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## ***N + H surface reaction under interstellar conditions: Does the NH/NH<sub>2</sub>/NH<sub>3</sub> distribution depend on N/H ratio?***

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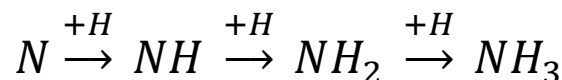
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### **ABSTRACT**

Astronomical observations have already reported that the abundances of NH, NH<sub>2</sub>, and NH<sub>3</sub> cannot be explained with gas phase chemistry modeling and depend strongly on the environment where these three N-hydrides have been detected. Consequently, dust grains may play a crucial role in the formation of these species through surface reactions. We have investigated the formation of NH, NH<sub>2</sub> and NH<sub>3</sub> through  $N \xrightarrow{+H} NH \xrightarrow{+H} NH_2 \xrightarrow{+H} NH_3$  solid state reaction at 3 and 10 K, in different environments. The N<sub>2</sub>-H<sub>2</sub> gas binary mixture is then plasma activated and the resulting gas from the microwave discharge made of H, H<sub>2</sub>, N, N<sub>2</sub> and NH<sub>3</sub> is deposited onto the surface of the sample holder maintained at 3 and 10 K. We show that, while at 10 K, NH, NH<sub>2</sub> and NH<sub>3</sub> have been detected in different abundance distributions, at 3 K the NH and NH<sub>2</sub> radicals have not been observed and the low amount of NH<sub>3</sub> present in our solid samples comes from the N<sub>2</sub>-H<sub>2</sub> plasma discharge. This is the first experimental study showing all the steps leading to ammonia formation, by detecting the final reaction product NH<sub>3</sub> and the two reaction intermediates NH and NH<sub>2</sub>. In addition to support the idea of NH and NH<sub>2</sub> formation on interstellar dust grains, we show that the environment where the reaction takes place plays an important role in the formation and stabilization of these two reactive unsaturated N-hydride radicals. We emphasize that NH and NH<sub>2</sub> are detected only if there are enough nitrogen molecules in the solid samples to isolate them from reacting, otherwise, directly exposed to H-atoms they turn into stable saturated species such as NH<sub>3</sub> and NH<sub>3</sub>-aggregates.

# 1. INTRODUCTION

Considered as one of the most important ingredient for the prebiotic chemistry in the interstellar medium and extragalactic system objects, ammonia has been the subject of several laboratory investigations carried out in the context of astrochemistry [1,5]. Many of these studies have been focused in the chemical transformation of  $\text{NH}_3$  which would lead to reactive radical species such as N, NH and  $\text{NH}_2$  usually met as functional groups in prebiotic blocks [6,8] such as CN, PN, HNCNH,  $\text{NH}_2\text{OH}$  and  $\text{NH}_2\text{CH}_3$ , as well as in more complex organic molecules [9] such as glycine ( $\text{NH}_2\text{-CH}_2\text{-COOH}$ ), the simplest possible amino acid. Many Laboratory studies [10, 16] have already shown that  $\text{NH}_3$  interacting with various energy sources (UV photons or energetic particles) is one of the most important sources of  $\text{NH}_2$  radical whose production may be induced by water molecules [17] through additional reaction pathways  $\text{NH}_3 + \text{OH} \rightarrow \text{NH}_2 + \text{H}_2\text{O}$ , in addition to the direct ammonia fragmentation  $\text{NH}_3 + \text{energy} \rightarrow \text{NH}_2 + \text{H}$ . In many of these studies the formation of  $\text{NH}_2$  radical has been characterized through the infrared detection of the bending mode signal at  $1500 \text{ cm}^{-1}$ . The N-H stretching IR signal of  $\text{NH}_2$  radical is hard to be measured in solid phase as it is obscured by the large IR-absorption bands of the reactants,  $\text{NH}_3$  and ammonia aggregates. We have recently investigated the formation [18] of NH and  $\text{NH}_2$  through  $\text{N} + \text{NH}_3 \rightarrow \text{NH} + \text{NH}_2$  reaction. Compared to the previous studies showing that UV or high energy particles irradiation of  $\text{NH}_3$  might be an important source of NH and  $\text{NH}_2$  radicals, the  $\text{N} + \text{NH}_3 \rightarrow \text{NH} + \text{NH}_2$  reaction involves non-energetic processes as the two reactants N and  $\text{NH}_3$  are taken in their ground state at temperatures as low as 3 and 10 K. However, all these laboratory studies would suggest that  $\text{NH}_2$  and probably NH radicals would form in the interstellar medium through energetic or non-energetic processing of  $\text{NH}_3$ , but this would require already the presence of ammonia as a reaction precursor. Nevertheless, it would be very plausible that ammonia as well as the two N-hydrides NH and  $\text{NH}_2$  might be formed through the obvious H-addition reaction on nitrogen atom:



Two experimental studies have been devoted to the solid state formation of ammonia through  $\text{N} + \text{H}$  reaction [19, 20]. In order to investigate the interaction between nitrogen and hydrogen atoms at cryogenic temperatures, the two groups adopted two different techniques where either nitrogen matrices containing N-atoms were bombarded by H-atoms at 10 K or ( $\text{N}_2 + \text{H}_2$ ) gas mixtures were plasma activated to form N and H species and condensed onto a cold

surface at 10 K. In these two studies related to the most relevant reaction in the interstellar medium, the hydrogenation processing, the formation of  $\text{NH}_3$  has been monitored by FTIR spectroscopy and temperature programmed desorption/mass spectrometry, showing that ammonia formation followed a successive hydrogenation of N atoms trapped in solid  $\text{N}_2$ . However, neither NH nor  $\text{NH}_2$  radicals have been detected as reaction intermediates in these two studies. Knowing that NH and  $\text{NH}_2$  species are stable at cryogenic temperatures, why these two reaction intermediates have not been detected at 10 K through N + H reaction? Is it due to the N/H ratios which would be low enough to favor the complete reduction of all the nitrogen atoms? This would raise another question related to influence of N/H ratios on the abundances of NH,  $\text{NH}_2$  and  $\text{NH}_3$ . The NH/ $\text{NH}_2$ / $\text{NH}_3$  distribution has been reported to be equal to 5/1/300 and 3/30/300 in class 0 protostars [21] and molecular clouds [22], respectively, showing that even if ammonia remains the most abundant species, the abundance of NH,  $\text{NH}_2$ , and  $\text{NH}_3$  depends strongly on the environment where these three species are found [23-25]. In the present study, we have investigated the formation of NH,  $\text{NH}_2$  and  $\text{NH}_3$  through N + H solid state reaction at 3 and 10 K, in various  $\text{N}_2$ - $\text{H}_2$  solid environments. While in many related studies,  $\text{NH}_2$  was characterized by infrared spectroscopy through its bending mode located at  $1500\text{ cm}^{-1}$ , we show for the first time a simultaneous measurement of the IR signatures of N-H stretching mode of the three N-hydrides NH,  $\text{NH}_2$  and  $\text{NH}_3$ .

