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Formation of N–O–H bearing species in HNO₃ and H₂O icy samples by heavy-ion irradiation: an infrared spectroscopic study

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Abstract

This article investigates the radiolysis of a mixture of nitric acid with water (HNO₃:H₂O) at 16 K in high-vacuum (residual pressure < 10⁻⁶ mbar). A nitric acid-water ice film was exposed to 40 MeV ⁵⁸Ni¹¹⁺ ion beam in a heavy ion accelerator facility in France. For this astrochemically- and atmospherically-relevant ice mixture of nitric acid and water, we analyze the possible formation and destruction processes of N-O bearing species, thus providing spectroscopic data in the infrared region for theoretical, laboratory and observational future studies. The irradiation synthesized eighteen species which were posteriorly examined by infrared spectroscopy: N₂O, NH₃, NO, NO₂ and H_xN_yO_z molecules, such as hydroxylamine (NH₂OH), nitrous acid (HONO) as well as other species with bonding N-O, N-H and H-O-N converting surface-adsorbed nitrogen oxides into astrochemically active NO_x. The interaction of HNO₃ and H₂O originates H-N-O molecular complexes, which were investigated as particular cases of the hydrogen-bonded species formed by a more electronegative atom (N or O) interacts intra or intermolecularly with a donor atom (N or O) and observed in the interstellar medium with higher quantities or great abundances. The HNO₃ and H₂O destruction cross sections have been determined to be 8.5 x 10⁻¹³ and 1.2 x 10⁻¹³ cm², respectively, for the mentioned experimental conditions.

Keywords: condensed phase; interstellar medium; infrared spectroscopy

1. Introduction

Nitrogen oxide molecules are supposed to play a significant role as a nitrogen reservoir in the interstellar medium. The term nitrogen oxides refer here to a broader list of chemical species, in which are included small molecules containing only N-O and N-H bonds (e.g., N_xO_y and N_xH_y), as well as some H-N-O species, in particular HNO (nitrosyl hydride). It has been also demonstrated that nitrogen oxides potentially participate in the formation of more complex species; for example, the ion processing of N_2O ice leads to formation of new species [1-3] and the solid-state hydrogenation of NO results in the formation of hydroxylamine (NH_2OH) [2], a species linked to the formation of prebiotic amino acids in space [3]. Until now, only NO, N_2O , HNO and HONO have been detected in the interstellar medium [4-6]. Nitric acid (HNO_3), which-plays a role in the Earth's atmospheric pollution, has not yet been detected in the interstellar medium (ISM).

Investigation of pure or mixed nitric acid ices were done in the context to understand heterogeneous chemistry on the surfaces of Earth polar stratospheric clouds (PSCs) [3,7]. Guillory et al. [7] reported the spectra of both the monomer and dimer; they hypothesized that the dimer has a cyclic structure. The photolytic properties of nitric acid were studied by Lee and colleagues [8]; they provided the spectra of HNO_3 in both argon and nitrogen matrices at lower temperatures. Chen et al. [9] found an IR absorption related to HONO after irradiating HNO_3 in solid Ar at 12 K with various sources of UV light. They claim that there is a substantial interaction between nitric acid and nitrogen based on the sizeable changes in the O-H stretching and NOH in-plane bending modes between argon and nitrogen matrices, but it seems that they did not look for a nitric acid-nitrogen complex in argon matrices. Barnes, A. J., Lasson, E., & Nielsen, C. J. [10-12] studied, by matrix isolation IR Spectroscopy, the molecular complexes of nitric acid with N, CO and NO; because of the HNO relative stability, they verify that it serves as a reservoir for NO, may be carried to the troposphere and subsequently dissipated there. It may also be integrated into aerosols by interaction with ammonia to generate ammonium nitrate.

Therefore, to comprehend the process of nitrous acid (HONO), nitrosyl hydride (HNO), nitric acid (HNO_3), nitrogen dioxide (NO_2), and nitrous oxide (N_2O) syntheses in the interstellar medium and the Earth's atmosphere, it is crucial to understand the reactivity between OH radicals and NO. Nitrous acid (HONO), which has been recently detected in ISM in addition to its significance in atmospheric chemistry, is a crucial precursor for the production of hydroxyl radicals [4]. Complex molecules have been identified in meteorites and in the ISM; their production in these environments from simple molecular species probably involves non-observed species in the chemical pathway evolution; the HNO_3 may be one of these species. In the current research, it is assumed its occurrence in water and products of their radiolysis is examined. Moreover, a method for simultaneous identification and abundance evolution measurement of molecular species in solids is treated; the laboratory setup combines Fourier Transform Infrared spectroscopy (FTIR) with heavy and swift ion beam irradiation. Aiming the understand the nitric acid and water ($\text{HNO}_3\text{:H}_2\text{O}$) ice radiolysis, we have analysed the effects produced by the heavy and swift ion irradiation of this mixture at low temperatures.

2. Methods

The measurements were conducted in a high vacuum chamber at the IRRadiation SUD (IRRSUD) beamline of the French National Heavy Ion Accelerator (GANIL), using the CASIMIR set-up of CIMAP; for further information on experimental procedures see [4,15]. By applying the corresponding partial pressure to both components in the pre-injection preparation ramp, a nitric acid (HNO_3) and water mixture with the relative concentration of 0.7:1 was produced around pressures 8×10^{-6} mbar. The nitric acid compound was acquired commercially from Sigma-Aldrich; the used (ultra pure) water had an electric conductivity of $10^7 \text{ } \Omega\text{cm}$ (Milli-Q). Both liquids were degassed through freeze-pump-thaw cycles and then they were both mixture in the pre-injection preparation ramp and

condensed at 16 K on a CsI substrate. The mixture was then deposited on the substrate via a capillary injection tube held approximately 10 mm away from the substrate. The deposit of the mixture also lasted for roughly 3 minutes. It is expected that the HNO_3 and H_2O components of the mixture would react between themselves, but – after the the condensation – the precursor compounds are regenerated [14].

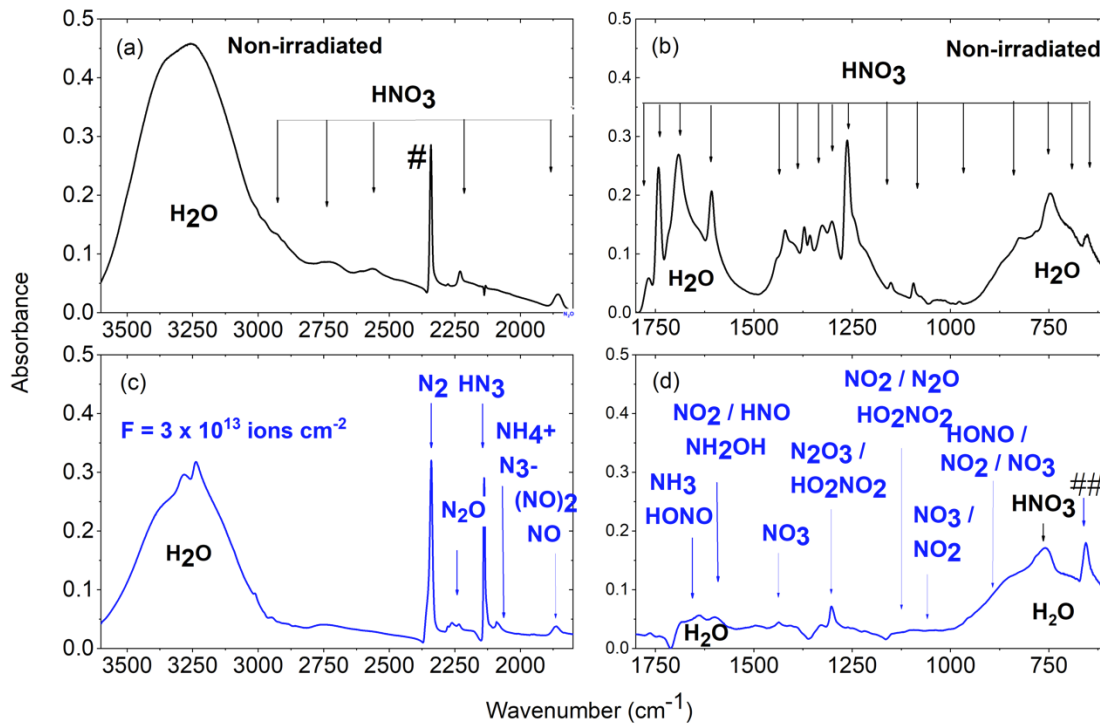


Fig.1 Mid-IR spectrum of $\text{HNO}_3:\text{H}_2\text{O}$ (0.7:1) at 16 K: (a) unirradiated sample from 3600 to 1800 cm^{-1} region, (b) unirradiated sample from 1800 to 600 cm^{-1} region, (c) sample irradiated with 40 MeV $^{58}\text{Ni}^{11+}$ at fluence 3.0×10^{13} ions. cm^{-2} from 3600 to 1800 cm^{-1} region, (d) sample irradiated from 1800 to 600 cm^{-1} region. The # refers to the possibility of a chemical reaction in the mixture of $\text{HNO}_3 + \text{H}_2\text{O}$ generating N_2 or $\text{NO}_2^+ - \text{NO}_3^+$ [13] and ## are unknown bands. The two peaks that appear on the top of water band located around 3300 cm^{-1} were also observed by Zondlo et. al. [14].

