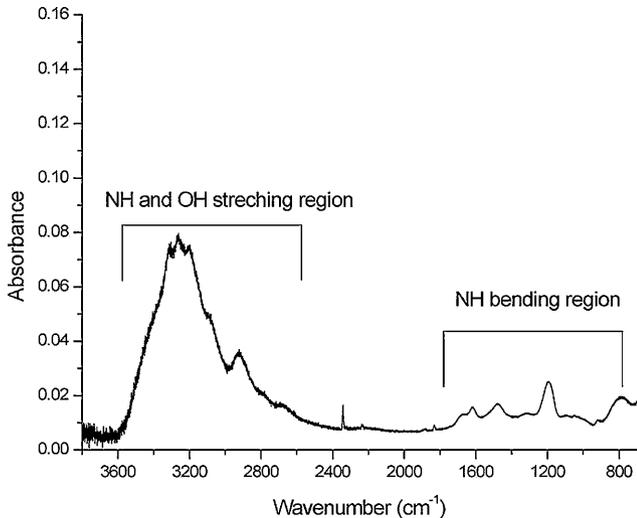
(ii) The thermal decomposition of  $(NH_2OH)_3H_3PO_4$  was co-injected and condensed with neon gas (‘Air liquide’; 99.9995%) at 3 or 10 K to create a neon matrix hosting  $NH_2OH$  molecules. This neon matrix isolation technique, which is frequently used to isolate specific chemical species in a neutral crystal, in addition to permit an accurate spectroscopic study of free isolated  $NH_2OH$  molecules, it would allow a better characterization of the purity degree of hydroxylamine derived from the heating of  $(NH_2OH)_3H_3PO_4$  salt. By co-injecting  $NH_2OH$  and neon gas simultaneously at 3 or 10 K, a neutral cage formed by neon atoms, is created where  $NH_2OH$  may be trapped and isolated. By heating, for a while, the neon matrix at temperatures higher than 15 K, the neon desorption temperature, all the neon atoms released from the solid sample leading to a formation of a neon-free solid  $NH_2OH$ .

To characterize the gas phase of our experiments and distinguish all the chemical species desorbing from our samples, a Quadrupole Mass Spectrometer (QMS – Hidden Analytical) is placed in front of the rotatable sample holder to monitor the evaporated species from the heated solid  $NH_2OH$ .

## 3 RESULTS

The infrared spectrum in Fig. 1 illustrates the result of the condensation, during 2 h at 10 K, of  $NH_2OH$  derived from the thermal decomposition of  $(NH_2OH)_3H_3PO_4$  salt. From this figure, we were barely able to assign the infrared signals around  $3000\text{ cm}^{-1}$  to  $NH$  and  $OH$  stretching modes and those below  $1600\text{ cm}^{-1}$  to  $HNH$  and  $NOH$  bending modes of solid hydroxylamine. In order to improve the specific vibrational mode assignments of  $NH_2OH$ , we need to perform the same condensation experiment of the thermal decomposition of  $(NH_2OH)_3H_3PO_4$  salt through a neon matrix isolation technique. In this context, a similar experiment was run using neon as carrier gas for the period of 30 min.

The results of this experiment is shown through the infrared spectrum of Fig. 2(a) where most of the detected absorption peaks for  $NH_2OH$  trapped in neon matrix are found to be similar to those investigated by other groups (Withnall and Andrews 1988; Luckhaus 1997). To compare our results to earlier matrix isolation hydroxylamine investigations, Table 1 gathers the vibrational mode frequencies of  $NH_2OH$  measured in our experiments and those given by previous studies. Through this experimental method, we can then, in addition to assign all the specific vibrational modes of  $NH_2OH$  molecule isolated in the rare gas matrix as shown in Fig. 2(a), better characterize the purity of our hydroxylamine arising from the



**Figure 1.** Infrared spectrum of  $\text{NH}_2\text{OH}-\text{H}_2\text{O}$  ice at 10 K in the 750–3700  $\text{cm}^{-1}$  spectral region. Sample formed by thermal decomposition of  $(\text{NH}_2\text{OH})_3\text{H}_3\text{PO}_4$  salt.

thermal decomposition of  $(\text{NH}_2\text{OH})_3\text{H}_3\text{PO}_4$  salt. The detection of  $\text{H}_2\text{O}$  vibrational modes in our IR spectrum as shown in Fig. 2(a), at 3744, 3651 and 1595  $\text{cm}^{-1}$ , prove that  $\text{NH}_2\text{OH}$  is found to be mixed with water molecules.

In order to connect the infrared spectrum of  $\text{NH}_2\text{OH}$  ice feathered in Fig. 1 which has been recorded after a direct condensation, during 2 h at 10 K, from the decomposition of  $(\text{NH}_2\text{OH})_3\text{H}_3\text{PO}_4$  salt

**Table 1.** Assignments of  $\text{NH}_2\text{OH}$  molecule vibrational mode frequencies ( $\text{cm}^{-1}$ ) compared to other references.

