The irradiation of ammonia ice studied by near edge x-ray absorption spectroscopy

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A vapor-deposited NH_3 ice film irradiated at 20 K with 150 eV photons has been studied with near-edge x-ray absorption fine structure (NEXAFS) spectroscopy at the nitrogen K -edge. Irradiation leads to the formation of high amounts (12%) of molecular nitrogen N_2 , whose concentration as a function of the absorbed energy has been quantified to 0.13 molecule/eV. The stability of N_2 in solid NH_3 has been also studied, showing that N_2 continuously desorbs between 20 and 95 K from the irradiated ammonia ice film. Weak concentrations (<1%) of other photoproducts are also detected. Our NEXAFS simulations show that these features own to NH_2 , N_2H_2 , and N_3^- . © 2009 American Institute of Physics. [doi:10.1063/1.3243849]

I. INTRODUCTION

Frozen ammonia (NH_3) and its hydrates ($\text{NH}_3 \cdot (\text{H}_2\text{O})_n$) have been observed or are predicted to be present in many icy objects of the outer solar system, as in the planetary satellites Enceladus,¹ Miranda,² and Charon,³ in the KBO Quaoar,⁴ and in the Oort cloud comets; NH_3 ices have also been detected as component of icy mantles on grains in the interstellar medium and in the circumstellar regions of massive (see, for instance, Ref. 5) and low-mass protostars.⁶ These ices are exposed to various radiation environments,⁷ and the knowledge of their radiation chemistry is important to understand the composition and the stability of these astrophysical ices.

In spite of its growing interest in astrochemistry, the photochemistry of condensed ammonia has been only sparsely characterized. Early, the release of molecular hydrogen (H_2), molecular nitrogen (N_2), and hydrazine (N_2H_4) from irradiated ammonia ice at $T > 70$ K has been reported.⁸ The amidogen radical (NH_2), hydrazine, and the azoimide acid (HN_3) have also been detected with infrared spectroscopy in UV irradiated ammonia ice.⁹ Recently, N_2 , H_2 , HN_3 [or the azide ion (N_3^-)], NH_2 , and N_2H_4 have been observed in 5 keV electron-irradiated ammonia ices by infrared spectroscopy and thermally induced desorption spectroscopy.¹⁰ In ammonia hydrates, the production of N_2 , H_2 , and NH_4^+ has been evidenced by infrared and mass spectroscopies after irradiation at 70 K with 100 keV protons⁶ and 0.8 MeV

protons at 10 K.⁷ Sputtering and destruction of NH_3 (Ref. 11) and amorphization of the ammonia ice structure^{7,10} have also been observed.

Most of these studies indicate that ammonia-rich ices could provide photochemical sources of N_2 in space. This is supposed to be the case, for example, for the Saturn's moon Enceladus, where the bombardment of its ammonia-rich icy surface by magnetospheric ions could be at the origin of the N_2 molecules observed by the Cassini spacecraft.¹² In the interstellar medium, irradiation of NH_3 -containing ices covering the grain surfaces in dense clouds could also lead to the production of molecular N_2 . Because of its symmetry, N_2 is difficult to detect by microwave or infrared techniques, and its abundance is deduced from observations of the dinitrogen monohydride ion (N_2H^+) predicted to be produced by gas phase reaction of N_2 with the protonated molecular hydrogen ion H_3^+ . Also NH_3 is observed in the gas phase. The abundance profiles of gaseous NH_3 and N_2H^+ in starless cores of dense clouds can be qualitatively understood as the result of the selective freeze-out of molecules onto cold dust grains as the gas becomes centrally concentrated during core formation.¹³ Thus, depending on the evolutive stage of an interstellar or circumstellar cloud, ammonia can be the major N-bearing species present in the icy mantles on dust grains. In other circumstances also solid molecular nitrogen can be present as a component of the icy mantles. In any case the knowledge of the production rate of N_2 from irradiated frozen NH_3 could allow an estimation of the N_2 minimum concentration in space environments where irradiated ammonia-rich ices are found. Moreover as the temperature of icy grains increases (e.g., because of star formation or because a

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comet passes near the Sun) frozen molecules are ejected in the gas phase where minor species are much more easily detected. Our results suggest the importance to consider energetic processing of ices in the chemical models of the gas phase. In other words not only molecular nitrogen but also NH_2 , the diimide molecule (N_2H_2), the isodiazenes radical ($\text{N}=\text{NH}_2$), and N_3^- are released upon warming up of irradiated ices.