A 40 MeV $^{58}\text{Ni}^{11+}$ (0.70 MeV u^{-1}) ion beam was used to irradiate the sample. A FTIR spectrometer (Nicolet Magna 550) was used in transmission mode for in-situ infrared (IR) data acquisition over the 4000 to 600 cm^{-1} wavelength range. Each IR spectrum was collected using 256 scans with 4 cm^{-1} resolution. When the radiation was applied, the chamber pressure was less than 2×10^{-8} mbar, and the beam flux was 1×10^9 ions. $\text{cm}^{-2}.\text{s}^{-1}$. **Fig. 1** displays two Mid-IR absorption spectra of $\text{HNO}_3:\text{H}_2\text{O}$ (0.7:1) mixture at 16 K: (a) the unirradiated sample and irradiated ion fluence ice (b) at 3.0×10^{13} ions. cm^{-2} .

For the ice thickness calculation the Beer-Lambert Law, $N_0 = \ln 10 S_0 / A_v$, and the thickness expression $L = (N_0 M) / (\rho N_A)$ have been used. N_0 is the initial column density of each precursor [cm^{-2}], S_0 is integrated absorbance [cm^{-1}], A_v is the A-value (band strength) [cm molec^{-1}], M is its molar mass [u], ρ is its density [g cm^{-3}], and N_A is the Avogadro's number. The HNO_3 and H_2O mass densities considered are 1.75 g.cm^{-3} [17] and 0.87 g.cm^{-3} , respectively [18]. The water component can be calculated from the IR absorption. The initial integrated absorbance for the water 3284 cm^{-1} band was measured to be $S_0 = 45 \text{ cm}^{-1}$; considering its A-value as $2.0 \times 10^{-16} \text{ cm.molec}^{-1}$, the water equivalent thickness is 8.0 nm. The nitric acid is approximately the same, so that the ice mixture thickness is roughly 16 nm. The calculated projectile penetration depth is 6.1 μm , which means that the

beam passes through the ice mantle without implantation. Thus, the molecular destruction cross-sections can be assumed constant along the projectile track in the sample. The projectile's electronic stopping power (S_e) calculated using the *Stopping and Range of Ions in Matter* (SRIM) [19] package is 5.9×10^3 keV/ μm , and the nuclear stopping power (S_n), 1.3 keV/ μm , is relatively negligible.

3. Results and Discussions

3.1 Possible formation of HNO_3

Nitric acid (HNO_3), which is produced by the interaction of NO_2 with OH radicals, is important in stratospheric chemistry [20]. It is a key component of polar stratospheric clouds, which are made of nitric acid ice with a sulphuric acid core. HNO_3 may also be absorbed into aerosols through a reaction with ammonia to create ammonium nitrate (NH_4NO_3). Additionally, other groups have reported infrared studies of gaseous and condensed nitric acid [21,22,23]. Experimental research on the hydrated nitric acid in the upper troposphere [24] shows that because of its relative stability, nitric acid may be carried down into the stratosphere, where it serves as a reservoir for NO. Ab-initio calculations predict that the interaction between nitric acid and ammonia produces a highly hydrogen-bonded complex, but no experimental examination of this complex has been documented [25]. McGraw et al. [21] completely assigned the vibrational spectrum of nitric acid in the gas phase, and a number of subsequent high-resolution investigations [26,27] have improved the wavenumber estimates for the band centers. The impact of hydrogen bonding in the liquid and solid phases, as seen by substantial changes of the O-H stretching, NOH in-plane bending, and NOH torsional modes, was also covered by McGraw et al. [21]. According to Belin and Potier's [28] study of the infrared spectra of the acid in these solutions in the OH stretching area, nitric acid weakly self-associates to form open chain dimers and trimers in chloroform and carbon tetrachloride solutions. In the gas phase, Millen and Samsonov [29] looked at the same complex as well as at those containing methyl n-propyl ether and diethyl ether as McGraw et al. [21] and Lund Myhre et al. [30].

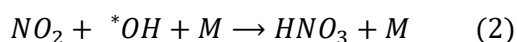
Nitric acid can be trapped in nitrogen matrices, as shown by the infrared spectra of the substances studied [23]. Guillory et al. reported the spectra of both the monomer and dimer, and they hypothesized that the dimer has a cyclic structure [22]. The photolytic properties of nitric acid were studied by Lee and colleagues [31]; they provided the spectra of HNO_3 in both argon and nitrogen matrices at lower temperatures. Chen et al. [9] found an IR absorption related to HOONO after irradiating HNO_3 in solid Ar at 12 K with various sources of UV light. They claim that there is a substantial interaction between nitric acid and nitrogen based on the sizeable changes in the O-H stretching and NOH in-plane bending modes between argon and nitrogen matrices, but it seems that they did not look for a nitric acid-nitrogen complex in argon matrices. Nowadays, relatively little research on solid nitric acid complexes has been published. Barnes, A. J., Lasson, E., & Nielsen, C. J. [32,33] studied, by matrix isolation IR Spectroscopy, the molecular complexes of nitric acid with N, CO and NO; because of the HNO relative stability, they verify that it serves as a reservoir for NO, may be carried to the troposphere and subsequently dissipated there. It may also be integrated into aerosols by interaction with ammonia to generate ammonium nitrate.

The photochemistry of nitric acid at 4.2 K has been studied using matrix isolation and Fourier transform infrared (FTIR) spectroscopy by Koch et al. [34]. Peroxynitrous acid (HOONO) was produced by UV photolysis of the matrix-isolated precursor in argon ($\text{MR} = 1/4000$) at 184.9 and 253.7 nm, most likely by cage recombination of $\text{OH} + \text{NO}_2$. HOONO seems to produce secondary NO and HO_2 by photolysis. They describe that, due to the equilibrium of catalytically active HO^* and NO^* , radicals in the stratosphere are significantly influenced by HONO_2 . It is well

known that, in Earth's troposphere, nitric acid (HNO_3) is one of the most common transformation products of NO_x species [35], generated via reactions involving nitrogen oxides and water [36], as shown in Eq. (1):



Molecules adsorbed on the surface of ice (as NO_x) can react with water vapor in heterogeneous reactions during deposition phase to form nitrous and nitric acids. In this case, the reactions are catalysed by the surface [37]. In this scheme, in Eq. (2) presents an important reaction to form HNO_3 in the atmosphere is the reaction of NO_2 with OH radicals (most likely from the water dissociation):



where M is any molecule in the gas phase [38,38a].

3.2 IR absorption of precursors: HONO_2 and H_2O

When in an aqueous medium, nitric acid has a strongly acidic behavior ($\text{pK}_a = -1.38$, at 298 K) [39], being deprotonated by hydronium ion ($\text{H}_3\text{O}^+(\text{aq})$), conjugate acid of water, and the nitrate ion ($\text{NO}_3^-(\text{aq})$), conjugate base of nitric acid, whose structure is stabilized by resonance.

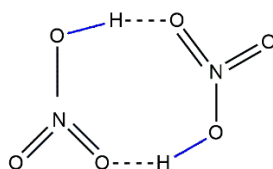


Fig 2. Schematic representation of the molecular structure of nitric acid in aqueous medium.

Fig. 2 represents the nitric acid dimer structure. The O-H bond (blue lines) undergoes a weakening due to hydrogen bonds (dotted lines) formed between nitric acid molecules.