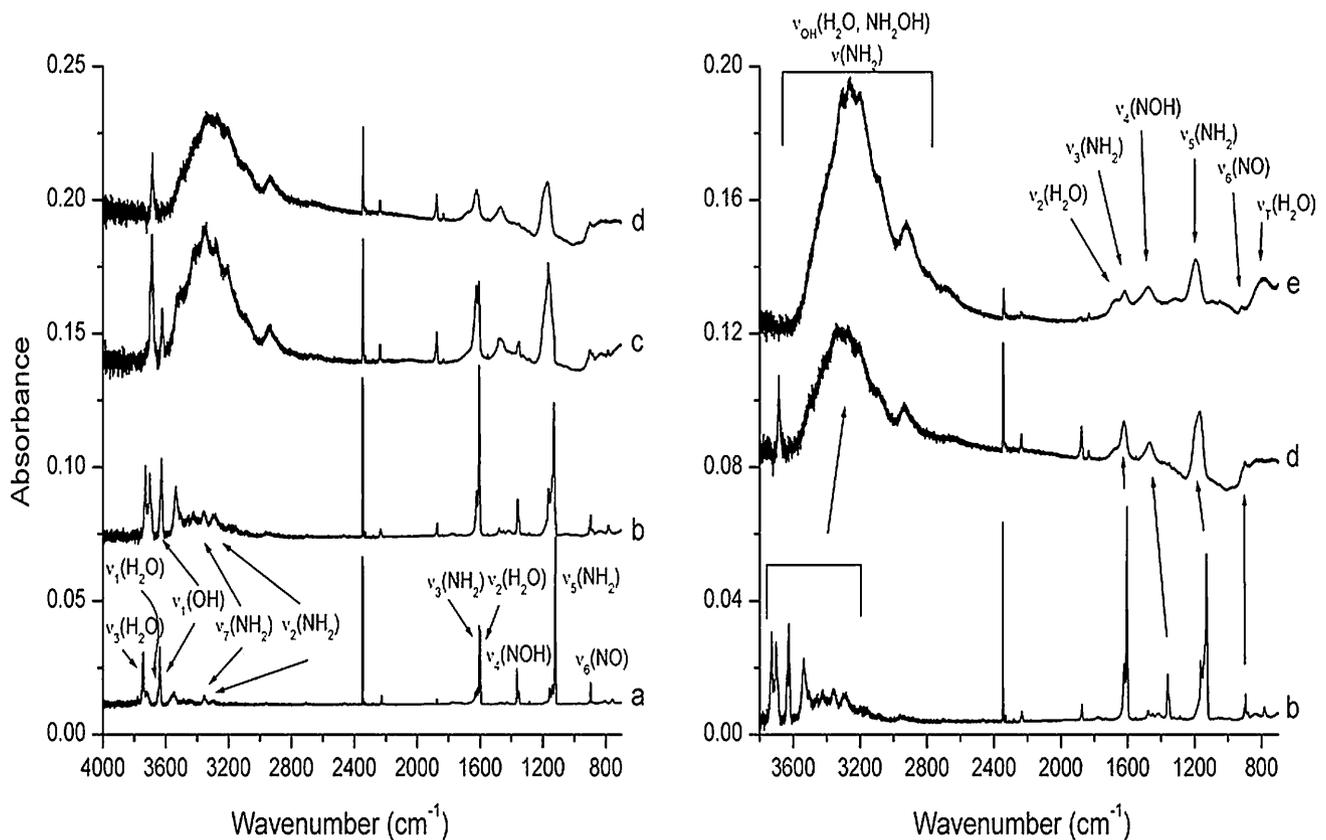
Vibrational mode	This exp	REF <sup>a</sup>	REF <sup>b</sup>
$\nu_1(\text{OH})$ str	3637.9	3634.7	3649.89
$\nu_2(\text{NH}_2)$ s str	3297.1	3289.7	32.94.25
$\nu_3(\text{NH}_2)$ sci	1598.4	1598.9	1604.52
$\nu_4(\text{NOH})$ bend	1351.7	1350.7	1353.3
$\nu_5(\text{NH}_2)$ wag	1117	1117	1115.47
$\nu_6(\text{NO})$ str	895.7	895.9	895.21
$\nu_7(\text{NH}_2)$ a str	3346.5	3353.3	3358.76
$\nu_8(\text{NH}_2)$ rock	–	–	1294.5
$\nu_9$ torsion	–	375.9	385.96

<sup>a</sup>Withnall & Andrews (1988).

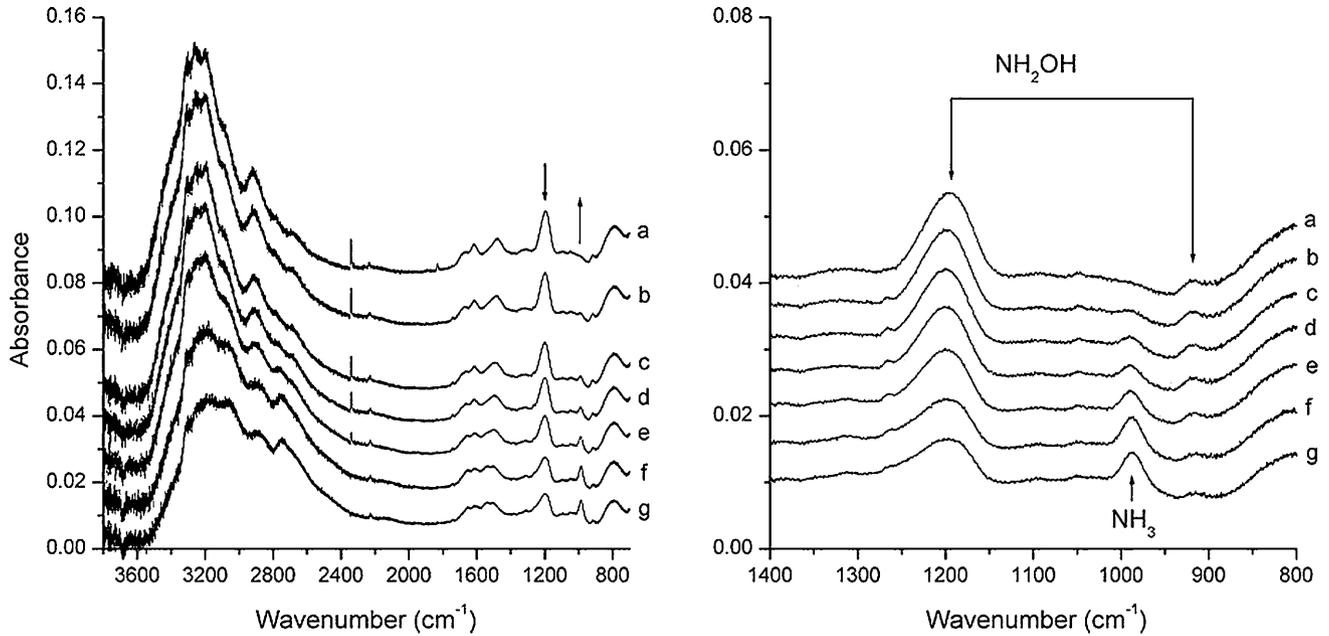
<sup>b</sup>Luckhaus (1997).

