CHEMICAL PROCESSING OF PURE AMMONIA AND AMMONIA-WATER ICES INDUCED BY HEAVY IONS

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ABSTRACT

Cosmic rays are possibly the main agents to prevent the freeze-out of molecules onto grain surfaces in cold dense clouds. Ammonia (NH₃) is one of the most abundant molecules present in dust ice mantles, with a concentration of up to 15% relative to water (H₂O). FTIR spectroscopy is used to monitor pure NH₃ and NH₃–H₂O ice samples as they are irradiated with Ni and Zn ion beams (500–600 MeV) at GANIL/France. New species, such as hydrazine (N₂H₄), diazene (N₂H₂ isomers), molecular hydrogen (H₂), and nitrogen (N₂) were identified after irradiation of pure NH₃ ices. Nitrous oxide (N₂O), nitrogen oxide (NO), nitrogen dioxide (NO₂), and hydroxylamine (NH₂OH) are some of the products of the NH₃–H₂O ice radiolysis. The spectral band at 6.85 μ m was observed after irradiation of both types of ice. Besides the likely contribution of ammonium (NH₄⁺) and amino (NH₂) radicals, data suggest a small contribution of NH₂OH to this band profile after high fluences of irradiation of NH₃–H₂O ices. The spectral shift of the NH₃ "umbrella" mode (9.3 μ m) band is parameterized as a function of NH₃–H₂O (1:10) ice compaction, measured by the OH dangling bond destruction cross-section. Ammonia destruction is enhanced in the presence of H₂O in the ice and a power law relationship between stopping power and NH₃ destruction cross-section is verified. Such results may provide relevant information for the evolution of molecular species in dense molecular clouds.

Key words: astrochemistry - cosmic rays - ISM: molecules - methods: laboratory: molecular

Online-only material: color figures

1. INTRODUCTION

Among the whole family of cosmic rays, the less abundant heavy ions (Z > 6) may play a dominant role in the chemical evolution of dense molecular clouds. As they penetrate into the clouds, they induce chemical reactions in the ice mantles that coat dust particles. In the interstellar medium (ISM), therefore, solid-state chemistry induced by ionizing radiation occurs well before the cloud collapses into stars and planets. In addition, due to thermal and non-thermal desorption, cosmic rays are possibly the main agents to prevent the complete freeze-out of gaseous species other than H and He onto grain surfaces in dense and cold (~10 K) regions of the clouds. Several direct and indirect mechanisms have been proposed to explain the amount of CO and N₂H⁺ (Alves et al. 1999; Bergin et al. 2001) observed in the gas phases in these regions (D'Hendecourt et al. 1982; Prasad & Tarafdar 1983; Léger et al. 1985; Duley & Williams 1993; Bringa & Johnson 2004).

Ices coating dust particles within molecular clouds are important reservoirs of ammonia (NH₃). In fact, NH₃ is one of the most abundant molecules present in the ice mantles, with a concentration of up to 15% relative to H₂O (Bottinelli et al. 2010). NH₃ ice is expected to be formed simultaneously with water (H₂O) and methane (CH₄) ices in early and low-density phases of the cloud by hydrogenation of N atoms (Tielens & Hagen 1982). The detection of solid phase NH₃ in molecular clouds is very difficult, even from data obtained by space telescopes (e.g., *Spitzer Space Telescope*), but recently it has been confirmed for a significant sample of low-mass young stellar objects (YSOs) based on observation of the ν_2 "umbrella" mode at 9.3 μ m

(Bottinelli et al. 2010). This band is weak and very close to the methanol (CH₃OH) v_4 CO stretching band at 9.7 μ m. The task of measuring it is further complicated due to the overlap with the broad 10 μ m silicate (Si–O stretch) absorption band. The shape and peak position of the NH₃ v_2 vibrational mode are especially sensitive to the molecular environment and physical properties of the grains and thus may provide additional constraints on the relative molecular concentration in the ice mantles (Zheng et al. 2009; Bottinelli et al. 2010).

In the solar system, signatures of NH₃ ice and its hydrates have been found in near-IR spectra of Saturn's satellites Mimas, Enceladus, Tethys, and Rhea (Emery et al. 2005; Verbiscer et al. 2006); Uranus' satellite Miranda (Bauer et al. 2002); Pluto's satellite Charon (Brown & Calvin 2000; Dumas et al. 2001; Cook et al. 2007); and Kuiper Belt Object (50000) Quaoar (Jewitt & Luu 2004; Schaller & Brown 2007). The feature at 2.2 μ m, corresponding to the v_3+v_2 combination mode, has been used as a diagnostic tool. In most cases, the features indicate crystalline ice at the surface of these objects, suggesting that NH₃ is frequently diluted in water and involved in cryovolcanic outgassing.

Recent investigations on the radiolysis of pure NH₃ ice have shown that molecular nitrogen (N₂), molecular hydrogen (H₂), diazene (N₂H₂), hydrazine (N₂H₄), hydrazoic acid (HN₃), and amino radical (NH₂) are the main products detected using Fourier transform infrared (FTIR) spectroscopy (Zheng et al. 2008). Experiments using time-of-flight mass spectroscopy have shown that MeV heavy ions (²⁵²Cf fission-fragments) induce desorption of positive (NH₃)_nNH⁴₄ and negative (NH₃)_nNH⁵₂ clusters from pure ammonia ices (Farenzena et al. 2005).

List of Experiments Analyzed in This work					
Projectile	Flux $(10^9 \text{ ion cm}^{-2} \text{ s}^{-1})$	Target	Ice Thickness (µm)	Total Fluence (ion cm ⁻²)	Total Dose (ion cm ⁻²)
536 MeV ⁶⁴ Ni ²⁴⁺	0.93 ± 0.06	NH ₃	2.3 ± 0.2	1×10^{13}	9.1
536 MeV ⁶⁴ Ni ²⁴⁺	1.26 ± 0.05	NH ₃	7.0 ± 0.5	1×10^{13}	9.1
536 MeV ⁶⁴ Ni ²⁴⁺	1.3 ± 0.1	NH ₃ :H ₂ O (1:1)	1.3 ± 0.3	6×10^{12}	5.4
536 MeV ⁶⁴ Ni ²⁴⁺	1.1 ± 0.1	NH3:H2O (1:10)	1.8 ± 0.3	1×10^{13}	8.8
606 MeV ⁷⁰ Zn ²⁶⁺	0.41 ± 0.01	NH ₃	2.2 ± 0.3	1×10^{13}	10.1

 Table 1

 List of Experiments Analyzed in This Work

Note. A mean density of 0.8 g cm⁻³ was adopted to determine the thickness of the ices (Wood & Roux 1982; Romanescu et al. 2010).