Marchand et al. [17] performed a spectroscopic study of the dissociation of nitric acid in ice, using different nitric acid/water ratios in mol percent. The authors argue that the absorption between 1300 and 1500 cm^{-1} , where the NO asymmetric stretching mode occurs, is on top of a continuous background absorption that is recognized as characteristic of the aqueous proton (H_3O^+) in aqueous solutions. The presence of this type of absorption, observed in the condensed phase, suggests that ionic dissociation of 5-15% of the molar fraction of nitric acid occurs, even at 45 K.

The bands observed in the condensed phase (1690 - 1700 cm^{-1} , 960 - 965 cm^{-1} , 1250 - 1450 cm^{-1}), analogous to the molecular nitric acid bands in the gaseous phase, strongly overlap the bands referring to the asymmetric vibrations of NO stretching of the nitrate ions (NO_3^-). As a consequence, it is extremely difficult to analyse the dissociation process in this frequency range. The observation of a weak band at 1044 cm^{-1} clearly indicates the presence of nitrate ions. In the current work, the referred band was not observed, which indicates that the ionic dissociation was inhibited; moreover, it was also not possible to visualize a broad band around 2700 cm^{-1} , usually attributed to the OH stretching vibrations of the hydrogen bond formed between the oxygen of the water and the hydrogen of the nitric acid molecule in the condensed phase.

On the other hand, it has been shown that nitric acid can form cyclic dimers through intermolecular hydrogen bonds [10,22], as proposed in **Fig. 2**. In this case, the OH stretching band undergoes a shift toward lower frequencies when compared to the monomer one, indicating the weakening of the O-H bond [8,11]. Analyzing

spectra of matrices with high concentration of nitric acid or in annealed matrices around 30 K, Barnes and coauthors [10,11] found absorptions attributed to the nitric acid dimer. Their findings in argon matrix are consistent with those observed by Guilfory and Bernstein [7], in which the vibrations of symmetric O-H stretching (ν_1) and antisymmetric stretching of NO_2 (ν_2) showed significant shifts to low frequencies. In the current work, using the (0.7:1) $\text{HNO}_3/\text{H}_2\text{O}$ mixture, the IR spectrum obtained at 16 K (see **Fig. 1**) shows a band at 3284.3 cm^{-1} (ν_1) and another one at 1690.7 cm^{-1} (ν_2) which may indicate dimer formation (**Fig. 2**). Chen et al. [9] irradiated HONO_2 in solid Ar at 12 K with various sources of UV light. Based on isotope shifts, they discovered HOONO IR absorption bands: four IR absorption lines, at 3545.5 , 1703.6 , 1364.4 , 952.0 , and 772.8 cm^{-1} , all attributed to HOONO vibrational modes.

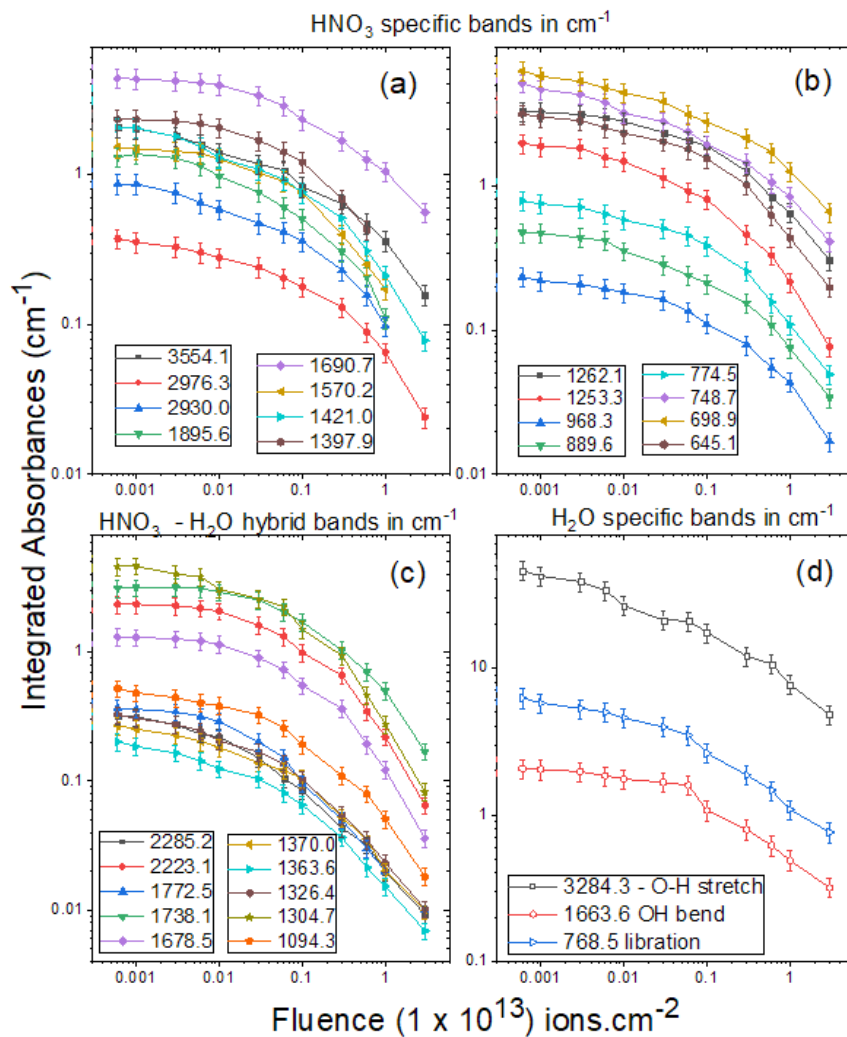


Fig. 3 Integrated absorbance (peak area, in cm^{-1}) evolution of HNO_3 and H_2O precursor bands with irradiation fluence: (a) for 8 fundamental bands, (b) for other 8 fundamental bands, (c) for 10 hybrid bands, and in (d) three specific H_2O bands. The behavior practically parallel of the curves confirms that they represent the HNO_3 column density decrease during the irradiation. Error bars are typically 5%.

It was determined that HOONO was present at a less stable position in the Ar matrix because, under certain experimental circumstances, a second set of lines was 5-18 cm^{-1} away from the first set of lines and shifted toward a higher wavenumber. These vibrational frequencies are comparable to those in the gas phase, but the vibrational frequencies of ν_1 (OH stretching) and ν_3 (HON bending) of HONO₂ in solid Ar were found to be substantially different from those previously reported for HONO₂ in solid N₂ by Guillory and Bernstein [22]. These unusual matrix alterations show that HONO₂ and N₂ molecules interact strongly with each other. Although the experiments by Chen and collaborators do not explain the nature of the matrix interaction between N₂ and HONO₂, the authors believe that nitrogen can interact with nitric acid by hydrogen bonds forming the HONO₂·N₂ complex, a six-membered ring that can be stabilized by resonance [23].

This fact raises the question whether the strong interaction between the matrix guest and host causes the photochemistry of HONO₂ isolated in solid N₂ to be different from that in solid Ar. Chen et al. [23] verified that after HONO₂ photolysis in the N₂ matrix, a very small peak attributed to nitric acid was observed at 1704.4 cm^{-1} in the same spectral region as the one reported by Joshi et al. [40]. The NO stretch normally occurs between 800 and 900 cm^{-1} , typical for nitrogen oxide systems such as nitrous acid (cis and trans) and has a corresponding shift of 10 to 15 cm^{-1} upon ¹⁵N substitution [15]. Between 600 and 700 cm^{-1} , the NO₂ valence bending motions are observed with a shift of 2 to 3 cm^{-1} upon ¹⁵N replacement. Applying these general principles to the matrix-isolated infrared spectra observed in the current work, it is reasonable to attribute the absorption seen at 889.6 cm^{-1} to the NO stretch. Contrarily, the absorption at 657.7 cm^{-1} is due to the NO₂ valence bending vibration.