In this paper, we present the near-edge x-ray absorption fine structure (NEXAFS) spectroscopy study of the irradiation of condensed ammonia. We have already applied this technique on a closely related system, the water ice. We have shown that NEXAFS provides detailed insights on the bulk and the surface structures of H_2O ice,¹⁴ its heterogeneous chemistry,¹⁵ and its bulk photochemistry.^{16,17} In the case of ammonia, this technique enables us to quantify the conditions of absorbed energy at which N_2 is produced at 20 K in NH_3 . In addition to N_2 , NEXAFS allows identifying all the other by-products, except hydrazine N_2H_4 , H, and H_2 . Since there were no available NEXAFS data for the species expected in irradiated NH_3 [except for N_2 (Ref. 18) and N_2H_4 (Ref. 19)], we have performed vibrationally resolved calculations of the core to bound-state transitions for the by-products reported in the literature cited above, namely, NH_2 , the imidogen radical (NH), N_2 , the dinitrogen monohydride N_2H , N_2H_2 , the N_2H_3 radical, N_3^- , and N_3H .

The paper is organized as follows. The experimental and the theoretical methods are presented Sec. II. An overall description of the experimental data begins in Sec. III. At this stage, the features corresponding to known species (as N_2) are assigned without help of calculations; some details on the evolution of the N_2 concentration upon irradiation are also given. The calculations are shown in the middle of Sec. III. They are used to assign the experimental features of the unknown species observed in the pre-edge region. Additional results obtained from the warming of the films are also shown. In Sec. IV, the photochemistry of NH_3 is discussed.

II. METHODS

A. Experiments

The experiments are performed at the Elettra synchrotron light source (Trieste, Italy) on the BL 2.2 R undulator beamline (100–1500 eV). The irradiation and the NEXAFS measurements are carried out under UHV conditions on the Super-ESCA end station connected to the beamline. The NEXAFS spectra are recorded at the nitrogen *K*-edge (400 eV) in the total electron yield (TEY) mode, monitoring the incident flux using the photocurrent of a semitransparent copper mesh. A crystalline NH_3 ice film is deposited on a clean polycrystalline copper substrate held at 95 K by dosing 300 L of NH_3 (99.96% purity, Air Liquide) at a rate of 0.4 L sec^{-1} over the background pressure of the experimental chamber (base pressure of 3×10^{-10} Torr). Assuming a sticking coefficient of 1, this exposure corresponds to a deposition of 300 ML. The electrons photoemitted by the substrate can damage the region at the interface between the film and the substrate within a depth of around 100 Å corresponding to their typical mean free path. This eventual en-

hancement of the irradiation effect must be excluded from our measurements; for this, the film thickness must be larger than the depth probed by the NEXAFS spectroscopy (100 Å in the TEY mode). Assuming a perfect layer-by-layer growth of the film in the densest [111] direction of the NH_3 cubic lattice²⁰ (the interplane distance is 2.94 Å), 300 ML corresponds to a film of 882 Å thick; if the direction of growth is the [100] axis (the interplane distance is then 3.6 Å), it corresponds to a film of 1080 Å thick. In reality, the film is not a single crystal; it is likely polycrystalline with grains oriented in various directions, but its thickness is certainly far above the probing depth of the NEXAFS technique. In order to reduce the diffusion and desorption of the by-products formed upon irradiation, the film is cooled down at the lowest temperature reachable on the experiment, which is 20 K. The irradiations are performed at this temperature at a photon energy of 150 eV. This energy is not of great importance because the irradiation process is dominated by interactions of the material with the low-energy secondary electrons predominantly produced after the primary photon interaction.^{17,21} At 150 eV and in our experimental conditions, the typical flux delivered by the beamline is 3×10^{12} photons/sec for a ring current of 100 mA at 2 GeV. This photon flux is not directly measured in our experiment, and, for the dose calculation, we rely on the photocurrent measured during the irradiation, which is 8×10^{-9} A at 150 eV in a spot size of 1.75×10^{-3} cm^2 . Assuming these electrons are created in the probed depth of the TEY method (i.e., 100 Å = 10^{-6} cm), their number (8×10^{-9} A = 510^{10} electrons/sec) is created in a volume of 1.75×10^{-9} cm^3 (1.75×10^{-3} $\text{cm}^2 \times 10^{-6}$ cm). As the density of condensed ammonia is 0.86 g/ cm^3 , there are 5.25×10^{13} molecules in a volume of 1.75×10^{-9} cm^3 . These molecules emit 5×10^{10} electrons/sec during the irradiation at 150 eV. Each molecule then emits $5 \times 10^{10} / 5.25 \times 10^{13} = 9.5 \times 10^{-4}$ electron/sec. In water ice, each electron of 500 eV leads to about 25 secondary electrons.²¹ This yield linearly decreases with the photon energy,²² here with a slope of 0.05; each absorbed photon of 150 eV then gives $0.05 \times 150 = 7.5$ electrons. If we transpose this value to NH_3 , the yield of 9.5×10^{-4} electron sec molecule thus corresponds to an initial excitation by a photon flux of 1.27×10^{-4} photon/sec. As the energy of each photon is 150 eV, this corresponds to an absorbed energy of $150 \times 1.27 \times 10^{-4} = 0.1905$ eV molecule sec. The irradiation dose given in this paper corresponds to this value multiplied by the irradiation time in second.