 Table 2

 Band Strengths (A-values) Adopted for Different Absorption Bands and Samples

Molecule	Ice	Mode	Position (cm ⁻¹)	A-value (cm molecule ⁻¹)	Reference
NH ₃	pure NH ₃	v ₂ "umbrella"	1070	1.7×10^{-17}	1
NH ₃	NH ₃ :H ₂ O (1:1)	v_2 "umbrella"	1070	1.8×10^{-17}	1
NH ₃	NH3:H2O (1:10)	v_2 "umbrella"	1070	1.3×10^{-17}	1
H_2O	NH ₃ :H ₂ O (1:1)	libration	800	2.8×10^{-17}	2
H_2O	NH3:H2O (1:10)	libration	800	$2.8 imes 10^{-17}$	2

References. (1) Kerkhof et al. 1999; (2) Moore et al. 2007.

Furthermore, the radiolysis of ammonia-water ices shows N₂, H₂, NH₂, ammonium ions (NH₄⁺), nitrogen oxide (NO), nitrous oxide (N₂O), and nitrogen dioxide (NO₂) as being the main products formed (Moore et al. 2007; Loeffler et al. 2010; Pilling et al. 2010a). Some of these species have been tentatively identified in molecular clouds. For instance, NH₂ and NH₄⁺ should be blended and their relative contributions to the ~1500 cm⁻¹ band are difficult to quantify. This is an interesting point since the observed absorption band in mid-infrared spectra of YSOs, 6.85 μ m, has long been a puzzle in the astrochemistry community (Schutte & Khanna 2003; Boogert et al. 2008; Maté et al. 2009; Zasowski et al. 2009).

Molecules and radicals produced by the radiolysis of NH₃ containing ices, therefore, should be involved in the surface chemistry of interstellar ices, providing the building blocks for the formation of more complex molecular species. Due to the high ionization power, MeV heavy ions induce chemical reactions at very high rates with nearly constant stopping power up to large penetration depths ($<10 \ \mu$ m). By performing experiments with such ions at high energies and thick samples $(2 \,\mu m < l < 10 \,\mu m)$, one is able to observe species with very low band strengths using the FTIR technique. Facilities such as the Grand Accélérateur National d'Ions Lourds (GANIL/ France) are suited for this task. Desorption rates, destruction, and formation rates due to solid-state radiolysis are required to feed astrochemical models concerning gas-grain chemistry (e.g., Hasegawa & Herbst 1993). However, experimental data of ices irradiated by heavy ions in the MeV range are scarce. To fill this gap, laboratory experiments have been performed at GANIL to determine desorption rates (sputtering yields) due to the direct interaction of ions with ice samples as analogs of interstellar agents and to investigate the chemical transformations on the ice samples (Seperuelo Duarte et al. 2009, 2010; Pilling et al. 2010a, 2010b; de Barros et al. 2011a, 2011b; Pilling et al. 2012; Andrade et al. 2013). In this contribution, we present our recent results obtained from FTIR spectroscopy of pure NH₃ and NH₃-H₂O ice samples irradiated by different heavy ions (Ni and Zn, ~500 MeV).

2. EXPERIMENTAL

All experiments reported in this work were performed in a stainless steel vacuum chamber mounted at the medium energy beam line (D1/SME) of GANIL. Solid ammonia and ammonia-water films were prepared at 14 K by vapor deposition on a CsI window. Full details concerning the experimental setup and methodology on ice preparation and analysis can be found elsewhere (Seperuelo Duarte et al. 2009). The infrared spectra $(5000-600 \text{ cm}^{-1})$ were recorded at 1 cm⁻¹ spectral resolution using a Nicolet Magna 550 FTIR spectrometer operating in transmission mode perpendicular to the surface of the sample. The spectra were taken after each partial irradiation. The list of experiments, including the ion beam, beam flux, target, initial ice thickness, total ion fluence, and respective doses for each experiment, is presented in Table 1. Ammonia-water ice samples were prepared by deposition of the mixtures containing the two gases previously mixed in an auxiliary chamber. The molecular concentrations were determined directly from the measurements of the band areas in the spectra of the samples. Possible products from gas-phase reactions in the auxiliary chamber that could contaminate the samples were not observed in the spectra. In order to minimize gas-phase reactions, the total pressure in the auxiliary chamber was not higher than 10 mbar. Column densities and ice thickness for pure NH₃ and NH₃-H₂O ices were determined from the v_2 "umbrella" (1070 cm⁻¹) band area for NH₃ and the libration (800 cm⁻¹) band area for H₂O by adopting the Beer-Lambert equation and the mean density 0.8 g cm^{-3} (Wood & Roux 1982; Romanescu et al. 2010). Band strengths (A-values) adopted throughout this work are presented in Table 2. Table 3 presents the electronic stopping power (S_e) and penetration depth for each system (ion/sample) obtained from the SRIM code.⁴ $S_{\rm e}$ values were used to estimate the total doses presented in Table 1.

Radiolytic products of pure NH_3 ice are difficult to detect using FTIR spectroscopy either due to the low band strengths of

⁴ Version SRIM-2008.04 (http://www.srim.org/).



Figure 1. (a) Infrared absorption spectra of NH₃ ice sample. The spectra taken after fluences of 0, 2.5×10^{11} , 6×10^{12} , and 1.0×10^{13} ion cm⁻² are drawn from the top to the bottom, respectively. (b) The spectrum of the unprocessed ice zoomed around the NH₃ absorption features.

 Table 3

 Electronic Stopping Powers and Penetration Depths for Each Studied System

Projectile	Target	$(\text{keV } \mu \text{m}^{-1})$	Pen. Depth (µm)
536 MeV ⁶⁴ Ni ²⁴⁺	NH ₃	2587	167
536 MeV ⁶⁴ Ni ²⁴⁺	NH3:H2O (1:1)	2473	178
536 MeV ⁶⁴ Ni ²⁴⁺	NH3:H2O (1:10)	2380	187
606 MeV ⁷⁰ Zn ²⁶⁺	NH ₃	2854	169

Note. The density 0.8 g cm⁻³ was adopted to calculate the electronic stopping power and the penetration depth using the SRIM code.

their vibrational modes (most species' A-values are unknown) or low relative formation yields, resulting in very low signal-tonoise ratios of their infrared absorption bands. In order to detect such species, two strategies were adopted. First, an additional thick pure NH₃ ice (7 μ m) was irradiated by 536 MeV ⁶⁴Ni²⁴⁺ with the aim to enhance the amount of product formed. The energy of the Ni projectiles was high enough to assure constant stopping power during their passage through the samples. In this case, excitations and ionizations of molecules and atoms in the samples are dominantly related to the release of electrons $(\delta$ -rays) from the ion track (inelastic interactions). Second, difference spectra (C = A - B) were calculated subtracting the one obtained after a given fluence (A) by its predecessor (B). As the spectra are consecutive, only small variations in the baseline and in the NH₃ strong bands occur and new weak absorption bands can be detected in the difference spectrum, C, even when they are blended with the strong NH₃ bands.