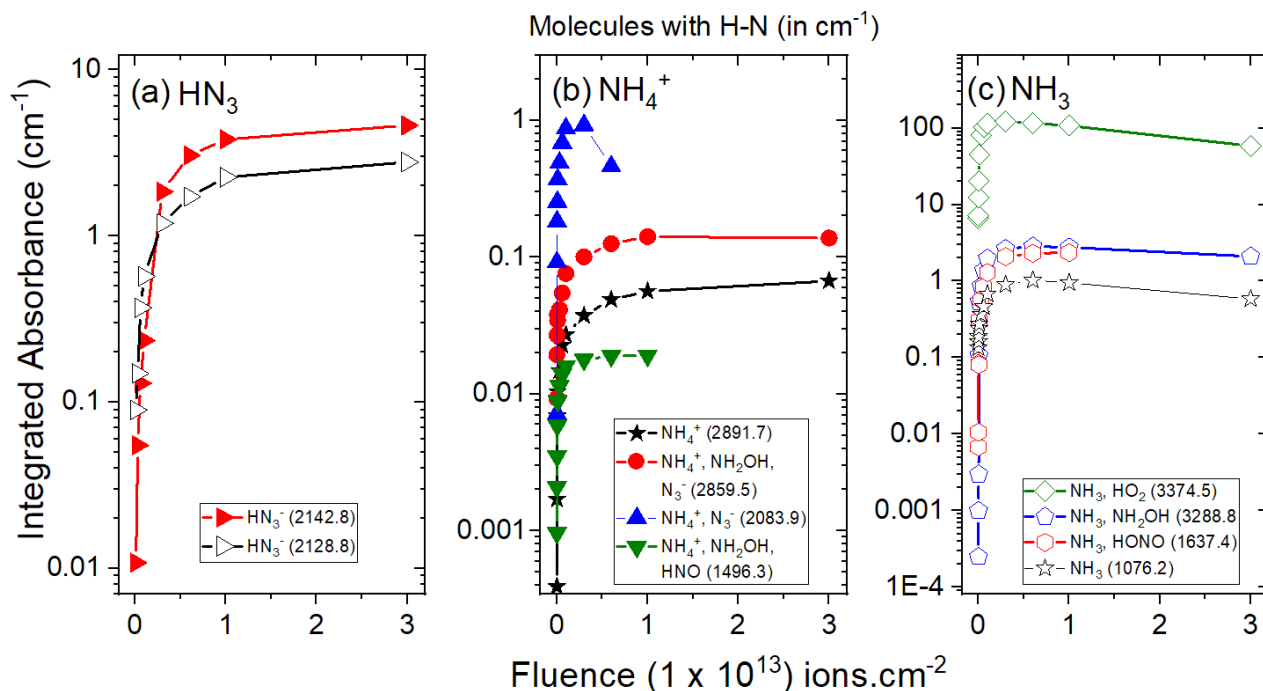


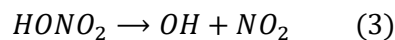
Fig. 4 Evolution of integrated absorbance, as a function of 40 MeV ⁵⁸Ni¹¹⁺ beam fluence, of selected band of the products: (a) HN₃, (b) NH₄⁺ and (c) NH₃.

Figure 3 shows absorbance decrease of the observed HNO_3 bands as a function of ion fluence, which indicates the loss of the precursor's column density. In this work, twenty six HNO_3 bands are identified: 3554.1, 2976.3, 2930, 2285.2, 2223.1, 1895.6, 1772.5, 1740, 1738.1, 1690.7, 1681.7, 1570.2, 1421.0, 1370.0, 1363.6, 1326.4, 1304.7, 1262.1, 1253.3, 1094.3, 968.3, ~ 870.5 , 778.6, 748.7, 698.9, 645.1 cm^{-1} , as well as three water bands: 3284.3, 1663.6 and 768.5 cm^{-1} . All of them are displayed and referenced in **Table 1**. Three water bands are observed at: 3284.3, 1663.6 and 768.5 cm^{-1} , respectively.

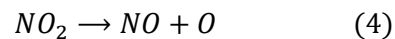
3.3 Formation of new species during irradiation

Figs. 4, 5, 6 and 7 show the absorbance evolution of the radiolysis products. The assignment of nitric acid bands is described in detail in [4,7,8,12,13,15]. **Table 1** summarizes, for precursors and products, the band positions before and after irradiation.

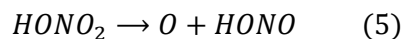
Chen et al. [23] describe some possible formation and destruction mechanisms during the HNO_3 irradiation, Eq. (3):



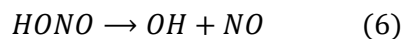
followed by



and



followed by



New molecular species appear during the irradiation of the $\text{HNO}_3:\text{H}_2\text{O}$ mixture, some of them also observed when comparing the photochemistry of HNO_3 imbedded in solid Ar and N_2 matrices. However, Burkholder et al. [41], using a high-resolution FTIR spectrometry coupled with a rapid-flow multipass absorption cell to study the gaseous reaction of OH with NO_2 (Eq.4), were unable to find any IR absorption in the range 1850-3850 cm^{-1} that could be attributed to HOONO.

3.3.1 Formation of the H-N species

Unlike Loeffler & Baragiola [42] and Bordalo et al. [43], we did not observe the H_2 band at 4128 cm^{-1} . Carlo et al. [44] reported that the initial reaction of HN_3 leads to the formation of azide ions (N_3^-), indeed observed in the current work at a 2083.9 and 2859.5 cm^{-1} .

Two bands observed at 2142.8 and 2128.4 cm^{-1} (**Fig. 4a**) are attributed to the HN_3 molecule (hydrazoic acid) [44, 45]. Zheng et al. 2018 [45] studied the infrared absorption spectra of amorphous solid ammonia at 10 K, before and after exposure to radiation. They found a band at 2088 cm^{-1} , corresponding to HN_3 , and a newly generated molecular nitrogen (N_2) correlated to the 2348 cm^{-1} absorption.

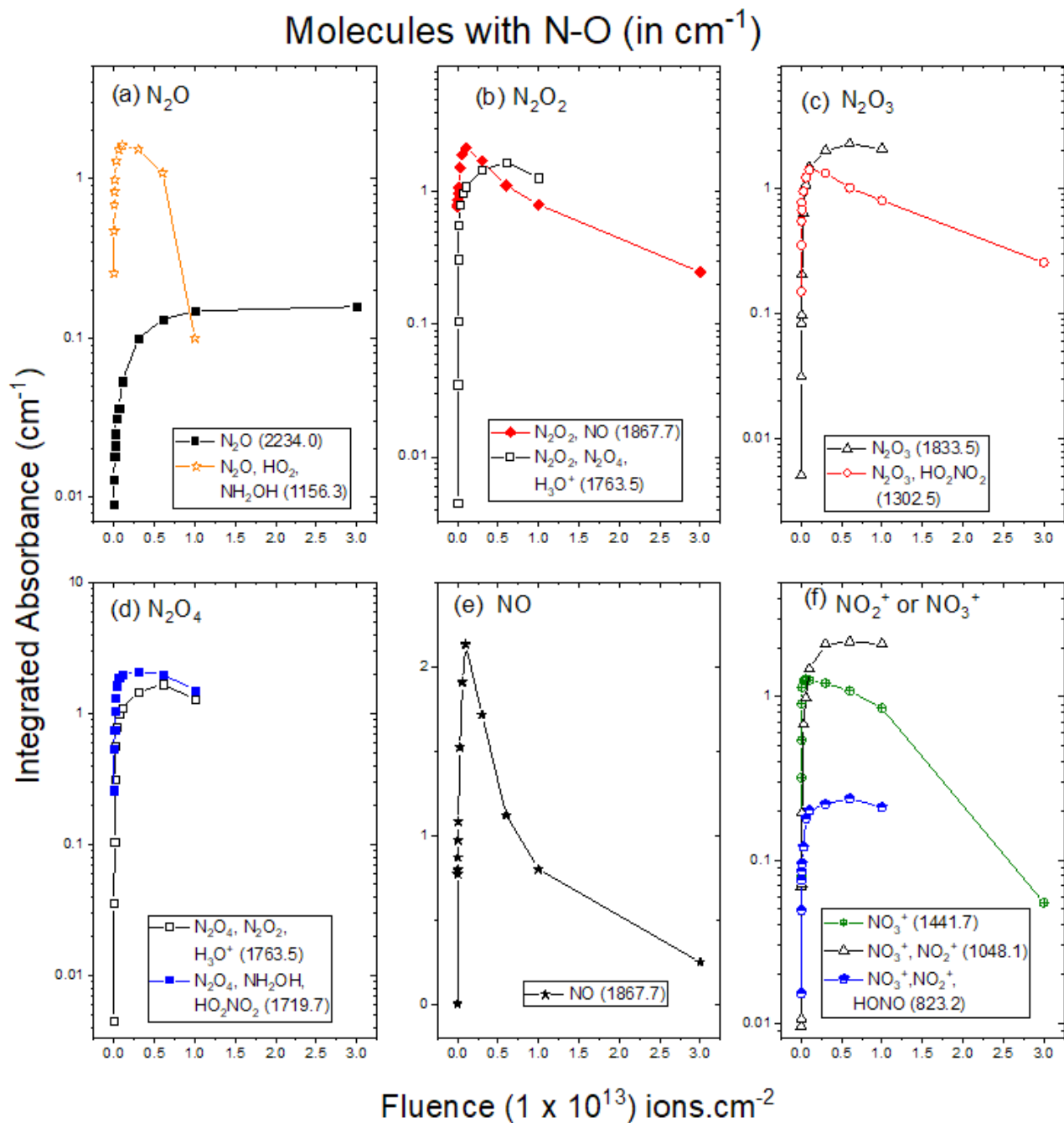


Fig. 5 Evolution of integrated absorbance, as a function of 40 MeV $^{58}\text{Ni}^{11+}$ beam fluence, of selected band of the products: (a) N_2O , (b) N_2O_2 , (c) N_2O_3 , (d) N_2O_4 , (e) NO and (f) NO_2^+ and NO_3^+ as a function of irradiation fluences.