The conditions of the NEXAFS recording were chosen to minimize further irradiation of the sample after each irradiation step was achieved. The irradiation dose during the acquisition of a spectrum was ten times lower than the dose used for irradiation at 150 eV. At the end of irradiation the sample was warmed step by step from 20 to 95 K at a rate of 1 K/min and spectra recorded at chosen temperatures.

We have also performed complementary N *K*-edge NEXAFS experiments at the Swiss Light Source, Paul Scherrer Institut, Villigen, Switzerland on the SIM (Surfaces Interfaces Microscopy) beamline, equipped with a cryostat allowing measurements at 1.7 K. The recordings are made

with the TEY method. The statistic of the data is improved compared with the data recorded at Elettra. The irradiation is performed at 400 eV; the measured photocurrent is 3×10^{-10} A in a spot size of 3 mm². Using the calculation method developed above, this gives a total energy dose of 4.15×10^{-5} eV molecule sec. The irradiation time is 100 min and the total absorbed dose is then 0.25 eV/molecule.

B. Calculations

As it will be shown, the range of interest of the NEXAFS spectrum for the identification of the by-products is the “pre-edge” region (394–402 eV). In our calculations, we only simulate the excitations we expect located in this energy range, i.e., those from the N 1s electron to the lowest unoccupied molecular orbital (LUMO), which all own an empty- p or π^* character. A correct assignment of these experimental features relies first on the accurate calculation of the energy of these excitations. When possible, a further and desirable step is to obtain their vibrational envelope. This is of great importance for the identification of the by-products, especially because vibrations can split or spread the π^* transitions in different peaks, which could be, by error, attributed to different species. Furthermore, the shape of the vibrational envelope, when it fits the experimental data, is a further confirmation of the assignment provided by the value of the transition energy.

From a theoretical point of view, such calculations give interesting insights on the dynamic of the core excitation, in particular, on the geometry of the excited state, which can differ greatly from the ground state. These calculations are quite straightforward in the case of diatomic [CO (Ref. 23)] or highly symmetrical molecules (CH_{4-*n*}Cl_{*n*}).²⁴ However, in most of the situations encountered here, the case is more complex because of the strong distortions occurring in the excitation.^{25–29} In such species, the excitation of a large number of low frequency modes and their overtones (bending and twisting) then contributes to the broadening or to the asymmetry of the line shape.

The calculations of the electronic structure are performed using the GAMESS (U.S.) package.³⁰ The geometry optimizations and the harmonic frequency calculations for the electronic ground state (isolated molecule) are performed at density functional theory (DFT) level of theory with the Becke 3-parameter hybrid exchange³¹ and the Lee–Yang–Parr (B3LYP) gradient-corrected correlation functional.³² A large aug-cc-PcVQZ basis set was used for nitrogen and hydrogen. The calculations of the transition energies are performed at Hartree–Fock (HF), post-HF, multiconfiguration self-consistent field with configuration interaction, and DFT levels of theories, providing vertical transition energies with only deviations of a few tenths of an eV from the experimental values. For the species considered here, the N(1s) core-excited states in the neutral geometry or in the fully optimized geometry are directly computed in a triplet form at a restricted open-shell Hartree–Fock (ROHF)/DFT level of theory with the Δ KS (Kohn–Sham) B3LYP scheme. In most of the cases, the initial ground state has a singlet electronic spin configuration. The excitation energies of the core-

FIG. 1. The NEXAFS spectra of a crystalline NH₃ ice film at 20 K before (bottom) and after photon irradiation at 150 eV at 11 eV/molecule (middle) and 91 eV/molecule (top). MS indicates the multiple scattering resonances observed before irradiation. The inset (a) presents a high-resolution recording around 401 eV, which evidences the fine structures of the N 1s $\rightarrow$ 1 π_g transition of N₂. In the pre-edge range, faint fingerprints of other nitrogen-bearing by-products can be observed [inset (b)].

excited singlet states are then determined using the sum method of Ziegler *et al.*³³ The relativistic correction of 0.3 eV for nitrogen is included.³⁴ In the case of NH₂, the spin configuration is a doublet in the excited state, which can be directly handled by computing the ROHF of the core-excited configuration.