The FTIR spectra were not entirely corrected for the baseline oscillations. However, to perform the band area measurements, the baselines and the absorption band profiles were simultaneously fitted using an appropriate polynomial function and single or multiple Gaussian functions, respectively.

3. RESULTS

3.1. Pure NH₃ Ice Processing

Figure 1(a) presents the spectra of the pure NH₃ ice sample (2.3 μ m) before and after three partial irradiations with 536 MeV

⁶⁴Ni²⁴⁺. These spectra represent the evolution of all three pure NH₃ ice samples analyzed in this work (see Table 1) quite well. Note that only subtle variations occur in the spectra taken at high fluences with respect to the spectrum taken before irradiation. The spectra show the decrease of the intense NH₃ bands related to the molecule destruction under irradiation. The infrared spectrum of the pure NH₃ sample before irridation is presented in detail in Figure 1(b) with the indication of several vibrational modes. Below, results concerning the radiolytic products obtained from the spectra of the thick NH₃ ice sample (7.0 μm) irradiated with 536 MeV ⁶⁴Ni²⁴⁺ are presented, since the absorption bands have a higher signal-to-noise ratio. The feature assignments and references for all absorption bands identified during processing of pure NH₃ ice are listed in Table 4.

Figure 2 shows two wavelength regions where the absorption features of H₂ (a) and N₂ (b) were detected (see discussion in Section 4.1). Their respective band area evolutions during radiolysis are shown in Figures 2(c) and (d). The small amount of CO₂ visible at 2341 cm⁻¹ in Figure 2(b) corresponds to less than 10^{15} molecules cm⁻² (1.2×10^{15} molecules cm⁻² at the beginning of the experiment) and it is due to the contamination by condensation of residual CO₂ gas. The H₂ band area evolution shows a fast increase, reaching a maximum value around a fluence of 1.2×10^{12} ion cm⁻² and a slow decrease afterward (Figure 2(c)). This behavior contrasts significantly with the monotonic increase of the N₂ band areas (Figure 2(d)).

The most conspicuous product of NH₃ detected after irradiation is N₂H₄ centered around 900 cm⁻¹ (Figure 3). The band has a double-peak shape and is free from contamination by other bands. The difference spectrum shown in the bottom panel of Figure 3 highlights the appearance of N₂H₄ (ν_6) and a *trans*-N₂H₂ isomer at 1280 cm⁻¹ (Rosengren & Pimentel 1965). Figure 4 presents the evolution of the area of both bands during irradiation. Figure 5 shows the bands associated with the N₂H₂ isomers *cis*- and *iso*-N₂H₂ (Zheng et al. 2009) highlighted by two difference spectra: (2.5–1) and (5–2.5) × 10¹¹ ion cm⁻². The three consecutive spectra are plotted in the same figure. The bands coincide with the long red wing of the ν_1 NH₃ band and have very broad profiles, which makes the band area measurements difficult. Both were more easily detected at the beginning of the irradiation with low fluences. The detection of NH₄⁴ (2 ν_4)



Figure 2. Evolution of band areas for products of pure NH₃ ice radiolysis: (a and c) H₂ at 4139 cm⁻¹ and (b and d) N₂ at 2325 cm⁻¹. The band corresponding to CO₂ at 2341 cm⁻¹ is due to the residual gas. The total amount of CO₂ in the sample was less than 10^{15} molecules cm⁻².

Absorption (cm^{-1})	References	Species	Feature Assignments
	NH	3 amorphous sample at 14	ι K
4994	1	NH ₃	$v_3 + v_4$
4478	1	NH ₃	$v_3 + v_2$
4361	1	NH ₃	$v_1 + v_2$
3478	1	NH ₃	$v_1 + v_L$
3459	1,2	NH ₃	v_3 deg. N–H stretch.
3211	1,2	NH ₃	v_1 sym. N–H stretch.
1880	1	NH ₃	$v_4 + v_1$
1625	1,2	NH ₃	v_4 deg. N–H deform.
1074	1,2	NH ₃	v ₂ sym. N–H deform./"umbrella"
		Radiolytic products	
4131	3	H ₂	v_1 H–H stretch.
~ 3040	4,11	cis-N ₂ H ₂	v_5 N–H stretch.
2890	5	NH_4^+	$2v_4$
~ 2780	4,11	iso-N ₂ H ₂	v_5 N–H stretch.
2326	3,4	N_2	v_1 N–N stretch.
2084-2060	4,6	$NH_4^+N_3^-$	N–N–N asym. stretch.
2022	6,7	N_3^-	N–N–N asym. stretch.
$\sim \! 1500$	5	NH_4^+	v_4 N–H bend.
	8,9,12	NH ₂	v_2 N–H bend.
~ 1280	10,11	$trans-N_2H_2$	ν_5, ν_6 N–H bend.
~ 895	4	N ₂ H ₄	v ₆ NH ₂ rock

 Table 4

 The Infrared Absorption Features of Solid Ammonia and Species Formed after Irradiation

References. (1) Zheng & Kaiser 2007; (2) Shimanouchi 1972; (3) Loeffler et al. 2010; (4) Zheng et al. 2008; (5) Schutte & Khanna 2003; (6) Carlo et al. 2001; (7) Tian et al. 1988; (8) Gerakines et al. 1996; (9) Suzer & Andrews 1988; (10) Rosengren & Pimentel 1965; (11) Biczysko et al. 2006; (12) Milligan & Jacox 1965.



Figure 3. Spectra around the NH₃ (ν_2) band showing the appearance of N₂H₄ and *trans*-N₂H₂ after irradiation of pure NH₃ ice (7 μ m thick) by 536 MeV ⁶⁴Ni²⁴⁺ (top). Difference spectrum (10¹³–0) ion cm⁻² (bottom). A small feature due to substrate alteration is seen at 1234 cm⁻¹.



Figure 4. Changes in N₂H₄ (895 cm⁻¹) and *trans*-N₂H₂ (1280 cm⁻¹) band areas as a function of fluence for pure NH₃ ice (7 μ m) irradiated with 536 MeV ⁶⁴Ni²⁴⁺.



Figure 5. Normal and difference IR spectra of processed pure NH_3 ice and identification of weak bands corresponding to *cis*- and *iso*- N_2H_2 , NH_4^+ , and NH_2 .

at 2890 cm⁻¹ confirms that the band corresponding to the v_4 mode must contribute to the 1500 cm⁻¹ feature (6.85 μ m). This feature is clearly visible in the two difference spectra and is composed of at least three components: a two-peak profile and a broad red wing. However, a possible significant contribution



Figure 6. Original and difference IR spectra of processed pure NH_3 ice. Weak bands in the difference spectrum, corresponding to $NH_4^+N_3^-$, N_3^- , and HN_3 , are identified. A dashed curve is drawn to guide the eye and acts as a reference baseline for the difference spectrum. Bands of CO and OCN⁻ species, probably formed due to the presence of residual CO₂ in the sample, are indicated as (res.).

of NH_2^- and NH_2 (ν_2 bend.) to this band cannot be discarded (Suzer & Andrews 1988; Milligan & Jacox 1965). It is interesting to note that a very similar feature was observed by Loeffler & Baragiola (2010) after photolysis of a NH_3 – H_2O (1:2) ice sample (see their Figure 5(b)).