Bordalo et al. [43] studied NH_3 and $\text{NH}_3+\text{H}_2\text{O}$ ices irradiated with heavy ions and observed nine features assigned to NH_3 absorption bands. As a products of NH_3 irradiation, they reported: N_2 , H_2 , NH_2 , ammonium ion (NH_4^+), nitrogen oxide (NO), nitrous oxide (N_2O), and nitrogen dioxide (NO_2); these are considered the most abundant products of the radiolysis of ammonia-water ices. Moreover, they found out that NH_2 and NH_4^+ should be chemically combined, and it is challenging to estimate how much each contributes to the ν_4 mode feature at 6.85

μm (1500 cm^{-1}) band. NH_4^+ ($2\nu_4$) is expected to be seen at 2890 cm^{-1} . In the current work, as shown in **Fig. 4b**, these two bands are also observed. **Fig. 4c** presents the 3374.5 , 3288.8 , 1637.4 and 1076.2 cm^{-1} bands, all attributed to NH_3 , fact that characterizes this molecule as a radiolysis product.

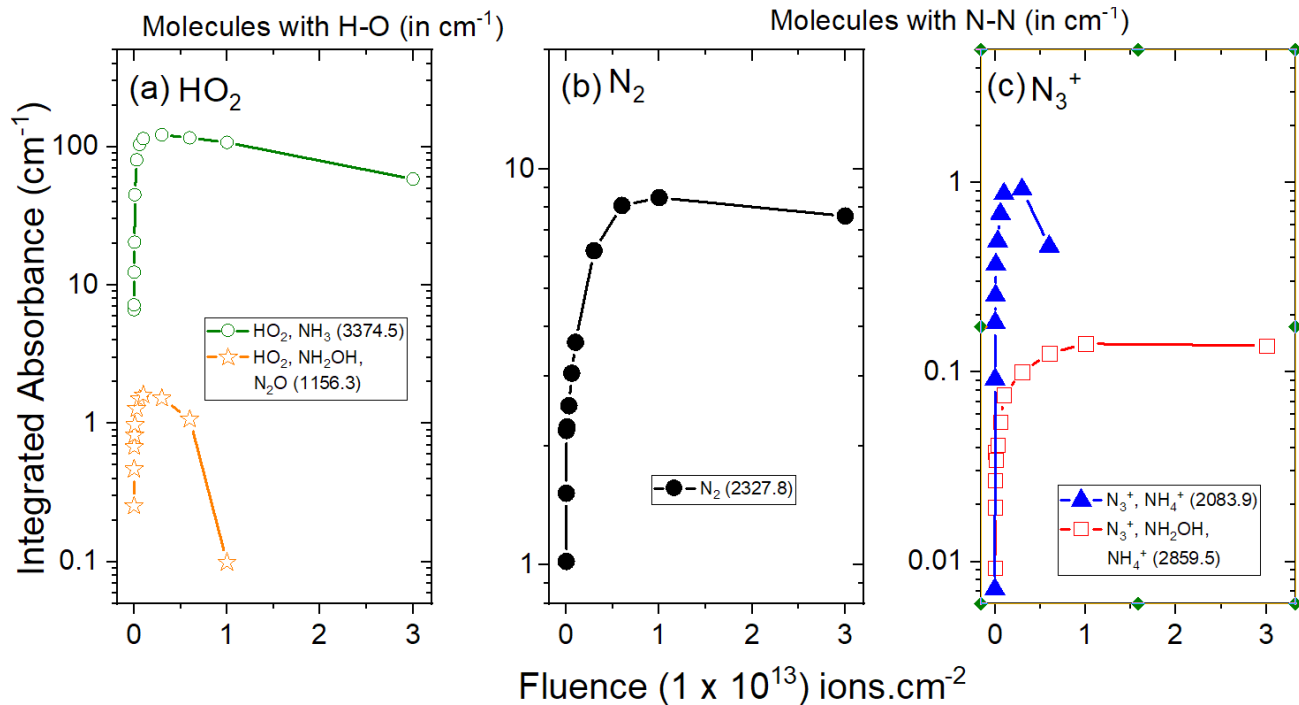


Fig. 6 Evolution of integrated absorbance, as a function of $40\text{ MeV }^{58}\text{Ni}^{11+}$ beam fluence, of selected bands of the products: (a) HO_2 , (b) N_2 , and (c) N_3^+ .

3.3.2 Formation of the N-O species

The IR spectrum of the non-irradiated ice presented in **Fig. 1(a)** shows a band at 2348 cm^{-1} that may be attributed to N_2 [47]. Two very small peaks at 1441.7 and 823.2 cm^{-1} are usually attributed to NO_3^- or NO_2^+ [35,45]. Jamieson et al. [48] identified the NN stretch at 2234.5 cm^{-1} assigned as nitrous oxide (N_2O) (**Fig. 5a**). A tentative band attribution for the dinitrogen trioxide (N_2O_3) [22] stretch, at 1833.5 cm^{-1} , is proposed; however, the slopes of the temporal traces for the other trioxide band around 1300 cm^{-1} also matched; they are due to other absorptions related to the peroxyntitric acid (HO_2NO_2) around 1293.7 cm^{-1} feature [35].

Observing the integrated absorbance evolution shown in **Fig. 5c**, one concludes that the N_2O_3 is related to the 1833.5 cm^{-1} band and the feature at 1763 cm^{-1} can be related to N_2O_2 or N_2O_4 [48, 49]. Some bands are attributed to the N-O bands: N_2O_2 (1867.7 cm^{-1}) in **Fig. 5b**; NO (1867.7 cm^{-1}) in **Fig. 5e**; NO_3 (1441.7 , 1048.1 and 823.2 cm^{-1}) and NO_2 (1048.1 and 823.2 cm^{-1}) in **Fig. 5f**.