For the vibrational analysis, different analytical and recursive techniques are used to derive the Franck–Condon factors using the full harmonic approximation coupled to Duchinsky transformation.^{35–38} The core-excited vibrational wave function is written as a product of 3N-6 one dimensional harmonic oscillators described by the same coordinates as those for the ground state, but with different frequencies and displaced from the ground state equilibrium position along the normal coordinates.³⁹ The analytical approach used is based on the expression for the overlap between two harmonic oscillators with ω'_k/v'_k (vibrational core-hole state) and $\omega_k/v_k=0$ (vibrational ground state) derived from Ref. 38. The vibronic coupling parameter S_k is calculated using the approach proposed by Thomas *et al.*⁴⁰ We successfully used the case of the nitrile molecules.^{26–28}

III. RESULTS

Figure 1 presents the N K-edge NEXAFS spectra of a crystalline ammonia ice film at 20 K before and after irradiation; for clarity, only the doses of 11 and 91 eV/molecule are shown. Before irradiation, the resonance observed at 401 eV is the N 1s $\rightarrow$ σ^* (N–H) (3a) excitation in NH₃. The transitions to the continuum of states start at 402 eV. In this energy domain, four wiggles are observed at 404.6, 411, 415, and 420 eV, resulting from the scattering of the N 1s photoelectron into the electronic potential of the surrounding NH₃ molecules. In the case of a highly ordered solid, as crystalline ammonia, the symmetrical arrangement of the molecular potential generates such modulation of the absorption cross section, known as the multiple scattering (MS) effect. This is

FIG. 2. Evolution of the N_2 and the NH_3 concentrations with the dose. On the left scale: crosses: amount of molecular N_2 in the film (in molecular percent); filled squares: amount of nitrogen in the film forming N_2 molecules (in atomic percent). On the right scale: open circles: amount of nitrogen forming NH_3 molecules (in atomic or molecular percent). The lines fit the data using Eq. (2). The dashed line fits the $[N_2]$ data using Eq. (3).

also observed on crystalline H_2O ice, but not on the amorphous phase, because of the lack of crystalline order.¹⁷ On NH_3 , these features are strongly damped at the first irradiation step (11 eV/molecule). This shows that the structural order is destroyed upon irradiation. Such radiation-induced disordering has been recently reported on condensed ammonia¹⁰ and also observed on H_2O .^{17,41,42} At a dose of 91 eV/molecule, only a broad resonance remains at 419.4 eV, related to the photoelectrons scattering within the first coordination shell in the amorphized ammonia structure. In this energy domain, a weak feature is also observed at 414 eV, which is due to the superimposed absorption of N_2 (see below).

The irradiation triggers a strong increase in intensity around 401 eV. This is due to the appearance of the $N\ 1s \rightarrow 1\pi_g$ excitation in molecular N_2 [400.87 eV (Ref. 18)], incidentally overlapping the $N\ 1s \rightarrow \sigma^*(N-H)$ (3a) transition. A high-resolution recording around 401 eV [Fig. 1, inset (a)] confirms this assignment: We observe the typical vibrational envelope of the $N\ 1s \rightarrow 1\pi_g$ transition of N_2 .¹⁸ Doing a linear combination of the N_2 and the NH_3 spectra, we can calculate the amount of N_2 trapped in the NH_3 matrix at each irradiation step. Figure 2 shows the evolution of the NH_3 and N_2 concentrations with the dose derived from these combinations. On the left scale, we have reported (1) $[N_2]$, the amount of N_2 formed in the film, in molecular percent (crosses), and (2) $[N]$, the amount of N atoms involved in N_2 (filled squares; it is twice the molecular concentration of N_2 : $[N]=2[N_2]$). On the right scale, we have reported $[NH_3]$, the percentage of N atoms forming NH_3 (open squares).

The number of N_2 molecules present in our sample as a function of time is given by the balance between formation and destruction processes,

$$d[N_2]/dt = \sigma_f \Phi [NH_3] - \sigma_d \Phi [N_2], \quad (1)$$

where σ_f is the N_2 formation cross section, σ_d is the N_2 destruction cross section, and Φ is the photon flux. By integrating Eq. (1) we get

$$[N_2] = \frac{\sigma_f}{2\sigma_f + \sigma_d} [NH_3]_0 (1 - e^{-(2\sigma_f + \sigma_d)x}), \quad (2)$$

where $x = \Phi t$ is the photon fluence and $[NH_3]_0$ is the ammonia concentration before the irradiation. Equation (2) is used for fitting the curves presented in Fig. 2. If we consider that the photon fluence x is low, then Eq. (2) is approximated by (taking $[NH_3]_0 = 1$)

$$[N_2] = \sigma_f x. \quad (3)$$

In this assumption, the production of N_2 is linear with the dose. As shown in Fig. 2 (dashed line), the $[N_2]$ concentration can be well approximated by a linear function, indicating that the irradiations are achieved in a low fluence regime. The slope of the linear of $[N_2]$ fits gives a formation cross section of 0.13 molecule/eV for $[N_2]$ at 150 eV.

If N_2 is by far the main species produced in the photolysis, hydrazine N_2H_4 is also expected to be an important by-product in the NH_3 photolysis. For instance, Zheng *et al.*¹⁰ reported a hydrazine concentration of about 10% of that of N_2 in radiolyzed NH_3 . Since, in our case, the maximum amount of N_2 in our films is 12%, this corresponds to a hydrazine concentration of around 1%. In any case, it cannot be detected with NEXAFS because its lowest resonance lies at 401.5 eV,¹⁹ therefore hidden by the absorption features of N_2 and NH_3 .