Figure 6 shows the difference spectrum $(1-0.6) \times 10^{13}$ ion cm⁻² in which ammonium azide $(NH_4^+N_3^-)$ and azide (N_3^-) ions are detected. CO is formed, and possibly OCN⁻, due to the small contamination of CO₂ in the ice (Grim & Greenberg 1987; Maté et al. 2012). Substrate solid residuals may have a contribution to the bands associated with OCN⁻ and N₃⁻, since features are observed in the background spectrum in these regions. HN₃ is tentatively identified at 2154 cm⁻¹. It is a possible intermediate to the formation of NH₄⁺N₃⁻ (see the more confident detection of HN₃ in Section 3.2). Carlo et al. (2001) have shown the formation of NH₄⁺N₃⁻ after X-ray irradiation of HN₃ adsorbed on Au substrate and H₂O ice at $T \sim 100$ K. The feature associated with HN₃ was also reported by Zheng et al. (2008) after electron irradiation of pure NH₃ ice.

3.2. NH₃-H₂O Ice Processing

In addition to pure NH₃ ices, two NH₃–H₂O samples in different molecular concentrations were irradiated with 536 MeV 64 Ni²⁴⁺. This allows a better comprehension of how the processing of NH₃ ice is affected in the presence of H₂O ice (Strazzulla & Palumbo 1998; Moore et al. 2007). It is relevant to astrophysics since NH₃ is quite diluted in dominant H₂O ices in many space environments.

Figures 7(a) and (c) show the overall spectral evolution of the NH₃–H₂O ice samples after irradiation with 536 MeV ⁶⁴Ni²⁴⁺. Figures 7(b) and (d) show the spectral region around the v_4 NH₃ band in detail for the two samples: (1:1) and (1:10), respectively. Figure 8 shows the fittings to the baseline NH₃ and H₂O band profiles for the two NH₃–H₂O samples, from which the initial concentrations were determined. Similarly to what occurs in pure NH₃ processing, no big change is observed in the spectra except the decrease of the NH₃ and H₂O band areas due to the molecular dissociation. However, new species are detected from their weak bands. The formation of NH₄⁺, which may contribute to the ~1500 cm⁻¹ feature, is confirmed



Figure 7. Infrared absorption spectra of (a and b) NH₃:H₂O (1:1) and (c and d) NH₃:H₂O (1:10) samples. The spectra after fluences of 0, 2.5×10^{11} , and 6×10^{12} ion cm⁻² are drawn from top to bottom in panels (a) and (b). Panels (c) and (d) show a fourth spectrum after fluence of 1.0×10^{13} ion cm⁻². A small feature due to substrate alteration is seen at 1234 cm⁻¹.

(A color version of this figure is available in the online journal.)



Figure 8. Simultaneous fittings to the baseline, NH₃ (ν_2) and H₂O (libration) band profiles (short dashed lines) for band area determinations of NH₃–H₂O (a) (1:1) and (b) (1:10) samples. The original and modeled spectra are plotted as dotted and dashed lines, respectively. (A color version of this figure is available in the online journal.)

after processing the NH₃-H₂O (1:10) sample. The difference spectrum presented in Figure 9 shows the NH_4^+ (2 ν_4) band at 2890 cm^{-1} . However, as mentioned before (Section 3.1), the contribution of NH₂ (or NH₂⁻) to the \sim 1500 cm⁻¹ feature cannot be discarded. Recently, hydroxylamine (NH₂OH) has been identified in electron-irradiated NH₃-H₂O ices (Zheng & Kaiser 2010) and via successive hydrogenation reactions of NO ice (Congiu et al. 2012). As shown in Figure 7(d), NH₂OH is detected (NH₂ rock mode) with a peak at 1261 cm⁻¹. The band is broad, ranging from 1288 to 1200 cm^{-1} . Since this band is stronger than its relative (NOH bend) at 1515 cm⁻¹ (Zheng & Kaiser 2010; Nightingale & Wagner 1954), we conclude that NH₂OH contributes to the $\sim 1500 \text{ cm}^{-1}$ feature, although it is not a major component. The appearance of $NH_2OH(1261 \text{ cm}^{-1})$ at high fluences also contrasts with the prompt appearance of the 1500 cm^{-1} feature after irradiation, indicating that other molecules or radicals are responsible for the total band profile.

Here we concentrate on the appearance of other new products more easily observed after irradiation of NH_3-H_2O (1:10) than (1:1) ice. Table 5 lists feature assignments and references for all absorption bands identified during radiolysis of NH₃-H₂O (1:10) ice. H₂ and N₂ are formed after the irradiation of NH₃-H₂O ices (not shown), following similar behaviors as those observed for NH₃ pure ice (Figure 2). As will be presented in Section 3.4.1, a small amount of H_2 is already present before irradiation starts due to H_2 residual gas diffusion into the sample. Hybrid species containing N and O atoms were identified and can be seen in Figure 10. N_2O (a), NO (b), and NO_2 (c) are clearly observed at high fluences and their band area evolutions are shown in Figure 11. Figure 12 shows the detection of some peculiar features after a fluence of 10^{13} ion cm⁻². The last two spectra after the fluence of 0.6 and 1×10^{13} ion cm⁻² are also shown. The broad band at 2100 cm^{-1} , which also appears in the spectra of pure NH₃ ice sample (not shown) during initial fluences, is observed. Gerakines et al. (1996) have reported the appearance of this band during photolysis of pure NH₃ ice, but it still remains unidentified. A small contamination of CO₂ in the NH₃-H₂O ice gives rise to the formation of CO and possibly OCN⁻. The remarkable band with peak at 2154 cm⁻¹ is identified as HN₃ based on its previous observation by Carlo



Figure 9. NH_4^+ is identified in the difference spectrum $(5-2.5) \times 10^{11}$ ion cm⁻². The original spectra of the NH_3 – H_2O (1:10) sample taken after the two fluences are also shown.