## 2. EXPERIMENTAL METHODS

The experimental methods used for the present study have been previously described [26,27]. Consequently, we remind the reader of the basic scheme. Hydrogen (99.9995%) and nitrogen (99.9995%) have been purchased from Messer. The solid samples are formed in our ultrahigh vacuum chamber at  $10^{-10}$  mbar by condensation of the reactants on a Rh-plated copper mirror maintained at 10 K using a closed-cycle helium cryogenerator (Sumitomo cryogenics F-70) and programmable temperature controller (Lakeshore 336). H and N atoms are formed by passing  $\text{H}_2$ - $\text{N}_2$  gas mixtures through a microwave driven atomic source (SPECS, PCS-ECR). We have investigated five samples corresponding to five relative hydrogen and nitrogen concentrations in the gas binary mixtures  $(100-X)\% \text{ N}_2 + X\% \text{ H}_2$ , where  $X = 10, 30, 50, 70$  and 90. For each gas binary mixture, the  $\text{H}_2$  and  $\text{N}_2$  dissociation yields have been measured using a Quadrupole Mass Spectrometer (QMS - Hidden Analytical). We have also calculated the N- and H- atomic fluxes which will be discussed in the results section. The microwave

discharge has been modified by adding to its output a curved Teflon tube to allow the thermalization of the species released from the atomic source and also to block the light from the plasma discharge to avoid possible photo-irradiation processing during the deposition of the sample. The H/H<sub>2</sub> + N/N<sub>2</sub> mixtures are deposited with a molecular flux of  $3 \times 10^{17}$  molecules cm<sup>-2</sup> s<sup>-1</sup> during 30 min on the sample holder maintained at low temperature. The resulting solid samples are then probed in the mid infrared spectral region 5000-500 cm<sup>-1</sup> with a resolution of 0.5 cm<sup>-1</sup>, using a Bruker Vertex 80v Fourier transform infrared (FTIR) spectrometer in the transmission–reflection mode with an incidence angle of 8°.

### 3. RESULTS AND DISCUSSIONS

#### 3.1) Characterization of the H- and N-atom fluxes

The N + H reaction depends strongly on the amounts of hydrogen and nitrogen atoms which are formed from the N<sub>2</sub> and H<sub>2</sub> molecular dissociations. In order to determine the optimal N<sub>2</sub>/H<sub>2</sub> molecular ratios for a simultaneous detection of NH, NH<sub>2</sub> and NH<sub>3</sub> in solid phase, the same experiments have been carried out with five molecular ratios N<sub>2</sub>/H<sub>2</sub> = 90/10, 70/30, 50/50, 30/70 and 10/90. The N<sub>2</sub>-H<sub>2</sub> gas binary mixture is then plasma activated and the resulting gas from the microwave discharge is deposited onto the surface of the sample holder maintained at 3 or 10 K. Before showing the IR spectra of the obtained ices to investigate the NH, NH<sub>2</sub> and NH<sub>3</sub> formation in solid phase, it is important to discuss under our experimental conditions the H<sub>2</sub> and N<sub>2</sub> dissociation yields, the N- and H-atomic fluxes and the N/H atomic ratios versus the N<sub>2</sub>/H<sub>2</sub> molecular ratios. In this context we have first measured, for each N<sub>2</sub>-H<sub>2</sub> gas binary mixture, the H<sub>2</sub> and N<sub>2</sub> dissociation yields which are shown in Table 1 and figure 1.

Table 1: H<sub>2</sub> and N<sub>2</sub> dissociation yields in plasma activated gas binary mixtures (100-X)% N<sub>2</sub> + X% H<sub>2</sub>, X = 10, 30, 50, 70 and 90

N <sub>2</sub> /H <sub>2</sub> Mixture	H <sub>2</sub> dissociation yields (%)	N <sub>2</sub> dissociation yields (%)
90/10	28	3
70/30	24	5
50/50	21	7
30/70	9	10
10/90	6	22

We notice that, the N<sub>2</sub> and H<sub>2</sub> dissociation rates depend strongly on the N<sub>2</sub>-H<sub>2</sub> gas binary mixtures. They vary from 6 to 28 % and from 3 to 22 % for H<sub>2</sub> and N<sub>2</sub>, respectively.

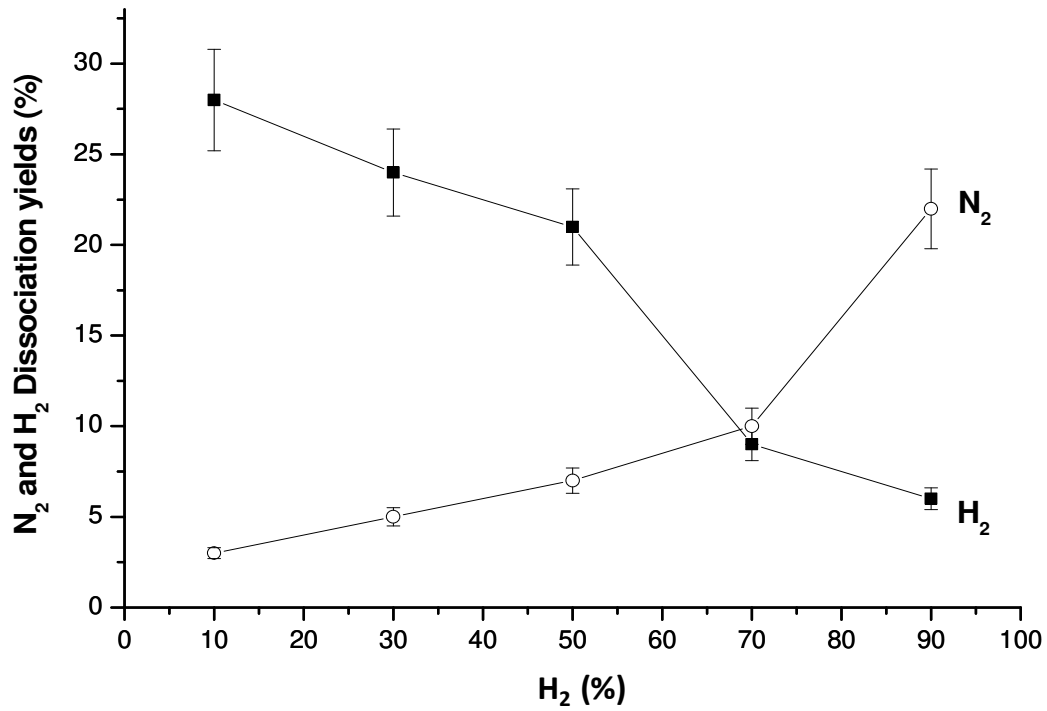


Figure 1: Dissociation yields of N<sub>2</sub> and H<sub>2</sub> versus the H<sub>2</sub> percentage in plasma activated gas binary mixtures (100-X)% N<sub>2</sub> + X% H<sub>2</sub>, X = 10, 30, 50, 70 and 90.

From table 1 and figure 1, we show that for both N<sub>2</sub> and H<sub>2</sub> molecular species, the lower is the concentration in the activated gas mixtures, the higher is the dissociation rate. This allows to deduce for each experiment by varying the N<sub>2</sub>/H<sub>2</sub> molecular ratios, the N/H atomic ratios and consequently, the N- and H-atomic fluxes. Figures 2 and 3 show the atomic fluxes and the N/H atomic ratios, respectively, for each plasma activated gas binary mixture (100-X)% N<sub>2</sub> + X% H<sub>2</sub>, where X = 10, 30, 50, 70 and 90.