As shown in the inset (b) of Fig. 1, other by-products are observed through features located in the pre-edge region (this is shown later in more details in Fig. 4). They have weak intensities below 1% that of N_2 . They do not correspond to any known NEXAFS features of nitrogen-bearing species molecules. Their identification has motivated our calculations of the $N\ 1s \rightarrow LUMO$ excitations (those potentially located in this energy domain) for several expected species:¹⁰ NH_2 , N_2 , NH , $N=NH_2$, N_2H , N_2H_2 , N_2H_3 , N_3^- , and N_3H .

The results of these simulations are presented in Fig. 3. For the amidogen radical (NH_2) (Fig. 3, NH_2 panel), the calculated transition is found at 394.53 eV; it corresponds to the excitation in the vibrational ground state. The symmetric stretching ν_{NH} mode at 3970 cm^{-1} (490 meV) mostly contributes to the vibrational structure of the excitation made of four levels separated from 490 meV. The NH_2 bending δ_{HNH} mode is calculated at 1510 cm^{-1} (187 meV), leading to a weak vibrational progression appearing as feet at the right side of the stretching mode levels. For the molecular nitrogen (N_2) (Fig. 3, N_2 panel), the maximum of the transition is at 400.7 eV, in good agreement with the experimental value of 400.87 eV. The vibrational profile is built on the activation of the ν_{NN} stretching mode at 2105 cm^{-1} (261 meV) close to the experimental value (235 meV). For the imidogen radical (NH) (Fig. 3, NH panel), the transition is found at 395.2 eV. The fundamental ($v=0$) and the first two vibrational levels ($v=1,2$) of the symmetric stretching ν_{NH} mode at 3857 cm^{-1} are the main contributors to the transition intensity. For the isodiazenes radical ($N=NH_2$) (Fig. 3, NNH_2 panel), the excitation from the terminal nonhydrogen-bonded nitrogen atom ($N^*=NH_2$) is located at 401 eV, while the core excitation from the other nitrogen atom ($N=N^*H_2$) is found at 397.4 eV; thus, only the latter

FIG. 3. Vibrationally resolved calculations of the core to bound-state transitions located in the NEXAFS region of interest (394–402 eV) for NH₂, N₂, NH, N=NH₂, N₂H, *cis*-N₂H₂, N₂H₃ (dotted vertical bar, see text), N₃[−], and HN₃. When it is relevant, the nuclear motions that mainly contribute to the vibrational envelope are indicated with the corresponding frequency calculated in the excited state.

contributes to the NEXAFS region of interest. The vibrational profile is mainly dominated by the ν NN stretching mode (1675 cm^{−1}) and both the symmetric and antisymmetric ν NH modes at 3309 and 3889 cm^{−1}, respectively. For these activated modes, the fundamental ($\nu=0$) and the first two vibrational levels ($\nu=1,2$) contribute to the broad asymmetric shape of the vibrational profile. In the dinitrogen monohydride (N₂H) (Fig. 3, N₂H panel), two inequivalent nitrogen atoms give two separate contributions for N^{*}–NH and N–N^{*}H excitations. The N^{*}–NH contribution is found at 398 eV; the vibrational profile is mainly built on the fundamental ($\nu=0$) and the first two vibrational levels ($\nu=1,2$) of the δ NNH bending mode at 1580 cm^{−1}. The N–N^{*}H contribution is found at 399.55 eV and the ν NN mode at 1460 cm^{−1} dominates the vibrational envelope. For the diimide molecule (H–N=N–H), the *cis*- and *trans*-geometries lead to the same result. The *cis*-N₂H₂ spectrum is shown in Fig. 3. The transition is found at 398.3 eV. The vibrational profile (Fig. 3, *cis*-N₂H₂ panel) is built on the deformation along the symmetric and antisymmetric δ NNH modes (1208 and 1265 cm^{−1}), the symmetric ν NN stretching (1538 cm^{−1}) and both the symmetric and antisymmetric ν NH modes at 3309 and 3889 cm^{−1}. For the N₂H₃ radical (dashed vertical bar in Fig. 3, *cis*-N₂H₂ panel), the core excitation produces a drastic change in the molecular geometry with an out-of-plane bent-up of the terminal nitrogen atom, and, in this case, the calculation of the vibrational profile is out of the scope of the paper. The vertical energy transition is calculated at 397.16 eV (H₂NN^{*}H), close to the band observed at 397.15 eV in the experimental data (see Fig. 4). For the azide anion (N₃[−]), the linear conformation is the most stable. The energy of the N^{*}NN transition is calculated at 399.7 and that of the NN^{*}N transition is found at 403.5 eV, which rules it out as a candidate in the 399–402 eV range.