 Table 5

 Infrared Peak Positions of New Species Formed in NH₃-H₂O (1:10)

 Ice after Irradiation with 536 MeV ⁶⁴Ni²⁴⁺

Absorption (cm ⁻¹)	References	Species	Feature
	NH ₃ :H ₂	O (1:10) products	3
4140	1	H ₂	v_1 H–H stretch.
2870	2	NH_4^+	$2\nu_4$
2326	1	N ₂	v_1 N–N stretch.
2231	1,4	N_2O	v_1 N–N stretch.
2154	5	HN ₃	N-N-N asym. stretch.
1870	1	NO	v_1 N–O stretch.
1605-1606	6	NO ₂	v_3 antisym. stretch.
1530-1380	2	NH_4^+	v_4 N–H bend.
	7	NH_2	ν_2 N–H bend.
	8, 9	NH ₂ OH	NOH bend.
1303	6	NO ₂	v_1 sym. stretch.
1288-1200	8, 9	NH ₂ OH	NH ₂ rock

References. (1) Loeffler et al. 2010; (2) Schutte & Khanna 2003; (3) Zheng et al. 2008; (4) Shimanouchi 1972; (5) Carlo et al. 2001; (6) Shimanouchi 1977; (7) Milligan & Jacox 1965; (8) Nightingale & Wagner 1954; (9) Nightingale & Wagner 1954.

et al. (2001). An additional broad feature at 1860 cm⁻¹ blended with NO (ν_1) is also detected but remains unidentified. As seen in Figure 12, full background subtraction was not possible, maybe due to substrate alteration after the beginning of the experiment. Nevertheless, these perturbations in the baseline of the spectra



Figure 11. Evolution of the band areas of N₂O (ν_1), NO (ν_1), and NO₂ (ν_3) during irradiation of NH₃-H₂O ice (1:10).



Figure 12. Original and difference IR spectra of processed NH₃–H₂O (1:10) ice. Weak bands in the difference spectrum $(1-0.6) \times 10^{13}$ ion cm⁻² are identified. A dashed curve is drawn to guide the eye and acts as a reference baseline for the difference spectrum.

are canceled after the subtraction procedure since the alteration was minimal after the two last irradiations.

3.3. Peak Shifts of the NH₃ Bands

Figure 13 (top) shows the $NH_3 \ 1070 \ cm^{-1}$ absorption band profiles for three ice samples before irradiation at 14 K: pure NH_3 , NH_3 – H_2O (1:1), and NH_3 – H_2O (1:10). The band peak shifts toward larger wavenumbers (shorter wavelengths)



Figure 10. Evolution of IR bands of new species formed after irradiation of NH_3 : H_2O (1:10) ice: (a) N_2O at 2230 cm⁻¹, (b) NO at 1870 cm⁻¹, and (c) NO_2 at 1606 cm⁻¹.

(A color version of this figure is available in the online journal.)



Figure 13. Ammonia band profiles of v_2 "umbrella" mode for the three samples with different molecule concentrations (top). Band peaks were normalized in other to better show their shifts. Wavenumber shifts of 1070 cm⁻¹ band peaks as a function of H₂O concentration including data from Bottinelli et al. (2010) (bottom). The solid line represents the exponential fit to the data (see the text).

as the percentage of water (%H₂O) in the sample increases. Wavenumbers at the maximum absorbance (band peak, λ) were plotted against %H₂O and the band shift was parameterized using an exponential fit to the data that also included peak positions obtained by Bottinelli et al. (2010; Figure 13, bottom). In both cases, FTIR spectra of amorphous ices containing different fractions of NH₃ and H₂O were taken in transmission mode. The exponential fit (solid line) yields the parameterization $\lambda(\%H_2O) = a + b[1 - \exp(-c\%H_2O)]$, where $a = (1070.1 \pm 1.3)$, $b = (98.6 \pm 32.5)$, and $c = (0.0074 \pm 0.0034)$. The parameterization does not imply a direct underlying physical relationship between the band peak and H₂O percentage. It intends mainly to provide an empirical method to determine NH₃/H₂O ratios in amorphous NH₃-H₂O ices using the peak position of the NH₃ band (1070 cm⁻¹).

Figure 14 shows the variation of the NH₃ 4478 cm⁻¹ band peak position as a function of %H₂O for amorphous NH₃-H₂O ices. The band peak positions from Zheng et al. (2009) and Zheng & Kaiser (2007) for crystalline and amorphous NH₃-H₂O ices are also plotted. The systematic difference between crystalline and amorphous cannot be accounted for by the experimental errors. It confirms the real difference between the shifts of the 4478 cm⁻¹ band for the two forms of ice, as also shown by Zheng & Kaiser (2007) using reflection mode FTIR spectroscopy. The exponential curve (dashed line) shown in Figure 14 is obtained from the 1070 cm⁻¹ band shifts (Figure 13), where an offset of the zero point to $a = (4478.1 \pm 1.3)$ cm⁻¹ was applied. The same exponential growth function remarkably represents both peak shifts.



Figure 14. Wavenumber shifts of 4478 cm⁻¹ band peaks as a function of H₂O concentration including data from Zheng et al. (2009) and Zheng & Kaiser (2007). The dashed line represents the exponential curve fitted to the data in Figure 13 shifted to $a = (4478.1 \pm 1.3) \text{ cm}^{-1}$ (see the text).

3.4. Initial Cross-sections

Initial destruction cross-sections (σ_d) for the original molecules in the sample can be obtained from the data in a straightforward procedure. Figure 15(a) shows the changes in normalized NH₃ (1070 cm⁻¹) band areas as a function of fluence for pure NH₃ ice samples irradiated by 536 MeV ⁶⁴Ni²⁴⁺ and 606 MeV 70 Zn²⁶⁺. If part of the decrement of NH₃ is due to loss by sputtering, the derived cross-section is overestimated. Assuming a sputtering yield of 10⁴ molecules per impact in both experiments-ignoring at first water layering from the residual gas that may prevent sputtering of NH₃ to some extent-the total loss of NH₃ after 2×10^{12} impacts cm⁻² would be 2×10^{16} molecules cm^{-2} . This represents less than 4% of the total NH₃ column density that is lost after a fluence of 2×10^{12} ions cm⁻² in both experiments: 5.5×10^{17} molecules cm⁻² (536 MeV Ni/NH₃) and 6.7×10^{17} molecules cm⁻² (606 MeV Zn/NH₃). Since this fraction would be highest in the case where no layering occurs, the effect due to sputtering on deriving initial cross-sections from simple exponential decay fits was considered to be negligible and within the experimental errors. Table 6presents all σ_d and their associated G-values (G) determined from single exponential fits to the data presented in Figure 15. Higher uncertainties associated with $\sigma_d(H_2O)$ and $G(H_2O)$ in Table 6 are due to the uncontrolled water layering during the experiment that affected the H₂O band areas (plots not shown).

It has been reported that NH_3 processing by ion irradiation in ice samples is enhanced in the presence of H_2O (Strazzulla & Palumbo 1998; Moore et al. 2007). This effect can be investigated by irradiating different samples containing NH_3 and H_2O with the same ion beam (projectile and energy) in different initial concentrations. Figure 15(b) shows the normalized NH_3 (1070 cm⁻¹) band areas as a function of fluence for the two NH_3 - H_2O samples. The exponential fit (dotted line) representing the loss of NH_3 after irradiation of the pure NH_3 sample by 536 MeV ⁶⁴Ni²⁴⁺ is also shown for comparison.