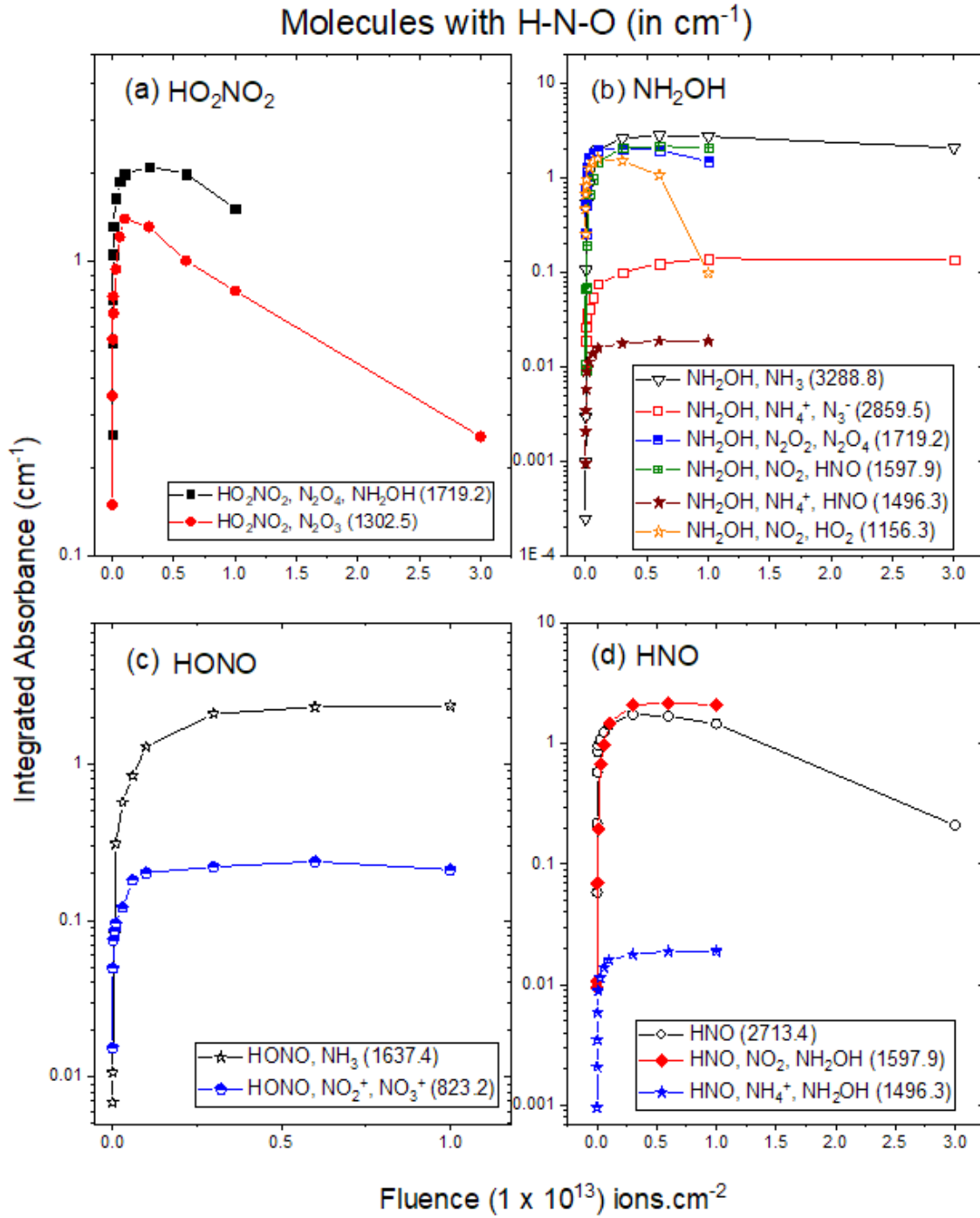


Fig. 7 Integrated absorbance evolution, as a function of 40 MeV $^{58}\text{Ni}^{11+}$ beam fluence, of selected bands of the products: (a) HO_2NO_2 , (b) HN_2OH , (c) HONO , (d) HNO .

3.3.3 Formation of the H-O species

The OH radical can be formed from a 10:100 (H₂O:He) mixture under microwave-discharges, as described by Zins and co-workers [50]. The OH stretch and HOH bend of water ice bands are responsible for the broad bands centered at 3400 and 1630 cm⁻¹, respectively. The 1763.5 cm⁻¹ feature may be related to the presence of hydronium (H₃O⁺) [51].

The band at 3689 cm⁻¹ in **Fig. 6a** is attributed to water ice-complexed OH radicals; HO₂ has been implicated in the weak broad absorption band with its center at 3374.5 and with another band at 1156.3 cm⁻¹ [52].

3.3.4 Formation of the N-N species

N₂ was observed at 2327.8 cm⁻¹ [51,53] (**Fig. 6b**). Two possible bands due to N₃⁺ are seen at 2859.5 and 2083.9 cm⁻¹ [51] in **Fig. 6c**.

3.3.5 Formation of the H-N-O species

Joshi et al. [40] identified three broad bands of HONO around 1640, 1420, and 1210 cm⁻¹, with shoulders and new absorption bands located at 1707.2 (HNO₃), 1606.7 (NO₂), 1563.7 (HNO), 1500.5 (HNO), 1301.4 (HNO₃), 1038.6 (O₃) and 1007.2 (HONO) cm⁻¹. This is an evidence how NO and OH radicals may combine to create new species. The shoulders at 1770.3 and 1861.5 cm⁻¹ are assigned to cis-(NO)₂ [53,54]. Following the Eq.5 and Eq.6, as described by Chen et al. [23] as a possible formation and destruction mechanisms during the HNO₃ irradiation.

A very common species in the atmosphere is nitric acid, which is created when OH reacts with NO₂. It serves as a temporary storage space for odd nitrogen in the stratosphere and a component of polar cloud stratosphere. Because nitric acid is a potent proton donor, it is important to understand the photochemistry of the molecular complexes that HNO₃ forms with other species in order to comprehend the chemistry taking place [23,31]. As part of a study of HNO's photolytic behavior in low-temperature matrices, Lee and coworkers [23,31] reported HNO spectra in both argon and nitrogen matrixes. They cite the significant differences in the O-H stretching and NOH in-plane bending modes between argon and nitrogen matrices as proof of a robust interaction between HNO and N, but it seems that they do not have searched for an HNO, *in* -N, complex in argon matrices.

In addition to the nitrogen oxides, HONO, HNO, and HNO₃ -species that were produced when OH radicals and NO reacted - were also seen. Nitric acid (HNO₃), nitrous acid (HONO), and nitrosyl hydride (HNO) production mechanisms are crucial for comprehending chemical processes in both the interstellar medium and in the Earth's atmosphere.

In addition to its impact on the chemistry of the atmosphere, nitrous acid (HONO) is an important precursor for the production of hydroxyl radicals. Pagsberg et al. [55] examined the gas phase kinetics of the interaction between NO and OH radicals that results in the generation of nitrous acid. In their study, the band attributable to nitrous acid at 1630.8 cm⁻¹ [15, 30] was noted. HNO is responsible for four distinctive absorption peaks at 1576.2 (ν₁), 1569.4, 1567.7, and 1564.9 cm⁻¹ (Jacox & Milligan [54]; Ioppolo et al. [56]). **Fig. 7** shows the integrated absorption of the H-N-O products. The two bands at 1719.2 and 1302.5 cm⁻¹ are attributed to the HO₂NO₂. We also observed six NH₂OH bands but comparing the absorbance evolution behavior of the bands with fluence, it is concluded that the 1156.3 cm⁻¹ band is probably due to the HO₂ instead of to NO₂ or NH₂OH (**Fig. 7b**). The two bands at 1637.4 and 823.2 cm⁻¹ in **Fig. 7c** are due to the HONO molecule. Finally, in **Fig. 7d**, three observed HNO bands, at 2713.4, 1597.9 and 1496.3 cm⁻¹ are shown.

4. Comments and Conclusions

The importance of a solid-state NO + H reaction channel as a starting point for prebiotic species in dark interstellar clouds is demonstrated by the inclusion of the experimental results in astrochemical gas-grain models. This opens up a fresh viewpoint on how molecules with biological significance may **be formed** in space. According to Nightingale & Wagner [57], Jacox & Milligan [54] and Krim & Lamome [58], studying isolated NH₂OH (1175, 1359, 1144 cm⁻¹), HNO (1561, 1507 cm⁻¹), and N₂O (2235, 1286 cm⁻¹) samples, the spectral features that appear upon solid NO hydrogenation are assigned to bulk NH₂OH (3317, 3261, 3194, 2899, 2716, 1608 cm⁻¹).

On the surfaces of icy dust grains in space, complex molecules develop catalytically. These compounds are produced by exothermic processes involving radical precursors and, primarily, hydrogen atom additions. Biologically significant byproducts include hydroxylamine (NH₂OH), a precursor molecule in the synthesis of amino acids. Congiu et al. [37], in their laboratory experiments, indicated the creation of NH₂OH in interstellar ice analogs by sequential hydrogenation reactions of solid nitric oxide (NO).

Zheng & Kaiser [59] observed many bands of hydroxylamine (NH₂OH) by infrared spectroscopy in electron-irradiated ammonia ices. In the current work, six bands have been observed at 3288.8, 2859.5, 1719.2, 1597.9, 1496.3, 1156.3 cm⁻¹ and can be related to the synthesis of hydroxylamine.

4.1 Chemical reactions during irradiation

The spectra of non-irradiated and irradiated HNO₃:H₂O (0.7:1) ice mixtures at fluences of 0 and 3.0 × 10¹³ ions.cm⁻² are depicted in Figs 1a and 1b, respectively. Table 1 presents the most prominent bands detected in the IR spectra of precursor and product molecules. In the current work, the distinct HNO₃ precursor bands in this spectral region were observed and identified. As a consequence, the bands that have appeared during the heavy ion beam irradiation belong to the synthesized molecular species; this is the first time that a careful analysis of their absorbance evolution has been done.