FIG. 4. (a) Detail of the pre-edge region of the NEXAFS spectra for different irradiation doses; on the inset is shown the evolution of the intensities of peaks 1–4 with the dose. (b) Calculated transitions. By comparison between (a) and (b), peaks 1–4 are assigned to NH₂ (peak 1), N₂H₃ or/and N=NH₂ (peak 2), N₂H₂ (peak 3), and HN₃ and/or N₃[−] (peak 4).

The presence of two degenerate electronic states in the N^{*}NN excitation induces a Renner–Teller effect that has required specific calculations incorporating the vibronic coupling between the two core-excited states;⁴³ their result is shown in Fig. 3 (N₃[−] panel). In the azoimide acid (HN₃), only the HN₃N^{*} excitation found at 399.5 eV is compatible with the experimental measurements; in this case, the singlet-triplet correction is important and shifts the peak to 400.02 eV (Fig. 3, HN₃ panel).

Figure 4(a) details the pre-edge region of the spectra where these features are experimentally observed. In this figure are presented the spectra obtained after different irradiation doses. Five peaks are observed: peak 1 at 394.34 eV followed by a weak feature at 394.8 eV, peak 2 at 397.25 eV, peak 3 at 398.4 eV, and peak 4 at 399.6 eV, the latter being only visible from a dose of 57 eV/molecule. The evolution of their intensity (integrated area) with the dose is also presented in the inset of Fig. 4(a). The calculated species owning spectral features incompatible with the experimental data are NH and N₂H. Those that fit the experiments are reported in Fig. 4(b): They are NH₂, N₂H₃ or N=NH₂, N₂H₂, N₃[−], and HN₃. Along the discussion, further considerations will allow improving this assignment.

Peaks at 394.4 and 394.9 eV are assigned to the N 1s → π^* transition in NH₂. This excitation owns a marked vibrational progression, leading to a series of peaks separated by 0.5 eV (Fig. 3). On the experimental data, only the second peak of the vibrational envelope is visible. Around 397 eV (peak 2), the calculations show that N₂H₃ and N=NH₂ could both contribute to this peak: In N₂H₃, the vertical energy of the N 1s → π^* excitation falls at 397.16 eV (H₂NN^{*}H)

FIG. 5. Evolution of the NEXAFS signal of the irradiated film for increasing temperatures (20–95 K). On the inset is plotted the evolution of the N_2 concentration as a function of the heating temperature.

[Fig. 4(b), vertical bar], and, in $N=NH_2$, the $N\ 1s \rightarrow \pi^*$ transition from the terminal N atom is located at 397.4 eV. Concerning peak 3, the $N\ 1s \rightarrow \pi^*$ transition of the diimide molecule (*cis*- or *trans*-) $HN=NH$ (398.4 eV) is very close to the experimental energy (398.6 eV). For peak 4 at 399.6 eV, both HN_3 and N_3^- might contribute to the experimental signal. In N_3^- , the $N\ 1s \rightarrow \pi^*$ transition from the uncharged terminal N atom (N^*-N-N^-) is located at the same energy than the experimental value. It owns a vibrational profile close to the experimental one, making N_3^- the most likely candidate for the attribution of peak 4, but HN_3 could underlie the N_3^- contribution.

Figure 5 presents the evolution of the high-resolution NEXAFS spectrum of the irradiated film during warming from 20 to 95 K (irradiations are stopped at this stage). We observe a strong and continuous decrease in the $N\ 1s \rightarrow \pi^*$ transition of N_2 due to its thermal desorption from the NH_3 matrix. In the inset of Fig. 5 is plotted the N_2 concentration as a function of the film temperature. It decreases exponentially from its initial value of 12% at 20 K down to 1% at 95 K. This is consistent with the findings of Zheng *et al.*,¹⁰ who observed the N_2 desorption in the 60–70 K temperature range, in coincidence with the phase transition from amorphous to crystalline ammonia.⁴⁴ This phase transition is not observed in our case: no MS features appear during the warming at 95 K (not shown); the recrystallization may be incomplete or delayed in temperature, as reported for irradiated crystalline H_2O ice.¹⁷ We also see that during the warm-up, the intensity of peak 4 at 399.6 eV remains quite stable. This indicates that N_3^-/HN_3 are less volatile than N_2 . This is consistent with a condensation temperature of 130 K for HN_3 .⁴⁵

Figure 6 shows a further NEXAFS experiment recorded at 1.7 K on the SLS facility at low irradiation dose (0.25 eV/molecule). At such dose, N_3^- and HN_3 are not visible because the amount of N_2 is not high enough. The improved signal to noise ratio allows a better comparison with the calculations, especially for the case of NH_2 (peak 1), where the vibrational progression is well evident. The energy separation of the three observed vibrational levels is 500 meV, which matches almost exactly the calculated val-

FIG. 6. NEXAFS experiments on irradiated NH_3 recorded at 1.7 K at the Swiss Light Source.

ues of 492 meV. Together with the case of N_2 discussed in Sec. II B (Fig. 1), this further shows the good agreement of the calculations and the experimental data.