and those recorded using rare gas matrix isolation experiments, the neon matrix samples formed at 3 K have been heated progressively between 3 and 20 K to release the neon atoms from the sample and generate a  $\text{NH}_2\text{OH}$  neon-free ice. The heating evolution of the neon matrix sample is shown in Figs 2(b)–(d). As shown in Fig. 2(c), at 15 K almost all the neon atoms leave the solid sample and a pure  $\text{NH}_2\text{OH}-\text{H}_2\text{O}$  ice mixture can be obtained at 20 K, characterized by wide absorption bands related to solid  $\text{H}_2\text{O}$  and  $\text{NH}_2\text{OH}$ . Once all the neon atoms are desorbed at 20 K from the sample, the resulting ice has been cooled down at 10 K, to compare the two sample deposition methods adopted to create a solid  $\text{NH}_2\text{OH}$ .

The comparison between Figs 1 and 2 shows that the thermal deposition of  $\text{NH}_2\text{OH}$ , under our experimental conditions with and



**Figure 2.** Left-hand panel: infrared spectrum  $\text{NH}_2\text{OH}$  and  $\text{H}_2\text{O}$  trapped in neon matrix. Right-hand panel:  $\text{NH}_2\text{OH}-\text{H}_2\text{O}$  ice deposition at 10 K versus neon matrix deposition. (a) Neon matrix deposition at 3 K. (b) Neon matrix heated at 10 K. (c) Neon matrix heated at 15 K and cooled down to 10 K. (d) Neon matrix heated at 20 K and cooled down to 10 K. (e) Direct  $\text{NH}_2\text{OH}-\text{H}_2\text{O}$  ice deposition at 10 K.



**Figure 3.** Heating of  $\text{NH}_2\text{OH-H}_2\text{O}$  ice. (a) Deposition at 10 K. Heating at (b) 100 K, (c) 130 K, (d) 140 K, (e) 150 K, (f) 160 K, (g) at 170 K.

without a carrier gas, lead mainly to the formation of samples containing  $\text{NH}_2\text{OH}$  and  $\text{H}_2\text{O}$  species. The right-hand panel of Fig. 2 allows to show the evolution of the vibrational modes of  $\text{NH}_2\text{OH}$  and  $\text{H}_2\text{O}$  at 10 K from a  $\text{NH}_2\text{OH-H}_2\text{O}$ -neon matrix to  $\text{NH}_2\text{OH-H}_2\text{O}$  ice. Fig. 2(b) shows the absorption bands of the trapped species in neon matrix at 10 K, while Fig. 2(d) shows the progress of those bands after heating of the sample, at 20 K for a while, to remove all neon atoms, followed by a cooling down of the sample to 10 K. The similarity between the spectrum of Fig. 2(d) and that recorded directly after a direct condensation during 2 h at 10 K of hydroxylamine in Fig. 2e, shows that even though the experimental methods are different but they may lead to the formation of the same solid sample, namely a  $\text{NH}_2\text{OH-H}_2\text{O}$  ice.

After the vibrational characterization of  $\text{NH}_2\text{OH-H}_2\text{O}$  ices at 10 K, our main interest was to study the thermal stability of  $\text{NH}_2\text{OH}$  in contact with water molecules at low temperatures. A scenario that might be used, to characterize the  $\text{NH}_2\text{OH}$  molecule evolutions in some icy grains of the interstellar medium and various planetary atmospheres. Our  $\text{NH}_2\text{OH-H}_2\text{O}$  ice samples obtained at 10 K have been gradually heated at higher temperatures until a total desorption of the sample. By increasing the temperature from 10 to 100 K, there were no visible changes in our infrared spectra, Figs 3(a) and (b). This phenomenon was not very surprising as most of the many previous experimental works related the chemistry of solid  $\text{NH}_2\text{OH}$  show that the desorption temperature of  $\text{NH}_2\text{OH}$  is higher than 160 K. Using the mass spectroscopy detection, where a mass signal at  $m/z = 33$  corresponding to  $\text{NH}_2\text{OH}$  molecules has been detected at temperatures ranged between 160 and 190 K, Congiu et al. (2012) and He et al. (2015) have already reported that  $\text{NH}_2\text{OH}$  may be formed through NO hydrogenation or ammonia oxidation in solid phase at very low temperature and might desorb into the gas phase when the solid sample is heated. In our case, by heating a  $\text{NH}_2\text{OH-H}_2\text{O}$  ice mixture between 100 and 200 K and as it is exposed in Figs 3(c)–(g), the recorded IR spectra show decreases of  $\text{NH}_2\text{OH}$  absorption signals and the appearance of new IR features, while the mass spectra, recorded during the sample heating show a very low signal at  $m/z = 33$  ( $\text{NH}_2\text{OH}$ ) when the desorption temperature of hydroxylamine is reached around 180 K. Such behaviours