Figure 16 shows the relation between $\sigma_d(NH_3)$ and the electronic stopping power (S_e). Data from the literature were compiled to derive $\sigma_d(NH_3)$ using the same methodology as described above. The power law $\sigma_d(NH_3) = (6 \pm 2) \times 10^{-19} S_e^{(1.4\pm0.1)}$ was obtained for S_e in units of keV μ m⁻¹ and σ_d in units of cm². Since $\sigma_d(NH_3)$ is normally higher in NH₃–H₂O than in pure NH₃ ices, as we have shown, error bars for the points related to the results of Loeffler et al. (2010) and Pilling et al. (2010a) were set taking this systematic difference into account.



Figure 15. Changes in normalized NH₃ band area (ν_2) as a function of fluence for (a) pure NH₃ samples irradiated by 536 MeV ⁶⁴Ni²⁴⁺ and 606 MeV ⁷⁰Zn²⁶⁺ ions and for (b) NH₃–H₂O (1:1) and (1:10) samples irradiated by the same ion beam, 536 MeV ⁶⁴Ni²⁴⁺. Dotted, dashed, and solid lines represent exponential fits to the data from which initial cross-sections were obtained (Table 6).



Figure 16. Destruction cross-section (σ_d) and stopping power (S_e) relationship. The power law $\sigma_d(NH_3) \propto S_e^{1.4\pm0.1}$ is derived from $\sigma_d(NH_3)$ obtained in this work and those compiled from the literature. See details in the text.

Very similar power laws have been obtained for CH_3OH and CH_4 (de Barros et al. 2011b). Theoretical reasons for and implications of this particular scaling relation is beyond the scope of the present work. However, we should mention that our results for different ices irradiated by MeV ions, including those compiled from the literature, have suggested the existence of a tight relationships between initial cross-section and the electronic stopping power with a typical power value of 1.5. Such relationship have largely been investigated in the material science context for ion beams ranging from keV to MeV (e.g., Papaléo et al. 1996).

3.4.1. OH Dangling Bond

The OH stretching band at 3692 cm^{-1} , also called the OH dangling bond (OHdb), was observed in the two NH₃–H₂O ices prepared at 14 K. This vibration mode is associated with H₂O molecules in the *walls* of microscopic cavities or pores in the



Figure 17. Changes in OH dangling bond and H_2 bands in the spectra of NH_3-H_2O (1:10) before irradiation. The elapsed times (in minutes) after the first spectrum obtained are indicated.

(A color version of this figure is available in the online journal.)

ice (Rowland & Devlin 1991). It can be perturbed in different ways by trapped molecules within the micropores, altering the band peak position with respect to that of pure H₂O ice (Buch & Devlin 1991). Figure 17 shows changes in the shape and peak positions of the OHdb band after the NH₃–H₂O (1:10) sample preparation. The sample was prepared and kept at 14 K for more than 2.5 hr (153 min) before irradiation started. The changes in the OHdb band are related to the prompt appearance of the H₂ (4137–4141 cm⁻¹) band, suggesting adsorption and migration of H₂ molecules from the residual gas to the ice micropores (Devlin 1992; Hixson et al. 1992). It was observed that the efficiency with which H₂ enters the micropores is nearly 100% without need for warming (Rowland et al. 1991).

Figure 18 (top) shows the evolution of the OHdb band observed in the spectra of NH_3 – H_2O (1:10) ice during irradiation.

Table 6 Destruction Cross-section and G-values					
Projectile	Target	$\sigma_d({ m NH_3}) \ (10^{-15} \ { m cm}^2)$	$G(NH_3)$ (molecules/100 eV)	$\sigma_d({ m H_2O}) \ (10^{-15}~{ m cm}^2)$	G(H ₂ O) (molecules/100 eV)
536 MeV ⁶⁴ Ni ²⁴⁺ 536 MeV ⁶⁴ Ni ²⁴⁺ 536 MeV ⁶⁴ Ni ²⁴⁺ 606 MeV ⁷⁰ Zn ²⁶⁺	NH ₃ NH ₃ :H ₂ O (1:1) NH ₃ :H ₂ O (1:10) NH ₃	39 ± 6 61 ± 11 102 ± 17 46 ± 6	$\begin{array}{c} 4.3 \pm 0.6 \\ 6.8 \pm 1.2 \\ 11.5 \pm 1.9 \\ 4.6 \pm 0.7 \end{array}$	11 ± 7 12 ± 9 	1.2 ± 0.8 1.4 ± 1.0



Figure 18. (Evolution of the OHdb band as a function of fluence (top). Evolution of the OHdb band area as a function of fluence (bottom). The solid line represents the exponential fit to the data and the inset shows the methodology to measure the OHdb band area by fitting a quadratic baseline and two Gaussian components. (A color version of this figure is available in the online journal.)

The band areas were obtained by fitting two Gaussian functions with a quadratic baseline to the band profiles, as seen in the inset. An exponential fit to the band area data is shown in Figure 18 (bottom). The estimated destruction cross-section is $\sigma_d(\text{OHdb}) = (1.0 \pm 0.1) \times 10^{-11} \text{ cm}^2$.

The OHdb is primarily present in the NH_3-H_2O (1:10) amorphous ice, as discussed above; however, during irradiation, pores are destroyed by ice "compaction" or local annealing, due to the passage of the ion, leading to a decrease of the OHdb band area (Pilling et al. 2010a; Palumbo et al. 2010). It is interesting to note that a reverse behavior has also been reported when the sample is annealed before irradiation. Loeffler et al. (2010) showed OHdb formation after the irradiation of an annealed NH_3-H_2O ice by 100 keV H⁺. Irradiated ice, therefore, presents an intermediate condition. The magnitude of compaction or amorphization can vary drastically for different ion beams and energies, ultimately being a function of the physical properties of the ion track, such as radius and energy density (Raut et al. 2008). Heavy ions seem to be much more efficient at compacting the ice than light ions.