In Table I are summarized the experimental energies, the calculated energies, and the assignments of the NEXAFS features observed in the pre-edge region.

IV. DISCUSSION

In this section, we discuss the possible photochemical routes leading from NH_3 to N_2 and to other by-products. It is admitted that the primary irradiation steps in ammonia lead to NH_2 , NH , H , and H_2 .^{46,47}

TABLE I. Experimental energies, calculated energies, and assignments of the by-products observed in the pre-edge region.

Species	Experimental values (eV)	Calculated values (eV)	Assignments
NH_2	394.34 (peak 1)	394.53	$\pi^*NH_2(1b_1)/\nu NH\ (0-0)$
	394.80	395.02	$\pi^*NH_2(1b_1)/\nu NH\ (0-1)$
	395.50	395.52	$\pi^*NH_2(1b_1)/\nu NH\ (0-2)$
	...	396.01	$\pi^*NH_2(1b_1)/\nu NH\ (0-3)$
$N=NH_2$	397.25 (peak 2)	397.40	$\pi^*(N=N^*H_2)(2b_1)$
<i>cis</i> - N_2H_2	398.40 (peak 3)	398.30	$\pi^*(HN=NH)(1b_g)$
N_3^-	399.60 (peak 4)	399.70	$\pi^*(N^*=N=N)(3b_2)$
HN_3	Underlying peak 4	400.02	$\pi^*(N^*=N=NH)(7a')$
N_2	400.87	400.70	$\pi^*N_2(1\pi_g)/\nu NN\ (0-0)$
	401.11	400.93	$\pi^*N_2(1\pi_g)/\nu NN\ (0-1)$
	401.33	401.17	$\pi^*N_2(1\pi_g)/\nu NN\ (0-2)$
	401.55	401.41	$\pi^*N_2(1\pi_g)/\nu NN\ (0-3)$

Photolysis experiments on ammonia trapped in solid matrix have shown that reactions (4)–(6) are possible at energies above 8 eV.⁴⁸ Gas phase irradiation experiments at 10 eV have confirmed these observations and shown that reaction (5) only accounts to 17% of the photolysis processes.^{46,49} Later, it has been found that in the gas phase UV irradiated at 10.2 eV, reaction (6) is a majority channel accounting for 90% of the NH₃ dissociation.⁵⁰ In our case, NH₂ is well observed, but NH is not clearly detected.

We see in Fig. 4(a) that the concentration of NH₂ decreases with the irradiation dose (peak 1), whereas a large amount of NH₃ remains available to produce NH₂ [reaction (4)]. This can be understood by the fact that NH₂ recombines with another NH₂ to form hydrazine [reaction (7)], a reaction that is a sink for NH₂,

This reaction is analog to the OH recombination in H₂O, leading to H₂O₂.¹⁷ The yield of reaction (7) increases when the concentration of NH₂ becomes high enough to allow the recombination of two neighboring NH₂ radicals, which only occurs at high doses (≥ 23 eV/molecule).

The decomposition of hydrazine is assumed to be route to the production of N₂. Little is known on the mechanism. In the early works done on the hydrazine photolysis, N₂, H₂, NH₂,⁵¹ and also NH₃ (Refs. 52 and 53) have been detected. It has been initially proposed that the formation of N₂ results in a succession of radical recombinations: After the photolysis of hydrazine into two NH₂ radicals [reaction (8)], reactions (9)–(11) may occur,

Later, photolysis studies on isotopically labeled N₂H₄ have shown that N₂ is actually formed from a single molecule of hydrazine, which rules out these recombination reactions.^{54,55} It has been proposed that the production of N₂ rather occurs through a series of dehydrogenation processes, which first removes one hydrogen atom from the initial excited hydrazine [reaction (12)], followed by disproportionation reactions of N₂H₃ with NH₂ [reaction (13)] and N₂H₃ [reaction (14)],

At the side of reactions (13) and (14), the direct dehydrogenation of N₂H₃ may also take place through reaction⁵⁴