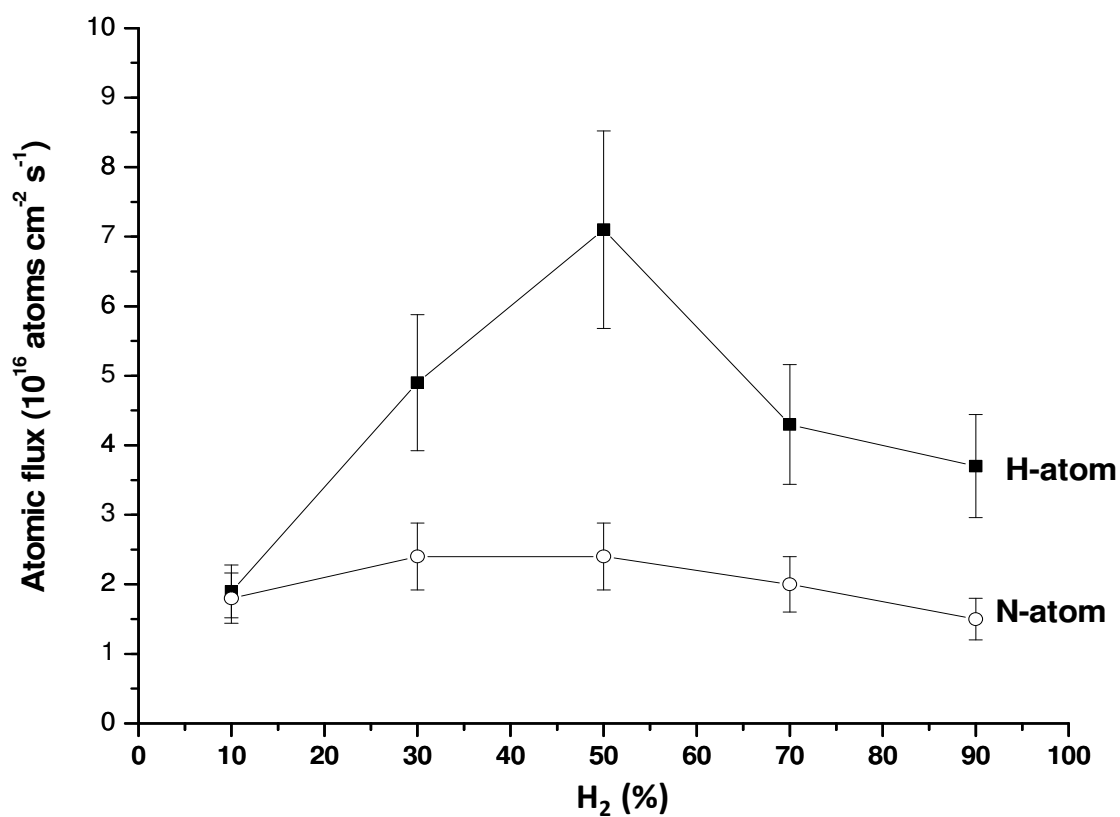


Figure 2: H-atom and N-atom fluxes versus the  $\text{H}_2$  percentage in plasma activated gas binary mixtures  $(100-X)\% \text{N}_2 + X\% \text{H}_2$ ,  $X = 10, 30, 50, 70$  and  $90$ .

Depending on the  $\text{H}_2$  and  $\text{N}_2$  concentrations in the gas mixture, the H-atom flux vary from 2 to  $7 \times 10^{16}$  atoms  $\text{cm}^{-2}$   $\text{s}^{-1}$ , however that of N-atoms seems almost constant ranged between 2 and  $3 \times 10^{16}$  atoms  $\text{cm}^{-2}$   $\text{s}^{-1}$ . This leads, as shown in figure 3, to N/H atomic ratios ranged between 1 and 0.4. Consequently, only in the experiment carried out with a  $\text{N}_2/\text{H}_2$  molecular ratio equal to 90/10, one nitrogen atom would be associated to one hydrogen atom while in the other cases one N-atom would be associated to 2 or 3 H-atoms.

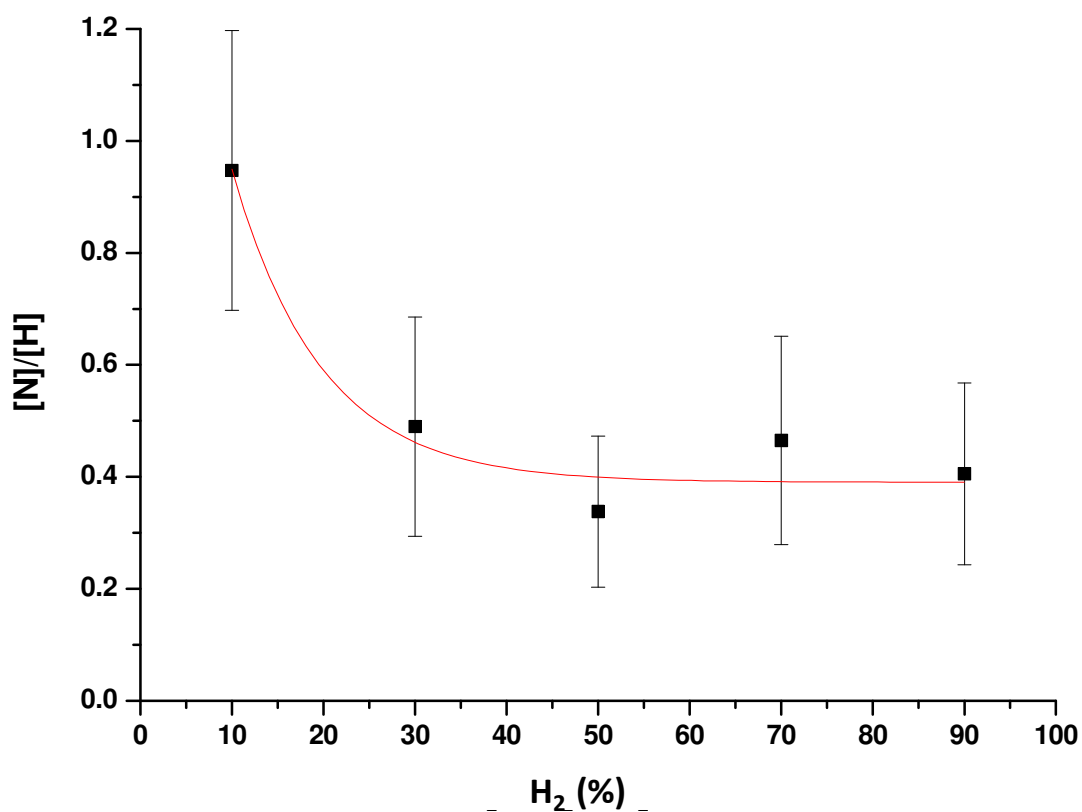


Figure 3: N/H atomic ratios versus the H<sub>2</sub> percentage in plasma activated gas binary mixtures (100-X)% N<sub>2</sub> + X% H<sub>2</sub>, X = 10, 30, 50, 70 and 90.

### 3.2) N + H solid state reaction

After the characterization of the H- and N-atom fluxes under our experimental conditions, the IR spectra of the ices formed by deposition at 10 K of plasma activated gas binary mixtures are shown in Figures 4 and 5 in the 900-1750 cm<sup>-1</sup> and 3000-3600 cm<sup>-1</sup> spectral regions, respectively.