4. DISCUSSION: ASTROPHYSICAL IMPLICATIONS

In the ISM, energetic particles such as cosmic rays interact directly with dust grains. As soon as grains are completely exposed to the galactic radiation field, they are rapidly amorphized (Kemper et al. 2004). Inside cold molecular clouds, dust grains act as catalyzers, favoring chemical reactions at their surfaces. Furthermore, at around 10 K all gases except H_2 and He condense onto their surfaces. UV photons and keV ions from the external field cannot penetrate deeply into these clouds; however, MeV–GeV cosmic rays and collisionally accelerated secondary ions interact with the icy grains, inducing chemical reactions. In the MeV regime, the chemistry is mainly induced by δ electrons released from the regions very close to the passage of the cosmic ray. Electrons penetrate deeply inside the grains with enough energy to promote excitations and ionizations. As part of the deposited energy is converted into thermal energy, nanometer-size grains are processed and can evaporate completely (Bringa & Johnson 2002). Micron-size grains can lose part of their molecules either by prompt desorption (nonthermal desorption, electronic sputtering) or thermal desorption (Bringa & Johnson 2004). If the grain is large enough to maintain its form, its inner molecular properties change slowly as the cloud evolves. Changes in dust grains or in their icy mantles are very complex since several different physicochemical mechanisms occur simultaneously. For instance, valuable information for the astrochemical models are the total desorption yield for a given cosmic ray spectrum (e.g., Shen et al. 2004). As mentioned, thermal and non-thermal desorption should occur. The ratio between the yields due to both mechanisms that replenish the gas phase molecular reservoir is, in principle and at least, a function of the dust size, its physicochemical properties, and the energy of the incident ion. In addition, some authors point out that a significant fraction of the yields can originate from explosive chemical desorption promoted by an excess of radicals in icy mantles (Greenberg 1976; Léger et al. 1985; Schutte & Greenberg 1991; Shen et al. 2004). Concerning the inner physicochemical alterations, MeV and keV ions have different roles. MeV ions can pass through several micron-size dust grains, inducing chemical reactions until they get implanted in a final grain. During deceleration, the way in which the energy is transferred to the solid particles also changes significantly as a function of penetration depth.

Laboratory experiments designed for astrochemical investigations can only provide information for simplified astrophysical conditions, which yields a fragmented knowledge of the physical processes that are playing a role in real situations. However, they can be useful to quantify the role of individual physicochemical processes. Improvements in astrochemical models can occur when processes are well understood and taken into account. In this contribution, we deal with one form of interaction-that of the MeV heavy ions with pure NH3 and NH₃-H₂O ices. Several chemical pathways have been proposed to explain the radiolysis of pure NH3 and NH3-H2O ices (Moore et al. 2007; Zheng et al. 2008; Pilling et al. 2010a; Loeffler et al. 2010; Loeffler & Baragiola 2010, 2012) and here we concentrate on the observability and the astrophysical implications of the observed products. It should be noted that since NH₃-H₂O ice samples were prepared by gas deposition containing both species, their spectra should better represent mixed NH₃-H₂O icy mantles.

4.1. OHdb, H₂, and N₂: Observability and the H₂O-rich Ice Mantle Structure

The absorption band due to the OHdb ($3.69-3.71 \ \mu m$) is a good probe of the structure of ices containing water molecules (Rowland et al. 1991; Palumbo et al. 2010). To our knowledge, this band has not yet been observed in astronomical spectra, which suggests that H₂O icy mantles are mainly compact with low surface area, at least in the ISM. At least three mechanisms have been proposed in the literature to explain the amorphous and compact nature of H₂O icy mantles: (1) formation via surface reactions between O₂ and H atoms (Oba et al. 2009); (2) rapid compaction by UV radiation and cosmic rays (this work; Pilling et al. 2010a; Palumbo et al. 2010; Raut et al. 2008; Palumbo 2006); and (3) compaction as

a consequence of surface reactions, leading to the formation of H_2 (Accolla et al. 2011). Icy mantles also seem to present a segregated structure resembling the union shells shape, i.e., layered ice. Accretion at different timescales and differential thermal desorption induced by localized energy input (e.g., cosmic rays and exothermic surface reactions) may play a significant role and have been invoked to explain the shape and peak positions of the CO band in the spectra taken toward YSOs (Tielens et al. 1991; Fraser et al. 2004). The "destruction crosssection" of the OHdb absorption band obtained in the present work for NH₃:H₂O (1:10) ice put an additional constraint on the lifetime of amorphous and porous icy mantles under the effect of passages of typical 500 MeV heavy ion cosmic rays. The OHdb band disappears at approximately the same rate $(\sigma_{\text{OHdb}} = 1 \times 10^{-11} \text{ cm}^2)$ for a significant range of ion (Ni) energies, 50-500 MeV, and different samples, H2O:NH3:CO (1:0.6:0.4; Pilling et al. 2010a) and NH₃:H₂O (1:10; this work). These ions are about three orders of magnitude more efficient to promote OHdb band disappearance in H2O-dominated ices than 200 keV H⁺ ($\sigma_{\text{OHdb}} = 4.13 \times 10^{-14} \text{ cm}^2$; Palumbo 2006).

H₂ and N₂ are the simplest molecules formed during pure NH₃ ice radiolysis at 15 K but they show very different behavior. The way in which the molecular symmetry is broken in order to become IR active depends on the molecular environment and the ice structure, both of which abruptly change after irradiation. The H₂ IR band seems to be strongly sensible to this latter effect. After formation, the stretching mode of H₂ is activated through interaction with ice surfaces as they are trapped within microcavities or pores. If the sample is significantly scratched due to the effect of the incident ions, some cavities are destroyed and the molecules can escape (Figure 2(c)). An additional explaination of the sudden decrease in H₂ band area after a given fluence is that it may be due to blistering (see below). In NH₃-H₂O samples, it is possible to observe an increase of H_2 concentration even before irradiation (Figure 17), which suggests that H₂ molecules of the residual gas in the vacuum chamber can also diffuse into the ice samples, filling the microcavities already present. In principle, this could also occur in the icy mantles of grains; however, the 2.4 μ m vibrational band of H₂ trapped inside the ice has not been observed toward cold molecular clouds. So far, the absence of H₂ and OHdb in the spectra toward molecular clouds suggests that icy mantles of grains are indeed compact. In contrast, N₂ is not observed before irradiation in any sample and presents a more common behavior for a radiolytic product. Unlike H2, N2 does not diffuse into the ice and is kept in the solid phase at 14 K, so the band area increase is mainly due to its formation during irradiation. However, the weakness of the corresponding band and proximity to the CO band make it unlikely to be detectable in astrophysical environments.

 H_2 and N_2 formation is indeed an important result of the radiolysis of pure NH_3 and NH_3-H_2O ices. Loeffler & Baragiola (2012) have directly observed the blistering effect caused (mainly) by trapped H_2 and N_2 gases in NH_3-H_2O (1:2) ices after radiolysis (T > 20 K) followed by heating. This has possible consequences for understanding the release of gas and grains by icy surfaces in the solar system, such as those by comets and icy satellites. H_2 trapped in the pure NH_3 sample analyzed here (Figure 2(c)) peaks at $\sim 1.2 \times 10^{12}$ ion cm⁻² in comparison with $\sim 1 \times 10^{15}$ ion cm⁻² for the 100 keV H⁺ irradiation of NH_3-H_2O (1:2) ices at 20 and 70 K (Loeffler & Baragiola 2010). Thus, MeV heavy ions may produce blisters three orders of magnitude faster than keV light ions. As blistering also causes abrupt changes in specular reflectance, as shown by Loeffler & Baragiola (2012), changes in absorbance due to scattering may also occur. Abrupt changes in band areas after initial fluences of different molecular species in several ice samples have been observed in our experiments with MeV heavy ions, suggesting that blistering is a common phenomenon that leads to explosive desorption and rapid changes in the optical properties of ice samples.