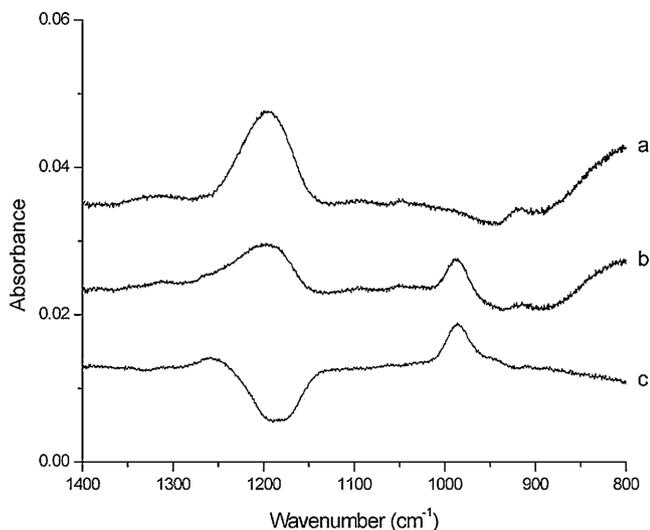
suggest that, instead of  $\text{NH}_2\text{OH}$  desorption, chemical transformations of  $\text{NH}_2\text{OH}$  molecules into water-hydroxylamine ice might occur between 100 and 170 K.

From our infrared spectra, we show that the new IR features are appearing clearly during the heating of  $\text{NH}_2\text{OH-H}_2\text{O}$  ices, before reaching the desorption temperature of  $\text{NH}_2\text{OH}$  but only at temperatures above 130 K. These results reveal that the  $\text{NH}_2\text{OH}$  desorption from the  $\text{NH}_2\text{OH-H}_2\text{O}$  ice may be very limited and most of  $\text{NH}_2\text{OH}$  molecules might be transformed between 130 and 170 K into new reaction products embedded into the sample ice.

Most of the detected new signals due to the formation of new species overlap with the  $\text{NH}_2\text{OH}$  absorption bands. However, one of these new chemical species shows an isolated spectral absorption band around  $980\text{ cm}^{-1}$ , far from the  $\text{NH}_2\text{OH}$  infrared signals. To quantify such a thermal chemical transformation of  $\text{NH}_2\text{OH}$  instead of its desorption, the right-hand panel of Fig. 3 shows a zoom of two distinguishing IR absorption bands at  $1194\text{ cm}^{-1}$  and  $980\text{ cm}^{-1}$ , corresponding to  $\text{NH}_2\text{OH}$  and one of the thermal reaction product from  $\text{NH}_2\text{OH}$  decomposition in water-hydroxylamine ice, respectively.

The  $980\text{ cm}^{-1}$  band appears in the  $\text{NH}_3$  vibration spectral region and it may be easily attributed to  $\text{NH}_3$  molecules trapped in  $\text{NH}_2\text{OH-H}_2\text{O}$  ice. Fedoseev et al. (2015) have already reported the absorption band signal of ammonia in solid phase at  $975\text{ cm}^{-1}$ . The appearance in our infrared spectra of a band at  $980\text{ cm}^{-1}$  is consistent with the presence of  $\text{NH}_3$  diluted in ice, and not as pure ammonia ice which has a characteristic band at  $1070\text{ cm}^{-1}$  (Richey & Gerakines 2012). In fact, when ammonia is present in solid phase as a minor species trapped in ice, its spectral position is shifted to lower frequency, which is also reliable with Fedoseev's work who detected ammonia as a minor reaction product in solid phase, around  $975\text{ cm}^{-1}$ . Comparison between Figs 3(a)–(c), to explore the decrease of the hydroxylamine absorption bands, shows that the  $\text{NH}_2\text{OH}$  transformations start occurring only at temperatures higher than 100 K and at 130 K only 15% of  $\text{NH}_2\text{OH}$  is transformed. The whole transformation takes place between 130 and 170 K.

The closeup of two infrared spectra recorded for two extreme temperatures, 10 and 170 K, associated to a subtraction spectrum, are shown in Fig. 4. The detection of ammonia under our



**Figure 4.** Infrared spectra in the  $800\text{--}1400\text{ cm}^{-1}$  region of  $\text{NH}_2\text{OH}$  ice. (a) After deposition at 10 K. (b) At 170 K. (c) Subtraction spectrum between 170 and 10 K.

experimental condition just by inducing a thermal reaction between water and hydroxylamine proves that  $\text{NH}_2\text{OH}$  molecules desorbing from  $\text{NH}_2\text{OH}\text{--H}_2\text{O}$  ice undergoes decomposition leading to the formation of new chemical species which may be formed and trapped into the  $\text{NH}_2\text{OH}\text{--H}_2\text{O}$  ice host between 100 and 170 K without any desorption (Collings et al. 2004; Zheng, Jewitt and Kaiser 2006; Brown & Bolina 2007; Martín-Doménech et al. 2014).