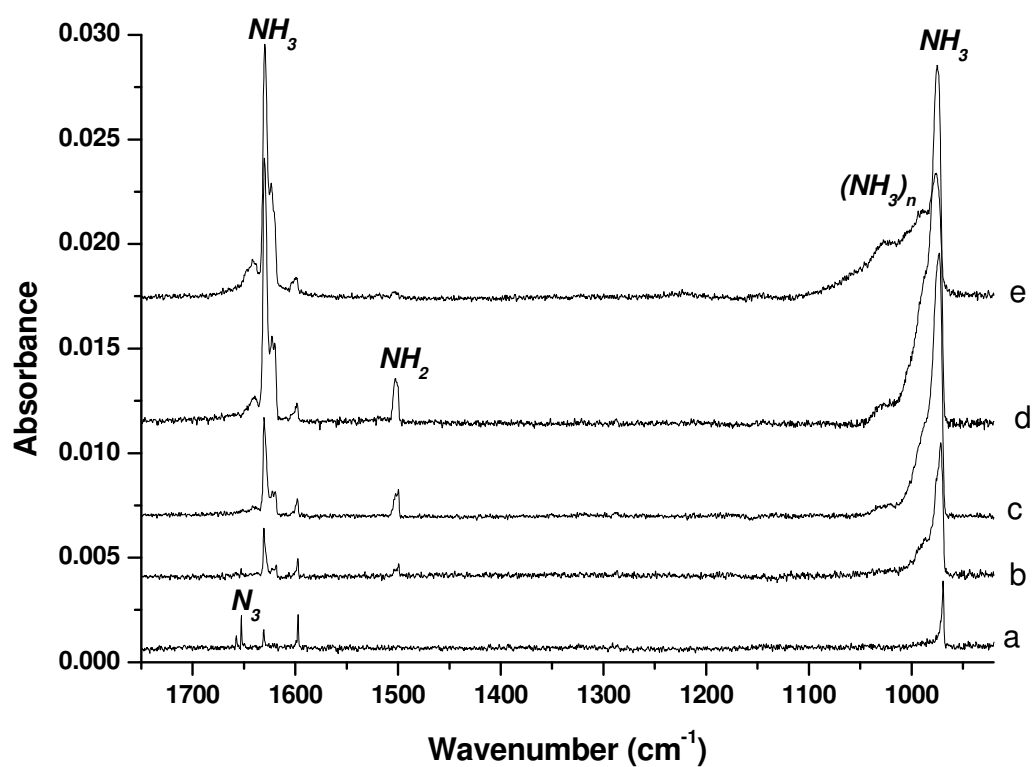


Figure 4. Ices formed by deposition on a surface at 10 K of plasma activated gas binary mixtures (100-X)% N<sub>2</sub> + X% H<sub>2</sub>, X = 10 (a), 30 (b), 50 (c), 70 (d) and 90 (e). The HNH bending region.

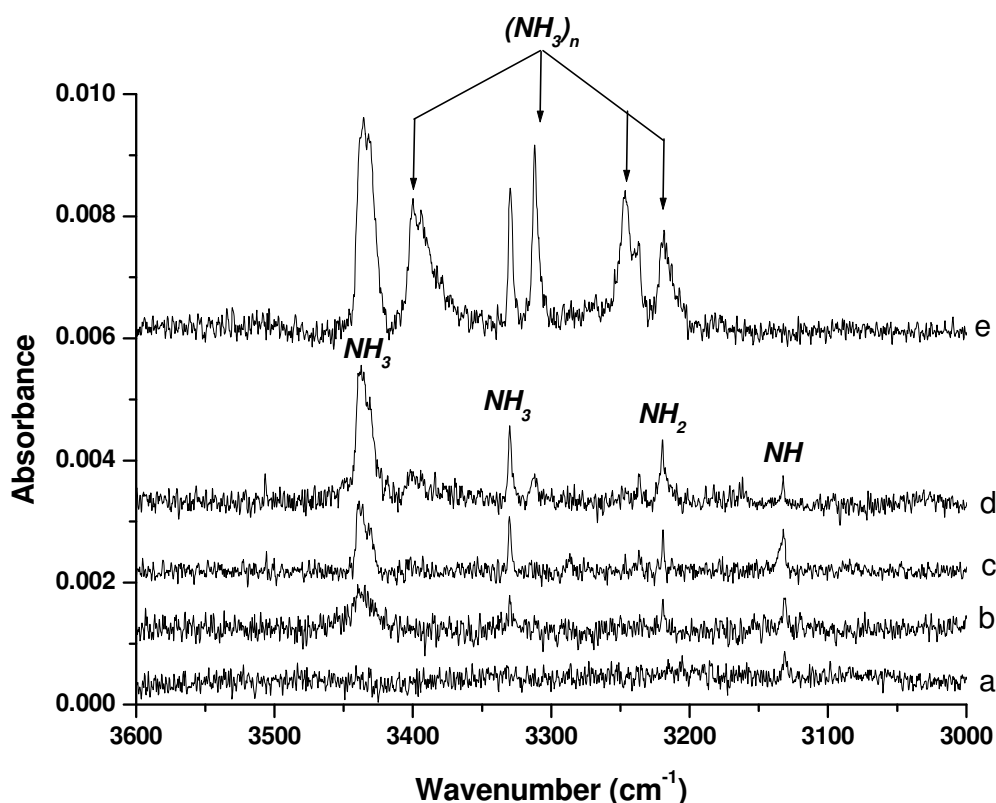


Figure 5. Ices formed by deposition on a surface at 10 K of plasma activated gas binary mixtures (100-X)% N<sub>2</sub> + X% H<sub>2</sub>, X = 10 (a), 30 (b), 50 (c), 70 (d) and 90 (e). The N-H stretching region.

Based on the literature, the vibrational attributions of the detected species are listed in table 2. From the acquired data we can see the varying range of products when the N<sub>2</sub>/H<sub>2</sub> molecular ratio varies.

Starting with the solid sample containing a molecular mixture of 10 % H<sub>2</sub> and 90 % N<sub>2</sub>, all the reaction products are trapped at 10 K in a mixed matrix mainly made of N<sub>2</sub>. The only products detected are N<sub>3</sub>, NH and NH<sub>3</sub> characterized by their characteristic IR signals at 1653, 3132, 1630 and 969 cm<sup>-1</sup>, respectively (Figures 4a and 5a). In such a configuration the atomic ratio N/H is equal to 1, showing that one N-atom is associated with one H-atom. This would suggest the formation of less reduced species such as NH and NH<sub>2</sub> rather than NH<sub>3</sub>. The NH radical has been detected through its N-H stretching mode at 3132 cm<sup>-1</sup>. Ammonia has been detected through its bending and umbrella modes at 1630 and 969 cm<sup>-1</sup>, respectively. These two NH<sub>3</sub> vibrational modes have very strong band strengths compared to that of N-H symmetric and asymmetric stretching modes which should be located in figure 5a at 3330 and 3435 cm<sup>-1</sup>, respectively. However NH<sub>2</sub> radical, a species more saturated than NH radical and

less reduced than  $\text{NH}_3$  molecule has not been detected. In fact, similarly to  $\text{NH}_3$ ,  $\text{NH}_2$  radical is easily characterized by its HNH bending mode which has a band strength higher than that of N-H stretching mode. From figures 4a and 5a, neither the HNH bending mode nor NH stretching mode which should be located at 1500 and 3220  $\text{cm}^{-1}$ , respectively, have been observed. This leads to a conclusion of a non-detection of  $\text{NH}_2$  radical for the deposition at 10 K of the plasma activated gas binary mixtures 90 %  $\text{N}_2$  + 10%  $\text{H}_2$ .

Table 2. Chemical species formed by deposition on a surface at 10 K of plasma activated gas binary mixtures (100-X)%  $\text{N}_2$  + X%  $\text{H}_2$ , X = 10, 30, 50, 70 and 90.

Species	Spectral position ( $\text{cm}^{-1}$ )	References
$\text{NH}_3$	969, 1630, 3330, 3435	[28]
$\text{NH}_2$	1500, 3220	[14]
NH	3132	[29]
$\text{H}_2\text{O}$	1598	[30]
$\text{N}_3$	1653, 1659	[31]

As shown in figures (4b, 4c, 4d and 5b, 5c, 5d), by increasing the amount of  $\text{H}_2$  in the plasma activated gas binary mixtures (100-X)%  $\text{N}_2$  + X%  $\text{H}_2$  from 30 to 70 % , the signal due to  $\text{N}_3$  radical disappears while the three nitrogen hydrides are simultaneously detected.  $\text{NH}_3$  is well characterized by its N-H symmetric and asymmetric stretching modes at 3330 and 3435  $\text{cm}^{-1}$ , respectively, in addition to its bending and umbrella modes at 1630 and 969  $\text{cm}^{-1}$ . Similarly,  $\text{NH}_2$  radical is well distinguished by its N-H stretching modes at 3220  $\text{cm}^{-1}$ , in addition to its HNH bending mode at 1500  $\text{cm}^{-1}$ . The NH radical is detected through its only IR signal at 3132  $\text{cm}^{-1}$ . However NH/ $\text{NH}_2$ / $\text{NH}_3$  distributions seem to depend strongly on the amount of  $\text{H}_2$  and  $\text{N}_2$  in the plasma activated gas mixtures, rather on the N/H atomic ratio. The NH and  $\text{NH}_2$  radicals are simultaneously detectable by increasing the amount of  $\text{H}_2$  in the binary mixtures. They reach their maximum for  $\text{N}_2/\text{H}_2$  molecular ratio equal to 50/50 and 30/70, respectively. However, for a  $\text{N}_2/\text{H}_2$  molecular ratio equal to 10/90, NH and  $\text{NH}_2$  are not observed while the only reaction products obtained are  $\text{NH}_3$  and  $\text{NH}_3$  aggregates (figures 4e and 5e). Ammonia being a polar molecule, it is very susceptible to form stable hydrogen bound aggregates easily observable in the N-H stretching region from 3500 to 3100  $\text{cm}^{-1}$  (figure 5e).