Reactions (13)–(15) end in the decomposition of diimide N₂H₂ in N₂+H₂,

Reactions (12)–(16) are consistent with the experimental detection of N₂H₂, H₂, N₂, and NH₃. Although N₂H₃ plays a central role in these reactions, it has never been detected, either because it may be difficult to observe with the techniques used so far, or because it owns a more transient character than, for instance, N₂H₂. The possible presence of N₂H₃ in the infrared spectrum of electron-irradiated NH₃ has been suggested,¹⁰ but its existence cannot be ascertained since its infrared bands overlap with the ammonia ones. In NEXAFS, our calculations show that N₂H₃ is a good candidate for peak 3, but it could be also isodiazene N=NH₂ (Fig. 4). It is then interesting to resolve whether it is N₂H₃ or N=NH₂ observed in our data. The high energy available in the photolysis process allows the three isomers of N₂H₂ to be formed. Since diimide HN=NH (*cis*- or/and *trans*-) is undoubtedly detected (peak 3), we expect isodiazene to also contribute significantly. From our calculations, it should lie in peak 2. It is to note that the *trans*- and *cis*-N₂H₂ have two equivalent nitrogen atoms contributing to this transition (H–N=N*–H and H–N*=N–H), while isodiazene has only one contribution from the hydrogen bonded N atom (N=N*H₂). If peak 2 is fully built on isodiazene, it must thus weigh half the intensity of peak 3, which is precisely what is observed [Fig. 4(a), inset]. This is a first clue to the fact that isodiazene could be the main contributor to peak 2. Second, we can see in the inset of Fig. 4(a) that peaks 2 and 3 evolve with the dose with the same slope. This shows that the corresponding species follow the same reaction route, and it is thus likely that the two peaks are related to the two isomers of N₂H₂. Then, these arguments make us assign peak 2 to N₂H₂.

The concentration of N₂H₂ decreases with the dose [Fig. 4(a)]. This is most likely due to the fact that the bimolecular reaction (17) starts when the N₂H₂ concentration increases,

Possible disproportionation reactions with N₂H₂-producing N₂H have been also evoked.¹⁰ No feature related to N₂H is observed in our NEXAFS data, but N₂H is very unstable and should readily decompose into N₂+H.⁵⁶

Peak 4 has been assigned to HN₃ or N₃[−]. We see in Fig. 4(a) that this peak becomes visible at high irradiation dose (≥ 57 eV/molecule) and is not observed on the spectra recorded at lower doses. HN₃ and N₃[−] are actually closely related, the former being the parent molecule of the N₃[−] anion: Once HN₃ is formed, its acidic nature allows a facile proton transfer to a solvating NH₃, leading to the formation of N₃[−], or, more precisely, to N₃[−]·NH₄⁺.⁵⁷ Thus, N₃[−] is more likely to be observed than HN₃, which would be therefore the main contributor to peak 4. HN₃ itself results from the hydrogenation of N₃, which has been detected with infrared spectroscopy in condensed N₂ irradiated with electrons and protons.^{58,59} The formation of N₃ starts with the homolysis of N₂,

followed by the capture of the N fragment by a further N₂ molecule,

Reaction (19) is favored when the N₂ molecule that dissociates is adjacent to another one. This is similar to what is observed with ozone in irradiated H₂O ice containing O₂. Ozone O₃ is not detected in pure water because the O₂ concentration remains always too low for the occurrence of the O+O₂ reaction;¹⁷ it only forms when H₂O ice is enriched with O₂.^{16,60}

Amounts of hydrogen atoms are liberated by almost all the reactions considered here. N₃ can capture a hydrogen atom,

HN₃ transfers its proton to a neighboring NH₃ molecule, leading to N₃[−]·NH₄⁺,

Since N₃[−] appears at irradiation doses between 23 and 57 eV/molecule, we deduce that the N₂ concentration necessary for the appearance of N₃ in irradiated NH₃ corresponds to the measured N₂ concentration at these doses, between 3.6% and 8.7%.

V. SUMMARY AND CONCLUSION

Our experimental data show that irradiation induces the amorphization of the NH₃ crystal, which partially recovers its crystalline structure after warming at 95 K. The initial photodecomposition of ammonia mainly produces NH₂, likely consumed to form N₂H₄, which spectral features, hidden by those of NH₃ and N₂, cannot be observed in our NEXAFS experiments. Hydrazine then decomposes in N₂ through a set of dehydrogenation reactions, where an intermediate, the diimide N₂H₂, is detected in its isodiazenes N=NH₂ and *cis*- and/or *trans*- HN=NH diimide forms. Molecular nitrogen is the most abundant species (12%). Its concentration almost linearly increases in the investigated dose range; its yield is 0.13 molecule/eV. When the N₂ concentration is high enough, N₃[−] is also formed through the production of HN₃. The molecular nitrogen is volatile and has almost fully desorbed at 95 K; N₃[−] is less volatile and remains trapped in the film at 95 K. These results stress the importance of considering the energetic and thermal processing of ammonia-rich ices in the release of nitrogen bearing molecules as N₂, NH₂, N₂H₂, and N₃[−] in the region of space where these ices are found.

By giving the exact excitation energies from each nitrogen atom within the same molecule, our NEXAFS calculations show that the observed features are related to distinct species and not to excitations from different nitrogen atoms of the same molecule, as in multifunctional molecules.⁶¹ Apart from the obvious cases of N₂ and NH, they show that, for some species (NH₂, N₂H, and N=NH₂), a limited number of nuclear motions contribute to the vibrational envelope of core excitations. For most of the molecules or radical con-

sidered here (*cis*-N₂H₂, HN₃, and N₃[−]), the excitation of numerous normal modes and their overtones leads to a broad envelope of the NEXAFS transition.

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