From the results exposed in Fig. 4 we can determine the column densities of our reactants and products  $N$  ( $\text{molec cm}^{-2}$ ), using the band strengths  $A$  ( $\text{cm molec}^{-1}$ ) of the detected species, in order to get an order of magnitude of the composition of our samples before and after the reaction occurs at 10 and 170 K, respectively. Table 2 gathers, the characteristic vibrational frequencies, the band strengths and the column densities of the three detected species which show specifically characteristic isolated band absorptions, namely,  $\text{H}_2\text{O}$ ,  $\text{NH}_3$  and  $\text{NH}_2\text{OH}$ .

We show through those column density calculations that just after the deposition of the sample, the amount of  $\text{NH}_2\text{OH}$  is 3 times higher than that of  $\text{H}_2\text{O}$ , and while the concentration of  $\text{H}_2\text{O}$  decreases by only 20%, approximately 60% of  $\text{NH}_2\text{OH}$  have been decomposed from 10 to 170 K to form new reaction products. Among others reaction products,  $\text{NH}_3$ , which may be simply identified in our IR spectra, could be associated to the formation  $\text{O}_2$ , a species, easier to distinguish with a mass spectroscopy detection. In fact, although the nature of all the formed species in the  $\text{NH}_2\text{OH}$  thermal transformation will be argued in the discussion part, from the mass spectroscopy point of view, the observation of a very low mass signal of the desorbed  $\text{NH}_2\text{OH}$  at 180 K, in comparison with other desorbed species such as  $\text{NH}_3$ ,  $\text{HNO}$ ,  $\text{H}_2\text{O}$  and  $\text{O}_2$ , might also

be a prove of hydroxylamine decomposition instead of its simple desorption. As an example, Fig. 5 shows the evolution of desorbed  $\text{NH}_2\text{OH}$  and  $\text{O}_2$  abundances.

$\text{NH}_2\text{OH}$  and  $\text{O}_2$  species start desorbing from the  $\text{NH}_2\text{OH}\text{--H}_2\text{O}$  refractory ice and reach highest desorption signals at 180 and 170 K, respectively. We show through this mass spectrum evolution that the signal due to the desorbed  $\text{O}_2$  starts increasing at low temperature but not lower than 120 K which is consistent with the infrared measurements exposed in Fig. 3. The analysis of the hydroxylamine IR absorption bands illustrate that 15% of  $\text{NH}_2\text{OH}$  is transformed between 100 and 130 K and a clear IR signature of  $\text{NH}_3$ , one of the reaction products in the alteration of  $\text{NH}_2\text{OH}$  during the heating of the solid sample, is obviously detected only at temperatures above 130 K. Similarly, the mass spectrum evolution of desorbed  $\text{O}_2$  reveals that oxygen may be another reaction product in the thermal transformation of  $\text{NH}_2\text{OH}$ . It is important to note that, the mass signal of desorbed  $\text{O}_2$  shown in Fig. 5 is almost 60 times higher than that of  $\text{NH}_2\text{OH}$ , while the  $\text{NH}_2\text{OH}\text{--H}_2\text{O}$  solid sample formed at 10 K contained simply  $\text{NH}_2\text{OH}$  and  $\text{H}_2\text{O}$  as primary reactants, with an amount of  $\text{NH}_2\text{OH}$ , 3 times higher than that of  $\text{H}_2\text{O}$ . As a reference, we have added the mass spectrum of pure  $\text{NH}_2\text{OH}$  recorded under our experimental conditions, during the sample deposition (Fig. 6) where the main mass signal situated at  $m/z = 33$  is due to  $\text{NH}_2\text{OH}$  molecules in addition to some low signals at  $m/z = 32$ , 31 and 30 due to the fragmentation patterns of hydroxylamine in the mass spectrometer.

#### 4 DISCUSSION

The presence of  $\text{NH}_2\text{OH}$ , the main precursor molecule in the formation of amino acids, on dust grain mantles is probable even if all the space observations conclude that  $\text{NH}_2\text{OH}$  is not detected in gas phase. This work is to see if there is any chemical transformation of  $\text{NH}_2\text{OH}$  occurring in the solid phase before its desorption from the mantle of interstellar icy grains. Such a chemical conversion of hydroxylamine, taking place in the solid phase, could be a consequence of its very low abundance in space and then it might explain its non-detection. In this perspective our investigations have been devoted to describe the behaviours of  $\text{NH}_2\text{OH}\text{--H}_2\text{O}$  ices between 10 and 200 K; to simulate the desorption  $\text{NH}_2\text{OH}$  in presence of water molecules and monitor the  $\text{NH}_2\text{OH}$  evolution during the solid–gas transitions.