The infrared signals of  $\text{NH}_3$  and  $\text{NH}_3$  aggregates overlap in the  $1650\text{-}900\text{ cm}^{-1}$  spectral region. However, in the  $3600\text{-}3000\text{ cm}^{-1}$  region, one can easily distinguish the signals of  $\text{NH}_3$  molecule from those of  $\text{NH}$ ,  $\text{NH}_2$  radicals and  $\text{NH}_3$  aggregates. This would help to identify the concentration distribution of the nitrogen hydrides  $\text{NH}/\text{NH}_2/\text{NH}_3$ , for each  $\text{N}_2/\text{H}_2$  molecular ratio. We have calculated the absorption band areas  $S = \int I(\nu) d\nu$  corresponding to  $\text{NH}_3$  and  $\text{NH}_2$  absorption bands.  $I(\nu)$  is the optical depth of a given absorption band as a function of frequency  $\nu$ . The band areas have been determined for the symmetric and asymmetric stretching modes of  $\text{NH}_3$  molecule, for the bending and asymmetric stretching modes of  $\text{NH}_2$  radical, and for the N-H stretching mode of  $\text{NH}$  radical.

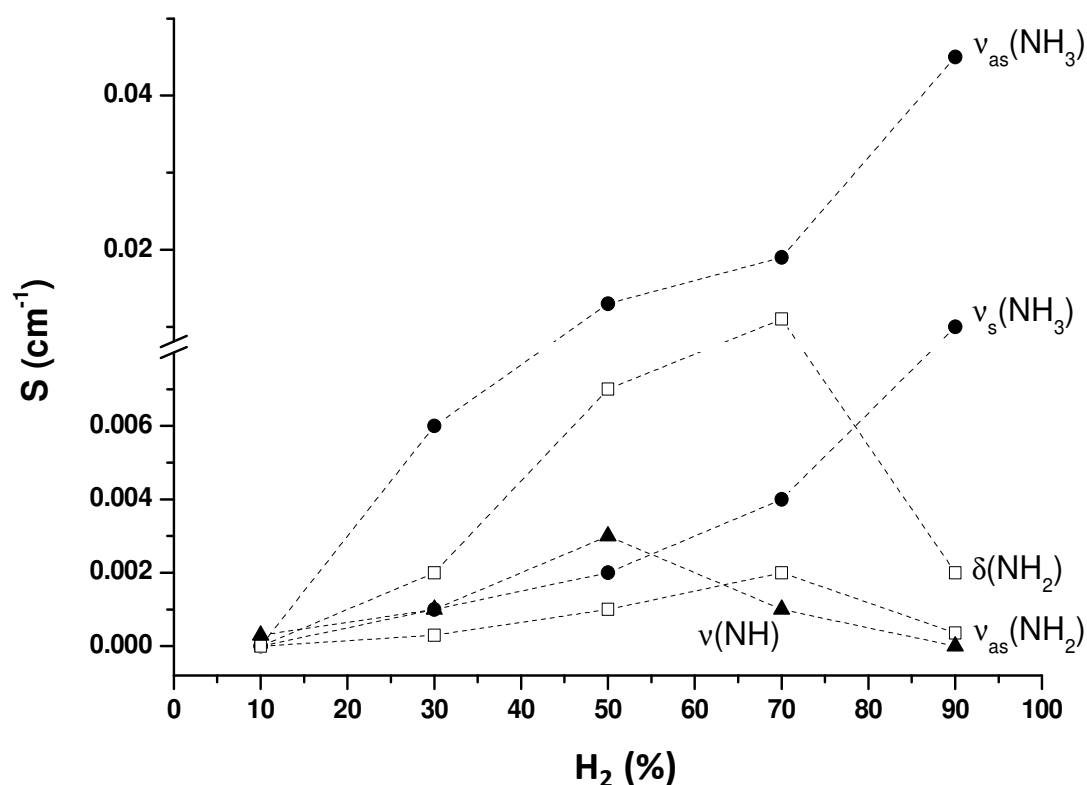


Figure 6. Integrated peak areas  $S(\text{cm}^{-1})$  for  $\text{NH}$ ,  $\text{NH}_2$  and  $\text{NH}_3$  formed at 10 K versus the  $\text{H}_2$  percentage in plasma activated gas binary mixtures  $(100\text{-}X)\% \text{N}_2 + X\% \text{H}_2$ ,  $X = 10, 30, 50, 70$  and  $90$ .

These absorption band areas are plotted against  $\text{H}_2$  amount which allows to characterize the behavior of each reaction product when the  $\text{N}_2/\text{H}_2$  molecular ratio varies. Figure 6 shows, for each  $\text{N}_2/\text{H}_2$  molecular ratio, the integrated band areas corresponding to N-H symmetric and asymmetric stretching modes of  $\text{NH}_3$ , to HNH bending and N-H stretching modes of  $\text{NH}_2$  radical and to N-H stretching mode of  $\text{NH}$  radical. We note that for  $\text{NH}_3$  molecule, the IR band strength of N-H asymmetric stretching mode is about 5 times higher than that of N-H

symmetric stretching mode. Similarly for  $\text{NH}_2$  radical, the bending mode at  $1500\text{ cm}^{-1}$  shows and IR band strength about 6 times higher than that of N-H stretching mode. By varying the  $\text{N}_2/\text{H}_2$  molecular ratio, the integrated peak areas of N-H symmetric and asymmetric stretching modes of ammonia behave likewise. Similarly, the band areas of HNH bending and N-H stretching modes of  $\text{NH}_2$  radical show the same behavior when the  $\text{N}_2/\text{H}_2$  molecular ratio varies. However, there is no information in the literature concerning the IR band strengths in solid phase of  $\text{NH}_2$  and  $\text{NH}$  radicals to estimate their column densities. Consequently, we can just estimate which chemical species is favorable during the  $\text{N} + \text{H}$  solid reaction for a given  $\text{N}_2/\text{H}_2$  molecular ratio. We notice that each nitrogen hydride responds differently by increasing the  $\text{H}_2$  amount in the gas binary mixtures.