Along the projectile paths, the principal radiation effects are ionization and molecular excitation. Ionization of molecules results in the formation of radicals, which can initiate chemical processes.

The integrated absorbance evolutions of the precursor's bands, depicted in Fig. 8, allow the determination of their destruction cross sections, σ_d . This figure illustrates the H₂O at 3220 cm⁻¹ and the HNO₃ at 698 cm⁻¹ band decay, and – for comparison – the integrated absorbance increase of the 1637 cm⁻¹ band of their product, the HONO. The precursor's data are fitted the sum of two decreasing exponentials, yielding $\sigma_d = 1.2 \times 10^{-13}$ cm² for the water ice and $\sigma_d = 8.5 \times 10^{-13}$ cm² for the HNO₃ ice; this quantity corresponds to the constant of the first (fastest) exponential. Note that the HNO₃ cross section is about 7 times greater than the water one, partially because it is formed by a larger number of atoms; indeed, higher is the number of atoms, larger is the number of links and higher is the probability that the projectile may break one of them.

Fig. 8 also shows that the precursor integrated absorbances practically level off at 2 × 10¹² cm⁻² fluence, which may indicate that HNO₃ and H₂O molecules are reforming. Indeed, the HONO integrated absorbance saturates at this fluence, evidence that the maximum abundance synthesis of this product was reached. Consistently, Figs. 5 – 8 shows that some products are strongly (NH₂OH, NO, NH₄⁺) or moderately (NH₃, N₂O₂, N₂O₃, HNO) destroyed at high fluences. Due to sputtering, the total number of atoms in the ice decreases continuously, so that precursor and product molecules must all decrease for long irradiations.

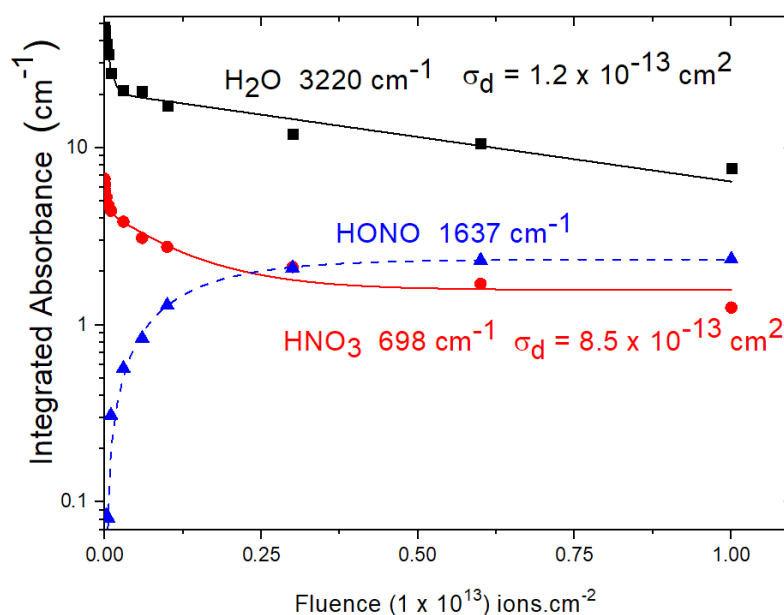


Fig. 8 Dependence of the integrated absorbance of H_2O 3220 cm^{-1} and the HNO_3 698 cm^{-1} bands on beam fluence. The solid lines are data fitting with the sum of two exponentials; σ_d , the (first) exponential constant, is taken as the destruction cross section. The dash line is the fitting of the integrated absorbance corresponding to the HONO 1637 cm^{-1} band, performed with a single exponential plus a constant.

In **Fig. 9**, a schematic depicting the probable molecules formed during radiolysis is proposed. Focusing on the H_2O dissociation, both H and O radicals can undergo radical–radical reactions either to form H_3O (1763.5 cm^{-1}) [13] and H_2O_2 at 1448.0 [52] and 2860 cm^{-1} [60]. H_2O_2 can form HO_2 (3374.5 cm^{-1}) [61]; losing an H radical, HO_2 then can dissociate into O_2 , the latter can subsequently combine with a O radical to form O_3 [62]. Since O_2 is a homonuclear molecule, it does not exhibit a band in the IR spectrum. However, O_3 formation is observed around the 1040 cm^{-1} ; unfortunately this band is not seen because it is very close to the NO_3^- , NO_2^+ and NO_3^+ bands in the same spectral region.

Under radiolysis, HNO_3 can proceed to HO_2NO_2 , HONO and HO_2 . HONO dissociates into HNO that can form NH_4 , by adding three radicals of H. Hydroxylamine NH_2OH , can be generated directly from HNO_3 , just adding one H radical and losing two oxygen atoms. NH_3 molecule can be formed by two processes: from NH_2OH just losing an oxygen, and from ammonium, NH_4 , losing an hydrogen.

H_2O and HNO_3 together can generate HO_2NO_2 , which in turn may dissociate to form the NO_3 , H_2NO_4 species. Both molecules can dissociate into NO_2 . Two or more NO_2 molecules can form N_2O_4 , N_2O_2 , N_2 or even NO by losing one oxygen radical.

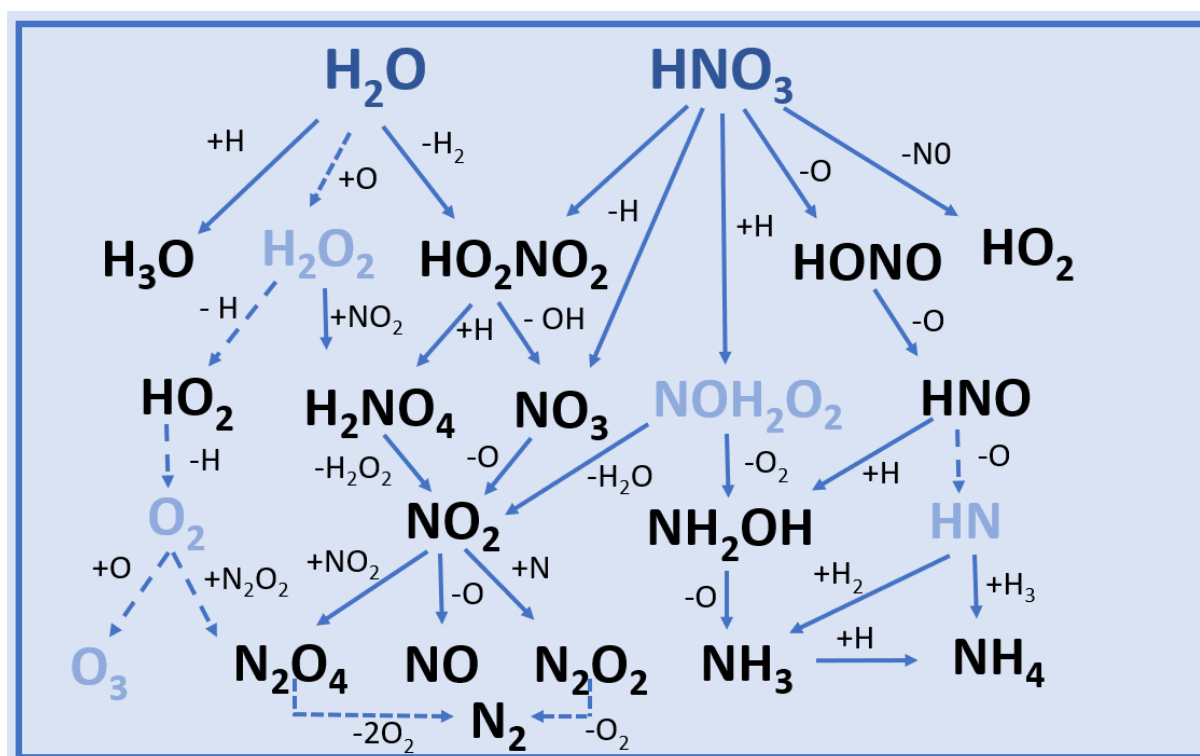


Fig. 9 Possible chemical reaction paths due to radiolysis of the HNO_3 and H_2O mixture. The names in light blue correspond to molecules unseen during the current experiment.