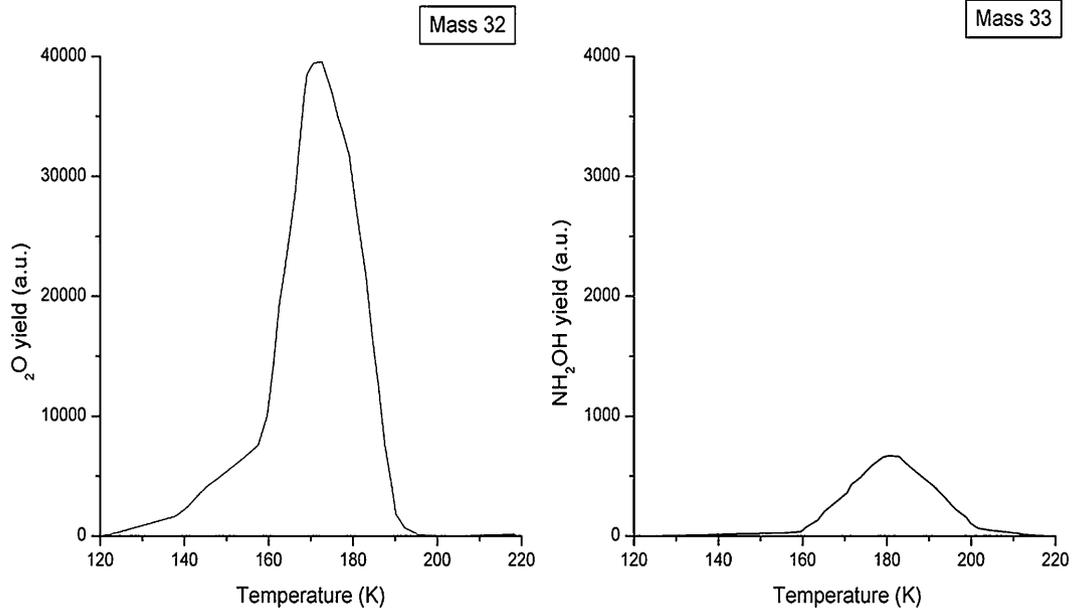
Our experimental results prove that by inducing progressively the evaporation of  $\text{NH}_2\text{OH}\text{--H}_2\text{O}$  ices; a reaction between water and hydroxylamine, the only main chemical species present in our samples, takes place even before the  $\text{NH}_2\text{OH}$  molecules start desorbing. By observing a decrease of  $\text{NH}_2\text{OH}$  infrared absorption signals and an appearance of new absorption bands, we conclude that a chemical transformation, leading to a decomposition of  $\text{NH}_2\text{OH}$  and a formation of some new chemical species, might be thermally induced. However some of the new detected absorption signals

**Table 2.** Characteristic vibrational frequencies, band strengths and column densities of  $\text{H}_2\text{O}$ ,  $\text{NH}_3$  and  $\text{NH}_2\text{OH}$ .

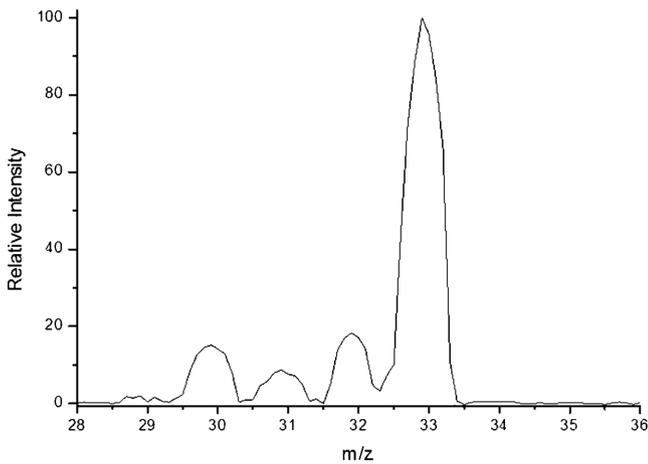
Characteristic vibrational frequency ( $\text{cm}^{-1}$ )	Molecule	Band strength <sup>a</sup>	Vibrational mode	Column densities ( $\text{molec cm}^{-2}$ ), at 10 K	Column densities ( $\text{molec cm}^{-2}$ ), at 170 K
760	$\text{H}_2\text{O}$	$3.1 \times 10^{-17}$	libration	$0.18 \times 10^{17}$	$0.14 \times 10^{17}$
980	$\text{NH}_3$	$1.2 \times 10^{-17}$	NH wag	0	$0.12 \times 10^{17}$
1194	$\text{NH}_2\text{OH}$	$1.2 \times 10^{-17b}$	NH wag	$0.59 \times 10^{17}$	$0.26 \times 10^{17}$

<sup>a</sup>Gerakines et al. (1995); Richey & Gerakines (2012).

<sup>b</sup>Adopted from the value of  $\text{NH}_3$ .



**Figure 5.** Mass evolution of desorbed  $\text{O}_2$  and  $\text{NH}_2\text{OH}$  during the heating of  $\text{NH}_2\text{OH}-\text{H}_2\text{O}$  ice. Desorbed  $\text{O}_2$  signal reaches a maximum at 170 K while that of  $\text{NH}_2\text{OH}$  at 180 K.

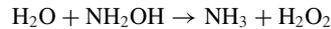


**Figure 6.** Mass spectrum  $\text{NH}_2\text{OH}$  recorded during the sample deposition: fragmentation patterns of  $\text{NH}_2\text{OH}$  in the mass spectrometer.

overlap with those of  $\text{NH}_2\text{OH}$ , as shown in Fig. 3 in 2800 and 1600  $\text{cm}^{-1}$  spectral regions, and this makes it impossible to separate the reactants, namely water and hydroxylamine from the new products. Thankfully, one of these new chemical products shows a strong and isolated spectral absorption band around 980  $\text{cm}^{-1}$ , in the  $\text{NH}_3$  vibration spectral region and it might be easily attributed to  $\text{NH}_3$  molecules, trapped in  $\text{NH}_2\text{OH}-\text{H}_2\text{O}$  ice, or coupled to other chemical species in the solid sample.