4.2. The NH_4^+ (6.85 μm) Hypothesis

Among several molecular species proposed to elucidate the origin of the observed 6.85 μ m band in the IR spectra toward protostars, the ammonium ion is the main candidate, originally proposed by Grim et al. (1989a, 1989b). However, most of the studies agree that to satisfactorily reproduce the observed band shape, at least one other species must be considered (e.g., Keane et al. 2001; Moon et al. 2010). Moreover, it has been suggested that the 5–8 μ m spectrum is better explained if icy mantles are at different temperatures along the line of sight and those with T > 100 K are the main contributors to the 6.85 μ m feature (Grim et al. 1989b). Pilling et al. (2010a) have shown that the 6.85 μ m band of an irradiated H₂O:NH₃:CO (1:0.6:0.4) ice sample presents strong absorption variations, for instance, relative to the 6.0 μ m band (H₂O and NH₃) during warm up (see their Figure 6(a)). The shape and peak position of the 6.85 μ m band at 150–200 K remarkably match those observed in the spectrum of the high-mass YSO W33A. Similar results were also obtained by Schutte & Khanna (2003), based on photolyzed H₂O:CO₂:NH₃:O₂ ice. Here, we have observed that NH_4^+ is likely to be formed after the irradiation of pure NH₃ and NH₃-H₂O ices with MeV heavy ions. The detection of the NH₄⁺ $2v_4$ for both cases put additional constraints on the contribution to the 6.85 μ m band due to the v_4 mode. Thus our results support the scenario proposed by Grim et al. (1989b) to explain the 5–8 μ m IR spectrum of W33A, where the processing of icy mantles (mainly due to MeV heavy ions) fits in. However, a more extensive spectral mixture analysis is required to better reproduce astronomical spectra.

4.3. Production and Destruction Yields

Since formation and destruction yields scale with stopping power, several new species can be observed after processing NH₃ pure and NH₃-H₂O ices by 500 MeV heavy ions at relatively low fluences (10^{13} ion cm⁻²). The stopping power for these projectiles is two orders of magnitude higher than for 1 MeV light ions (H⁺, α -particle). N-bearing species, however, seem to present relatively low IR-band strengths in comparison with O- and C-bearing species. Hence, band strengths, even for the simplest N-bearing species in NH₃ or NH₃-H₂O rich ices, are poorly known.

Here we observe N₂H₄ as the main stable product of pure NH₃ ice at 15 K. The band assigned as ν_6 mode at 895 cm⁻¹ indicates that a fraction of N atoms from NH₃ dissociation is stored in N₂H₄ molecules. In ISM, however, this band would hardly be detected since it would be blended with the broad H₂O (libration mode) and silicate bands. A different perspective to find constraints on the processing of NH₃ in icy mantles may come from hybrid species formed from NH₃–H₂O ice processing. N₂O with its strongest vibrational band at 4.484 μ m (ν_1) is a good candidate (see Figure 12) since it lies in a relatively free spectral region between the ¹³CO₂ and OCN⁻ bands. Based on the data of Figure 11 and band strengths provided

by Grim et al. (1989a) and Fulvio et al. (2009), we estimate a corresponding production of $N(N_2O) = (1.1-1.4) \times 10^{15}$ molecules cm⁻² and $N(NO) = 5.4 \times 10^{15}$ molecules cm⁻² after a fluence of 1.3×10^{13} ion cm⁻² from an initial column density of $N_0(NH_3-H_2O, 1:10) = (4.9 \pm 0.2) \times 10^{18}$ molecules cm⁻², giving yields of $125 \pm 15 \text{ N}_2\text{O}$ and $540 \pm 40 \text{ NO}$ molecules formed per ion impact. This suggests that the simple N₂O and NO molecules may be present in relatively high amounts in interstellar ices but are still undetected through IR spectroscopy. This may be true not only for N₂O and NO, but also for other N-bearing molecules detected in this work.

5. SUMMARY

We investigated the chemical processing (radiolysis) of pure NH₃ and NH₃-H₂O ices in different concentrations at 14 K, induced by energetic (500–600 MeV) heavy ion beams (Ni, Zn) in vacuum conditions using FTIR spectroscopy. The following conclusions can be drawn.

- 1. Several new species are formed and identified during the radiolysis of pure NH₃ ice, including H₂, N₂, N₂H₂ isomers (cis-, iso-, trans-), N_2H_4 , and NH_4^+ . We tentatively identified $NH_4^+N_3^-$, N_3^- , and HN_3 , suggesting an even more complex chemistry of NH₃ ice radiolysis.
- 2. New species formed and identified during NH₃-H₂O ice radiolysis are H₂, N₂, NH⁺₄, NO, N₂O, NO₂, HN₃, and NH₂OH.
- 3. The wavelength peak position of the NH₃ "umbrella" IR band at 1070–1120 cm⁻¹ (8.93–9.35 μ m) of amorphous ices is parameterized as a function of the concentration ratio, NH₃/H₂O, to provide an empirical concentration determination.
- 4. The NH₃ destruction cross-section, $\sigma_d(NH_3)$, increases slightly as a function of the initial H₂O concentration in the sample: from $(4.5 \pm 1.1) \times 10^{-14}$ cm² for pure NH₃ to $(9.8 \pm 1.4) \times 10^{-14} \text{ cm}^2$ for NH₃:H₂O (1:10) ice samples. Based on our results and data collected in the literature, a power law relationship between $\sigma_d(NH_3)$ and stopping power (S_e), $\sigma_d(NH_3) \propto S_e^{1.4\pm0.1}$, is verified.
- 5. The rate for "ice compaction" from a porous amorphous initial state, porous or amorphous, is estimated by the destruction cross-section of the OHdb, $\sigma_{d}(OHdb) = (1.0 \pm$ 0.1) × 10⁻¹¹ cm², for NH₃:H₂O (1:10) ice bombarded with 536 MeV ⁶⁴Ni²⁴⁺. The "ice compaction" hypothesis is strengthened by the simultaneous observation of the OHdb band and the fundamental vibration of H₂, indicating the existence of H₂ trapped in the ice pores.
- 6. Besides NH_3 and possibly OCN^- and NH_4^+ , N-bearing molecules, including those with simple structures as NO, NO₂, and N₂O, may be present in interstellar icy grains in relatively high amounts. They are direct products of the NH₃-H₂O ice processing and their IR bands have very low band strengths. These molecules are, however, good candidates to be observed in interstellar ices in the near future.

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