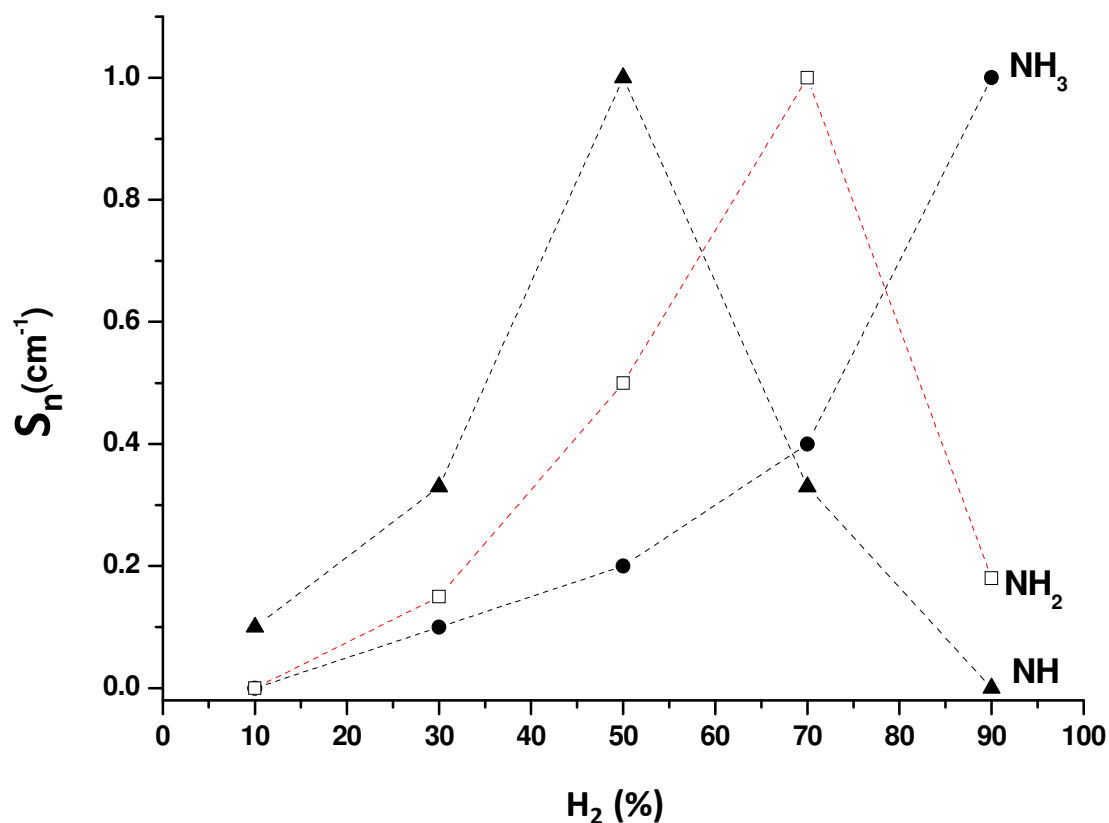


Figure 7. Normalized integrated peak areas  $S_n$  ( $\text{cm}^{-1}$ ) for  $\text{NH}$ ,  $\text{NH}_2$  and  $\text{NH}_3$  formed at 10 K versus the  $\text{H}_2$  percentage in plasma activated gas binary mixtures  $(100-X)\% \text{ N}_2 + X\% \text{ H}_2$ ,  $X = 10, 30, 50, 70$  and  $90$ .

Figure 7 shows the normalized integrated peak areas of NH, NH<sub>2</sub> and NH<sub>3</sub> versus N<sub>2</sub>/H<sub>2</sub> molecular ratio. The formation of NH and NH<sub>2</sub> radicals is favored for N<sub>2</sub>/H<sub>2</sub> equal to 50/50 and 30/70, respectively. For N<sub>2</sub>/H<sub>2</sub> molecular ratios ranged between 30/70 and 10/90, the amount of NH and NH<sub>2</sub> decreases while that of NH<sub>3</sub> increases. This result is very puzzling as the NH/NH<sub>2</sub>/NH<sub>3</sub> distribution should depend on N/H ratio. However, under our experimental conditions the N/H ratio is approximately equal to 0.4 for different H<sub>2</sub> amounts in the plasma activated gas binary mixtures, as shown in figure 3. Consequently, the NH/NH<sub>2</sub>/NH<sub>3</sub> concentration distribution is more related to its solid phase formation instead of the N/H atomic ratio. By varying the N<sub>2</sub>/H<sub>2</sub> molecular ratios from 70/30 to 10/90, the N/H atomic ratio is constant while the composition of the ice at 10 K and then the environment where the three nitrogen hydrides are formed would change considerably.

From these experimental results, we conclude that the best experimental conditions to favor the simultaneous formation of NH, NH<sub>2</sub> and NH<sub>3</sub> through N + H solid state reaction are reached when the N<sub>2</sub>/H<sub>2</sub> molecular ratio is ranged between 50/50 and 30/70. As shown in figure 4d, the highest IR signal of NH<sub>2</sub> radical is obtained for ices formed by deposition on a surface at 10 K of the plasma activated gas mixtures 30% N<sub>2</sub> + 70% H<sub>2</sub>.

Starting from these experimental conditions, we have to show that NH, NH<sub>2</sub> and NH<sub>3</sub> are effectively formed in solid phase at 10 K and not in the gas phase in the N<sub>2</sub>-H<sub>2</sub> plasma discharge followed by condensation in solid phase. We have then investigated the same experiments of condensation of plasma activated (N<sub>2</sub> + H<sub>2</sub>)-mixtures onto a cold surface at 10 and 3 K with the molecular ratio N<sub>2</sub>/H<sub>2</sub> = 30/70. Generally, all reactions occurring in the solid phase depend highly on the mobility of the reactants on the surface of the sample which enhances at higher deposition temperatures.

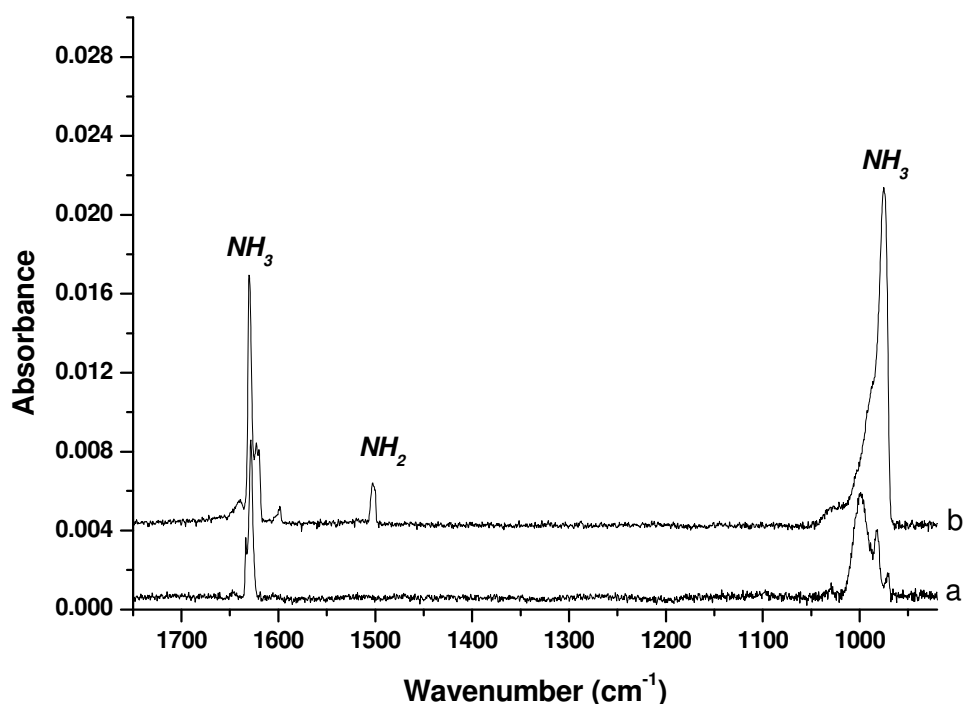


Figure 8. Ices formed by deposition of plasma activated gas binary mixtures 30% N<sub>2</sub> + 70% H<sub>2</sub>, on a surface at: a) 3 K, b) 10 K