To have a clear description of  $\text{NH}_2\text{OH}-\text{H}_2\text{O}$  reaction in solid phase at cryogenic temperatures, lower than that of  $\text{NH}_2\text{OH}$  desorption, we have first to discuss the reaction pathways leading to a decomposition of hydroxylamine. Regarding such a molecule with N–H, N–O and O–H chemical bonds,  $\text{NH}_2\text{OH}$  may decompose into several fragments, depending on involved reaction mechanisms and on the nature of the chemical bonds engaged in such a decomposition. Several theoretical investigations have been interested in the formation and decomposition reactions of hydroxylamine. Accord-

ing to Feller & Dixon (2003)  $\text{NH}_2\text{OH}$  may react with water to form  $\text{NH}_3$  and  $\text{H}_2\text{O}_2$ :



This reaction is found to be exothermic, showing a heat of formation  $\Delta H = -11 \text{ kcal mol}^{-1}$ . Such a reaction may take place under our experimental conditions, as we have detected a very specific signal characteristic of ammonia, and then it might explain the low stability of hydroxylamine in contact with water at temperatures lower than that of hydroxylamine desorption. In this situation  $\text{H}_2\text{O}_2$  may be considered as the other reaction product formed during the thermal decomposition of  $\text{NH}_2\text{OH}-\text{H}_2\text{O}$  ices. However, an accurate analysis of our infrared spectra show no characteristic signals related to  $\text{H}_2\text{O}_2$  which can be understandable, as many investigations have already shown that  $\text{H}_2\text{O}_2$  might decompose into  $\text{H}_2\text{O} + \text{O}$  (Giguère & Liu 1957).

The association of our experimental results and Feller's group calculations allows asserting that the thermal decomposition of  $\text{NH}_2\text{OH}-\text{H}_2\text{O}$  ices leads to the formation of ammonia and probably atomic oxygen as new reaction products. As, the reaction is occurring in solid phase at cryogenic temperatures, those oxygen atoms may complex with ammonia molecules to form  $\text{NH}_3\text{O}$  or recombine to form molecular oxygen. In this case the heated  $\text{NH}_2\text{OH}-\text{H}_2\text{O}$  ice may decompose into  $\text{NH}_3 + \text{O}_2 + \text{H}_2\text{O}$  instead of simple desorption of  $\text{NH}_2\text{OH}$  and  $\text{H}_2\text{O}$ .

Similar calculations have been carried out to study the decomposition of  $\text{NH}_2\text{OH}$  aggregates and  $\text{NH}_2\text{OH}$  in contact with water molecules. Wang et al. (2010) investigated a thermal decomposition of  $\text{NH}_2\text{OH}$  more deeply by varying the amount of the reactants, namely  $\text{NH}_2\text{OH}$  and  $\text{H}_2\text{O}$ . They proposed a decomposition mechanism involving dimers or aggregates of hydroxylamine. They show that the association of two hydroxylamine molecules lead to the formation of  $\text{H}_2\text{O}$ ,  $\text{NH}_3$  and  $\text{HNO}$  as reaction products:



$\text{HNO}$ , molecules is characterized by three IR absorption signals at 2685, 1565 and 1500  $\text{cm}^{-1}$  corresponding to NH stretching, NO

stretching and HNO bending vibrational modes (Clough et al. 1973). The formation of HNO as a new reaction product, in addition to ammonia, in the thermal decomposition of  $\text{NH}_2\text{OH}-\text{H}_2\text{O}$  ices may be possible as the analysis of our infrared spectra, exposed in Fig. 3, shows an increase of a signal around  $2700\text{ cm}^{-1}$  which may be due to the NH stretching mode of HNO molecules, while that of  $\text{NH}_2\text{OH}$  is decreasing. Also, in the spectral region between  $1500$  and  $1600\text{ cm}^{-1}$ , even though partially overlap with  $\text{NH}_2\text{OH}$  signals, new appearing signal may be due to the two other vibrational modes of HNO.

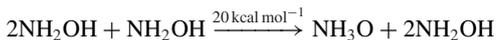
Wang's group calculations show that  $\text{NH}_2\text{OH}$  dimmer lead to a decomposition of  $\text{NH}_2\text{OH}$  to form ammonia, which is consistent with our experimental condition where solid samples were prepared using a direct condensation of pure  $\text{NH}_2\text{OH}$  favouring the formation of  $\text{NH}_2\text{OH}$  aggregates and also  $\text{NH}_2\text{OH}-\text{H}_2\text{O}$  clusters. The role of those aggregates can be underlined by analysing the reaction of  $\text{NH}_2\text{OH}$  decomposition from formation and activation energies point of view. Starting from one  $\text{NH}_2\text{OH}$  molecule, Wang et al. (2010) showed that hydroxylamine molecule undergoes isomerization into ammonia oxide:



This reaction is highly endothermic, showing a very high activation energy and it probably needs an initiating energy to convert  $\text{NH}_2\text{OH}$  into  $\text{NH}_3\text{O}$ . However by passing from monomolecular mechanism to bimolecular mechanism, a situation more favourable in solid phase, the energy barrier decreases from  $50\text{ kcal mol}^{-1}$  to  $25\text{ kcal mol}^{-1}$ , and the energy formation decreases from  $+25\text{ kcal mol}^{-1}$  to  $+15\text{ kcal mol}^{-1}$ .



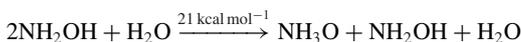
Wang et al. limited its calculations to the isomeric conversion reaction for only three  $\text{NH}_2\text{OH}$  molecules.



$$\Delta H = +10\text{ kcal mol}^{-1}$$

Similarly, with three  $\text{NH}_2\text{OH}$  molecules the conversion mechanism leading to the formation of  $\text{NH}_3\text{O}$  confirm a decrease of both activation and formation energies showing that the reaction is more favourable in solid phase by increasing the  $\text{NH}_2\text{OH}$  aggregate size, which is consistent with our experimental conditions. From these calculations, we can imagine that by increasing the number of  $\text{NH}_2\text{OH}$  molecules, the activation energy might decrease to zero and the  $\text{NH}_2\text{OH}$  conversion reaction would become highly exothermic. In such a situation, calculations are required to validate or invalidate this conclusion.