From the results presented in this work, especially those shown in **Table 1** and the corresponding mechanism illustrated in **Fig. 9**, we conclude that many species of astrophysical interest can be produced from the irradiation of astrophysically-relevant ice mixtures such as the $\text{H}_2\text{O}:\text{HONO}_2$ mixture exploited here. Among those species special attention should be given to N-H, N-O, and N-O-H-bearing species found in the ISM, such as hydroxylamine (NH_2OH), nitrous acid (HONO), nitrous oxide (N_2O), nitroxyl (HNO), nitric oxide (NO), ammonium ion (NH_4^+), and of nitrogen oxides. Note that some species have not yet been detected in the ISM, such as nitrate (NO_3), dinitrogen trioxide (N_2O_3), and dinitrogen tetroxide (N_2O_4), but are of great interest to astrochemists and astrobiologists [16, 63-68].

Despite the fact that nitric acid (HNO_3) has not yet been found in the ISM, many of its radiolysis products have been observed. This could be an indication that either the reaction between the HONO_2 and H_2O occurs too rapidly to yield a measurable abundance, similar to what happens in Earth's stratosphere, or that the detection techniques used by observational astronomers are not yet powerful or resolved enough to allow the detection of this species. Nevertheless, this work is an initial step in the laboratory study of astrophysically-relevant HONO_2 model ices and the results found here have potential to provide better understanding of the nitrogen-oxygen (N-O) chemistry of the outer space.

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Conflict of interest

The authors declare no competing financial interest.

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Table 1: Position and assignment of the vibrational bands of HNO₃:H₂O detected by FTIR spectroscopy before and after the sample processing by heavy and swift ions.

Position (cm ⁻¹)		Literature reference	Possible Assignment	Observations	References
Before irradiation	After irradiation				
3554.1		3556.8, 3548.1, 3545.5	HNO ₃	ν_1 OH stretch	[21, 23, 34, 40]
	3374.5	3372	NH ₃ , HO ₂	ν_3 NH ₃	[34, 61]
	3288.8	3288.6, 3281.5, 3292.0, 3302.0	NH ₃ / NH ₂ OH	2 ν_4 NH ₃ / ν_7 (a ₃) antisym., N-H stretch	[34, 59, 61]
~ 3284.3		3298, 3257	H ₂ O	ν_1 s-str., ν_3 a-str.	[31, 16, 18, 24, 61, 64]
2976.3		2980, 3104	HNO ₃	ν_1 (bonded)	[21, 65]
2930.0		2930	H ¹⁵ NO ₃	ν_1 (bonded)	[21]
	2891.7	2890, 2870	NH ₄ ⁺	2 ν_4	[43]
	2859.5	2867, (2855-2864), 2860	NH ₂ OH, NH ₄ ⁺ , N ₃ ⁻ , H ₂ O ₂	2 ν_4	[44, 45, 62]
	2713.4	2710.6; 2708, 2715.4	HNO	-	[23, 34]
2348.0		2347.5, 2375	N ₂ , NO ₂ ⁺ and NO ₃ ⁺	N=N stretch / ν_3	[67, 45, 48]
	2327.8	2328.4	N ₂	ν_1 - N-N-N asym. stretch	[52]
2285.2		2288, 2290	HNO ₃	ν_2 + ν_7	[21, 65]
	2234.0	2233, 2238, 2232.6, 2235, 2231, 2235.5	N ₂ O	ν_3 , ν_1 N-N stretch.	[2, 23, 34, 37, 67, 44, 48, 66]
2223.1		2200	HNO ₃	ν_4 + ν_5	[21]
	2142.8	2143	HN ₃	ν_1 , ν_2 N-N-N asym st	[51, 65]
	2128.4	2127	HN ₃	monomer	[66]
	2083.9	2080, 2088	NH ₄ ⁺ , N ₃ N=N=NH,	N-N-N asym. stretch.	[4, 44]
1895.6		1905	HNO ₃	2 ν_5	[21]
	1867.7	1869, 1873, 1870, 1874, 1871, 1874.1, 1862	NO, (NO) ₂	ν_1 , ν_1 (NO), ν_1 N-O stretch.	[23, 34, 44, 66]
	1833.5	1836, 1833	N ₂ O ₃	(ν_1) asym-N ₂ O ₃	[48,49]
1772.5		1787*, 1765	HNO ₃	ν_3 + ν_9	[21, 66]
	1763.5	1764, 1750, 1765, 1740	N ₂ O ₂ , N ₂ O ₄ , H ₃ O ⁺	(ν_5) c-N ₂ O ₂ , ν_6 + ν_{11} (N ₂ O ₄), ν_9	[22, 48, 49, 51]
1738.1		1737	HNO ₃	-	[66]
	1719.2	1719, 1697 1726.2	N ₂ O ₄ , NH ₂ OH, HO ₂ NO ₂	2 ν_6	[34, 49, 59]
1690.7		1693, 1698.3 1687, 1693, 1697	HNO ₃	ν_2 + lattice mode	[21, 22, 23, 34, 40, 65]
1678.5		1670, 1677.6, 1681.5, 1680	HNO ₃	-	[23, 34, 51,53]
~ 1663.6		1630.8, 1599	H ₂ O	-	[16, 18, 61,-64]
	1637.4	1640, 1625, 1635, 1629.9	HONO, NH ₃ ; cis-HONO	ν_4 NH ₃ , ν_4 deg. N-H deform.	[34, 40, 43]
	1597.9	1606.7, 1564, 1563, 1599	NO ₂ , NH ₂ OH, HNO	ν_3 (a ₂) NH ₂ bend	[34, 37, 40,59]
1570.2		1551	HNO ₃	2 ν_8	[21]

	1496.3	1500.5, 1501, 1499, 1515	HNO, NH ₄ , NH ₂ OH	ν_4 (a ₂) NOH bend	[34, 37, 40, 43, 45]
	1441.7	1437.3, 1450, 1440, 1448	NO ₃ , NO ₃ ⁻ , H ₂ O ₂	-	[14,53, 65]
1421.0		1420, 1413	NO ₃ ⁻ , HNO ₃ , NO ₂ ⁺ and NO ₃ ⁺	ν_3	[21, 65]
1397.9		1392, 1400, 1384	HNO ₃ , NO ₂ ⁺ and NO ₃ ⁺	ν_1	[34, 66, 67]
1370.0		1369.9	HNO ₃	-	[34]
1363.6		1362.2	HNO ₃	-	[23, 34]
1326.4		1324.9, 1327, 1325	HNO ₃ , H ¹⁶ NO ₃	-	[21, 23]
1304.7		1301.4, 1305, 1300	HNO ₃ , H ¹⁶ NO ₃	-	[21, 23, 40, 65]
	1302.5	1293.7, 1292.7, 1303, 1300, 1305, 1295.7	HO ₂ NO ₂ , N ₂ O ₃	trans -HONO ν_3 , asym-N ₂ O ₃	[23, 34, 48,49]
1262.1		1265, 1265.3* 1260	HNO ₃ , ¹⁵ N ₂ O, HN ₃	ν_3 - NO-stretch	[44, 46, 65], 66]
1253.3		1255, 1256	HNO ₃	ν_4	[21, 53]
	1156.3	1165, 1142, 1144	N ₂ O, HO ₂ , NH ₂ OH	2 ν_2	[37, 49]
1094.3		1098, 1090, 1099*, 1094*	HNO ₃ H ¹⁶ NO ₃ *	$\nu_7 + \nu_9$, $\nu_5 + \nu_9$	[21, 61]
	1076.2	1074	NH ₃	ν_2 sym. N-H deform., umbrella	[43]
	1048.1	1040, 1050	NO ₃ ⁻ , NO ₂ ⁺ and NO ₃ ⁺	ν_1	[34,51, 67]
968.3		954, 1016.3, 955, 958, 952	HNO ₃	ν_6	[21, 23, 34, 51, 53]
889.6		881, 896, 895, 894	HNO ₃	2 ν_9 , ν_5 ON - stretch	[22, 23, 40]
	823.2	822, 824	trans – HONO NO ₂ ⁺ and NO ₃ ⁺	ν_2	[34, 67]
774.5		773, 780, 767, 793.6, 776, 771.5	HNO ₃	ν_8	[21, 22, 23, 65]
~ 768.5		810, 792	H ₂ O	libration band	[16, 18, 61, 64]
748.7		748, 747 737, 743	HNO ₃	ν_9 , ν_8 ONO ₂	[21, 23, 65. 66]
698.9		710, 707, 702	HNO ₃	ν_6 NO ₂ scissors, ν_7	[21, 53, 65]
657.5		660	HNO ₃	NO ₂ valence bend	[22]
645.1		646.6*, 640	HNO ₃	ν_6	[21, 65]
	639-624	-	Unknown	-	-