Figure 8 shows the results obtained for the deposition of plasma activated (N<sub>2</sub>+ H<sub>2</sub>)-mixture at 3 and 10 K with the molecular ratio N<sub>2</sub>/H<sub>2</sub>= 30/70 which would correspond, as shown in figure 3, to an average atomic ratio N/H= 0.4. We have obtained at 10 K, measurable amounts of NH, NH<sub>2</sub> and NH<sub>3</sub> formed through  $N \xrightarrow{+H} NH \xrightarrow{+H} NH_2 \xrightarrow{+H} NH_3$  solid state reaction. However, the same experiment carried out at 3 K leads to small amounts of NH<sub>3</sub> while no traces of NH and NH<sub>2</sub> have been detected. This indicates that the NH, NH<sub>2</sub> and also a large part of the NH<sub>3</sub> are formed in solid phase at 10 K where both H and N are mobile on the surface of the sample. At 3 K, all the reactants are frozen and the interaction probability between H and N on the surface of the sample is almost null. If the formation of NH, NH<sub>2</sub> and NH<sub>3</sub> had taken place in gaseous phase in the N<sub>2</sub>-H<sub>2</sub> plasma just before the sample deposition, we would have detected the same amount of the three species at 3 and 10 K. However as at 3 K the N and H atoms are motionless, this cannot explain the detection of NH<sub>3</sub> while neither NH nor NH<sub>2</sub> have been observed. Accordingly, the small amount of NH<sub>3</sub> detected at 3 K would have been probably formed in N<sub>2</sub>-H<sub>2</sub> plasma and then deposited on the surface of the sample. This would suggest that the chemical species resulting from N<sub>2</sub>-H<sub>2</sub> plasma discharge are N and H atoms, in addition to N<sub>2</sub>, H<sub>2</sub> and NH<sub>3</sub>. NH and NH<sub>2</sub> would probably form in N<sub>2</sub>-

H<sub>2</sub> plasma discharge but they probably react to form NH<sub>3</sub> or dissociate into N + H and N + H<sub>2</sub> in the gas phase before reaching the surface of the solid sample.

We have estimated the amount of ammonia formed at 3 and 10 K by calculating the NH<sub>3</sub> column densities, using the integrated peak areas of the umbrella vibrational mode, associated to its proper band strength ( $A = 1.2 \times 10^{-17}$  cm molec<sup>-1</sup>) in solid phase [32]. The column [33] densities  $n$  are defined as:

$$n = \frac{\ln 10 \int I(\nu) d\nu \cos(8^\circ)}{A \cdot 2}$$

With the integral being the band area (cm<sup>-1</sup>) of the considered vibration mode. The correction factor  $\cos(8^\circ)$  takes into account the angle of the IR beam with respect to the normal of the deposition mirror, and the division by two corrects the fact that our samples are analyzed twice in the transmission-reflection mode. Under the same experimental conditions,  $11 \times 10^{15}$  and  $31 \times 10^{15}$  molec cm<sup>-2</sup> of NH<sub>3</sub> are formed at 3 and 10 K, respectively. As mentioned above, the  $11 \times 10^{15}$  molec cm<sup>-2</sup> of ammonia measured at 3 K are probably formed in the gas phase and then condense on the surface of the sample. Consequently, by increasing the temperature of the sample from 3 to 10 K, the amount of NH<sub>3</sub> formed exclusively on the surface of the sample is  $20 \times 10^{15}$  molec cm<sup>-2</sup>. The enhancement of NH<sub>3</sub> formation by 200% and the detection of NH and NH<sub>2</sub> radicals as reaction intermediates by increasing the temperature of the sample deposition from 3 to 10 K, prove that the formation of the three hydrides NH and NH<sub>2</sub> and NH<sub>3</sub> occurs through the solid phase H-addition reaction on nitrogen atom. The non-detection NH and NH<sub>2</sub> radicals at 3 K shows that under our experimental conditions, the plasma activated gas binary mixtures (100-X)% N<sub>2</sub> + X% H<sub>2</sub> before the deposition of the sample contains mainly H, N, H<sub>2</sub>, N<sub>2</sub> and NH<sub>3</sub> in gas phase. The resulting mixture H + N + H<sub>2</sub> + N<sub>2</sub> + NH<sub>3</sub> condenses on the surface of the sample at 10 K which leads to the formation of NH, NH<sub>2</sub> and NH<sub>3</sub> in solid phase.

### 3.3) Reaction Mechanisms

The chemical composition of our plasma activated (N<sub>2</sub>+ H<sub>2</sub>)-mixtures is in good agreement with previous studies related to plasmas containing N<sub>2</sub>-H<sub>2</sub> mixture [34, 35] for applications to surface treatments. Many of these investigations have already shown that N<sub>2</sub>-H<sub>2</sub> plasmas lead mainly to N, H, N<sub>2</sub>, H<sub>2</sub> and NH<sub>3</sub> where ammonia is generally formed directly on the surface of the reactor through NH<sub>2</sub>s + H → NH<sub>3</sub> and NHs + H<sub>2</sub> → NH<sub>3</sub> surface reactions. H and H<sub>2</sub> in the gas phase react with NH and NH<sub>2</sub> adsorbed at the plasma reactor surface to form NH<sub>3</sub>.



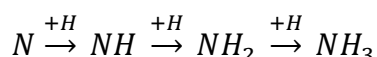
Additionally, Helden et al [35] investigated the contribution of NH and NH<sub>2</sub> radicals formed in the N<sub>2</sub>-H<sub>2</sub> plasmas in the N, H densities at the output of the plasma discharge. Using cavity ring-down spectroscopy, they measured the densities NH and NH<sub>2</sub> at different positions in the plasma flow. They showed that NH and NH<sub>2</sub> radicals form in the first part of the plasma expansion and turn below into N and H atoms and N<sub>2</sub>, H<sub>2</sub> and NH<sub>3</sub> molecules.

As mentioned in the introduction part, two experimental studies [19,20] have been already devoted to the solid state formation of ammonia through N + H reaction. In these previous studies, the formation of NH<sub>3</sub> has been monitored by FTIR spectroscopy and temperature programmed desorption/mass spectrometry, showing that ammonia formation followed a successive hydrogenation of N-atoms trapped in solid N<sub>2</sub>. However, in these two studies, neither NH nor NH<sub>2</sub> have been detected as reaction intermediates. We show through the disposition of H/H<sub>2</sub> + N/N<sub>2</sub> mixture at 10 K that NH, NH<sub>2</sub> and NH<sub>3</sub> are formed in solid phase with NH/NH<sub>2</sub>/NH<sub>3</sub> distributions depending strongly on the environment. As for almost the same atomic ratio N/H = 0.4, different NH/NH<sub>2</sub>/NH<sub>3</sub> concentration distributions have been observed depending on the amounts of the molecular nitrogen and hydrogen forming the ices where the H + N reaction takes place. From the same N/H atomic ratio, the three hydride species may co-exist. However NH, NH<sub>2</sub> reach their maximum for N<sub>2</sub>/H<sub>2</sub> ratios around 50/50 and 30/70, respectively. Ammonia becomes the main reaction product for N<sub>2</sub>/H<sub>2</sub> ratios lower than 30/70.

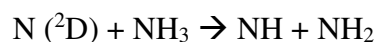
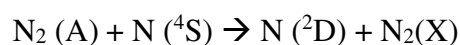
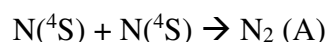
In fact, the H + N reaction, occurring in solid phase at 10 K leads mainly to the formation of saturated species NH<sub>3</sub>, unstable radical species such as NH and NH<sub>2</sub> need a neutral cage made of N<sub>2</sub> molecules to be stabilized. The reaction occurring with a molecular ratio N<sub>2</sub>/H<sub>2</sub> = 90/10 corresponding to N/H=1 leads mainly to N<sub>3</sub> and NH radical trapped in nitrogen matrix. NH radicals are then surrounded by N<sub>2</sub> molecules which reduce their reactivity to form NH<sub>2</sub> and NH<sub>3</sub>. By varying the molecular ratio N<sub>2</sub>/H<sub>2</sub> from 90/10 to 70/30, 50/50, 30/70 and 10/90 which leads to N/H=0.4, NH, NH<sub>2</sub> and NH<sub>3</sub> are simultaneously observed. However the NH, NH<sub>2</sub>, radical species are detected only if there are enough nitrogen molecules in the solid sample to isolate them from reacting with H-atoms. In samples made of 10 % of N<sub>2</sub> and 90 % of H<sub>2</sub>, the N<sub>2</sub>-matrix isolation effect is considerably reduced and almost all the NH and NH<sub>2</sub> radicals formed are directly in interaction with H-atoms to form more stable species such as NH<sub>3</sub> and NH<sub>3</sub>-aggregates.