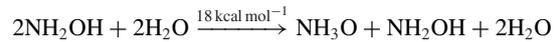
From Table 2, we show that even if 60% of  $\text{NH}_2\text{OH}$  decompose between 10 and 170 K to form new reaction products, concentration of  $\text{H}_2\text{O}$  also decreases by 20%, showing that water molecules may also play a role in  $\text{NH}_2\text{OH}$  transformations. Wang et al. investigated the influence of the number of water molecules into the  $\text{NH}_2\text{OH}$  alteration reaction:



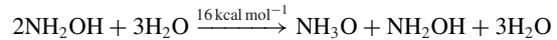
$$\Delta H = +13\text{ kcal mol}^{-1}$$

By comparing reactions involving three  $\text{NH}_2\text{OH}$  molecules to that obtained by substituting one of the three  $\text{NH}_2\text{OH}$  molecules by one  $\text{H}_2\text{O}$  molecule, we notice that the  $\text{NH}_2\text{OH}$  conversion into

$\text{NH}_3\text{O}$  occurs slightly under the same energetic condition. Both of the reactions are endothermic with almost the same activation energy, around  $20\text{ kcal mol}^{-1}$ . However by increasing the number of water molecules, the  $\text{NH}_2\text{OH}$  conversion into  $\text{NH}_3\text{O}$  become more favourable showing a considerable decrease of the energy barrier.



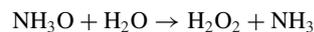
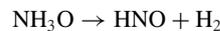
$$\Delta H = +7\text{ kcal mol}^{-1}$$



$$\Delta H = +4\text{ kcal mol}^{-1}$$

Wang et al. limited these calculations to three water molecules and two hydroxylamine molecules. From those calculations we can also conclude that by increasing the number of water molecules in contact with hydroxylamine, we would probably transform the  $\text{NH}_2\text{OH}$  into  $\text{NH}_3\text{O}$  through a barrierless and exothermic process.

Connected to our experimental results, Wang et al. show that, since ammonia oxide is less stable than hydroxylamine, further reactions may occur, leading to a decomposition of  $\text{NH}_3\text{O}$ , in absence of water molecules, into HNO and  $\text{H}_2$ . They also, showed that, in contact with water, ammonia oxide  $\text{NH}_3\text{O}$  may decompose, leading to the formation of ammonia and hydrogen peroxide as new reaction products in the transformation of  $\text{NH}_2\text{OH}$ .



The association of our experimental results and those calculations, enables to affirm that the heating of  $\text{NH}_2\text{OH}-\text{H}_2\text{O}$  ices may lead to a decomposition of  $\text{NH}_2\text{OH}$  before reaching its desorption temperature. The decomposition of  $\text{NH}_2\text{OH}$  instead of its desorption may be clearly proved though the infrared spectroscopy used as a probe method to show that the decrease of  $\text{NH}_2\text{OH}$  infrared signals is accompanied by an increase new IR signals due to the appearance of new reaction products. We showed that among those new signals, the most important one is that strong and isolated signal located at  $980\text{ cm}^{-1}$  in the  $\text{NH}_3$  vibration spectral region and which it may be due to  $\text{NH}_3$  molecules as well as to  $\text{NH}_3\text{O}$  molecule. The latter species has never been detected experimentally. However even though the other new signals overlap partially with the  $\text{NH}_2\text{OH}$  absorption bands, we are able to associate the final reaction products predicted by the theory and those detected experimentally, namely, HNO and  $\text{O}_2$  which have characteristic absorption signals in the spectral region between  $1500$  and  $1600\text{ cm}^{-1}$  (Bennett & Kaiser 2005).

## 5 CONCLUSION

Our investigations on the evolution of hydroxylamine via a thermal chemistry during the desorption of  $\text{NH}_2\text{OH}-\text{H}_2\text{O}$  ices in the temperature range of 10–200 K allow the characterization of  $\text{NH}_2\text{OH}$  stability, by coupling infrared spectroscopic analysis and temperature-programmed desorption. Knowing that the  $\text{NH}_2\text{OH}$  desorption temperatures range from 160 to 190 K, we show, through this study, there is a competition between  $\text{NH}_2\text{OH}$  desorption into the gas phase and its chemical transformation in the solid phase, occurring at low temperature and leading to the formation of into HNO,  $\text{NH}_3$  and  $\text{O}_2$ . This is the first infrared spectroscopic experimental study probing at different temperatures an ice formed

directly by condensing  $\text{NH}_2\text{OH}$  molecules. From our experimental results, we prove that the chemical transformation of  $\text{NH}_2\text{OH}$  starts occurring in solid phase at 120 K, a temperature far lower than that of  $\text{NH}_2\text{OH}$  desorption and this may reduce considerably the abundance of  $\text{NH}_2\text{OH}$  molecules releasing in the gas phase. We also show that the hydroxylamine chemical transformation is due mainly to the presence of high amount  $\text{H}_2\text{O}$  aggregates, thus consistent with the solid phase icy interstellar grain chemistry. Finally, those results might be the primary explanation for the non-detection of hydroxylamine in space.

## ACKNOWLEDGEMENTS

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