To list all the processes involved into the formation of the three N-hydrides under our experimental conditions, one should underline that the formation of NH and NH<sub>2</sub> in solid

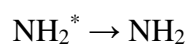
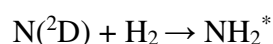
phase through H/H<sub>2</sub> + N/N<sub>2</sub> reactions is not only due to the N + H, NH + H and NH<sub>2</sub> + H radical recombination:



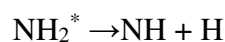
In fact, reactions involving excited state N-atoms N(<sup>2</sup>D) with stable molecule such as H<sub>2</sub> and NH<sub>3</sub> should be also taken into account. We have recently investigated [18] the N + NH<sub>3</sub> → NH + NH<sub>2</sub> solid state reaction which is triggered by N(<sup>4</sup>S)-N(<sup>4</sup>S) atomic recombination to form N<sub>2</sub>(A) metastable molecular nitrogen as follows:



During its energy relaxation to form ground state N<sub>2</sub>(X), metastable molecular nitrogen N<sub>2</sub>(A) may be a source of NH<sub>3</sub> dissociation or N-atom excitation N(<sup>4</sup>S) → N(<sup>2</sup>D). Excited state N-atom N(<sup>2</sup>D) may react with NH<sub>3</sub> to form NH and NH<sub>2</sub>. It would also react with molecular H<sub>2</sub> to form excited NH<sub>2</sub> [36-40] which might relax into its ground state or dissociate to form NH + H as follows:



or



Finally, our results would exclude all solid state reactions of the type NH<sub>3</sub> + H → NH<sub>2</sub> + H<sub>2</sub> or NH<sub>2</sub> + H<sub>2</sub> → NH<sub>3</sub> + H. Quantum calculations [41-44] have been carried out for the gas phase to investigate the H-abstraction reaction H + NH<sub>3</sub> ⇌ H<sub>2</sub> + NH<sub>2</sub>, showing that the formation of NH<sub>2</sub> from H + NH<sub>3</sub> is endothermic by 12 kJ/mol with an activation energy of the order of 58 kJ/mol. While the formation of NH<sub>3</sub> from H<sub>2</sub> + NH<sub>2</sub> reaction is exothermic, with an activation energy equal to 46 kJ/mol. Although these activation energies are high, they have been calculated for the gas phase and the exothermic process leading to the transformation of NH<sub>2</sub>

and  $H_2$  from  $NH_3 + H$  reaction could take place in solid phase at cryogenic temperatures, probably, through tunneling, as shown in figure 9.

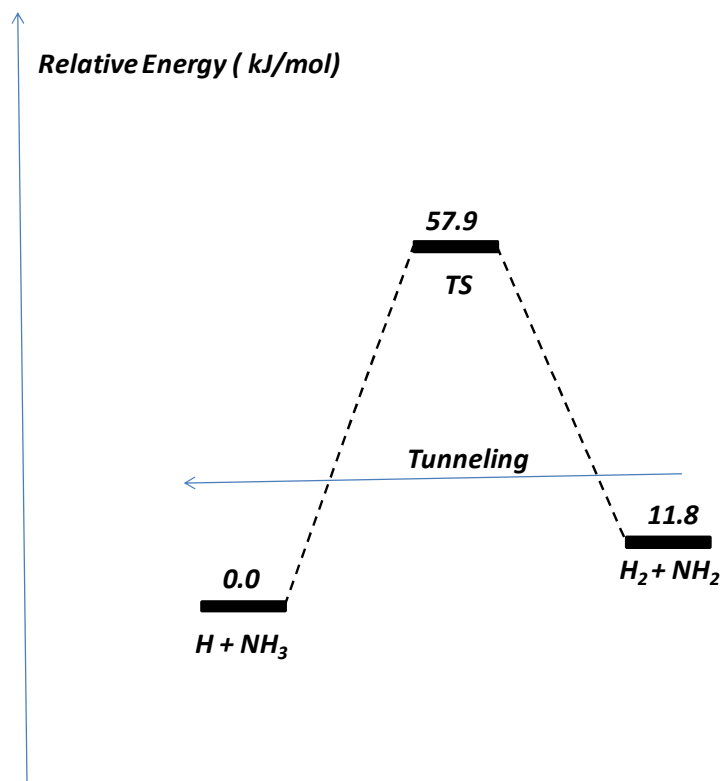


Figure 9: Energy diagram for  $H + NH_3$  reaction pathway versus  $H_2 + NH_2$  (Taken from Reference 41).

Consequently, if tunneling processes would take place under our experimental conditions, all our samples containing  $NH_2$  radicals and  $H_2$  molecules trapped in nitrogen matrix would show transformation of  $NH_2$  into  $NH_3$ . In this context, we have heated gradually our samples from 10 to 30 K to favor the  $H_2$ -mobility in  $N_2$ -matrix in order to favor the  $NH_2$ - $H_2$  interactions. Our measurements were not convincing to establish a link between  $NH_2 + H_2$  and  $NH_3$ . The heating of the samples leads to a decrease of  $NH_2$  and  $NH_3$  IR signals and an increase of those due  $NH_3$ -agregates. However we did not observe a clear transformation showing that  $NH_2$  radical is converted into  $NH_3$  molecule.

#### 4. CONCLUSIONS

The observation of  $NH$ ,  $NH_2$  and  $NH_3$  in the interstellar medium cannot be explained with gas phase chemistry modeling. The catalytic role of dust grains may play a crucial role in the formation of these three nitrogen hydrides through surface reactions. Astronomical observations have already reported that the abundances of  $NH$ ,  $NH_2$ , and  $NH_3$  depend strongly

on the environment where these three species are detected. We have investigated the formation of NH, NH<sub>2</sub> and NH<sub>3</sub> through N + H solid state reaction at 3 and 10 K, in different environments. Plasma activated (N<sub>2</sub> + H<sub>2</sub>)-mixtures have been deposited at 3 and 10 K under the same experimental conditions by varying the amounts of N<sub>2</sub> and H<sub>2</sub>. At 10 K, measurable amounts of NH, NH<sub>2</sub> and NH<sub>3</sub> are formed through  $N \xrightarrow{+H} NH \xrightarrow{+H} NH_2 \xrightarrow{+H} NH_3$  solid state reaction. While at 3 K the NH and NH<sub>2</sub> radicals have not been observed and the low amount of NH<sub>3</sub> detected in our solid sample at such low temperature comes mainly from its gas formation in the N<sub>2</sub>-H<sub>2</sub> plasma discharge. This study shows for the first time all the steps leading to solid state ammonia formation, by detecting the final reaction product and also the two reaction intermediates. Additionally, we show that the environment where the reaction takes place plays an important role in the formation and stabilization of NH and NH<sub>2</sub> radicals. The two unsaturated N-hydrides are detected only if there are enough nitrogen molecules in the solid samples to isolate them from reacting, otherwise, directly exposed to H-atoms they turn into stable saturated species such as NH<sub>3</sub> and NH<sub>3</sub> aggregates.

#### ACKNOWLEDGMENT

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