

Formation of Hydroxylamine in Low-Temperature Interstellar Model Ices

Published as part of *The Journal of Physical Chemistry virtual special issue "W. Lester S. Andrews Festschrift"*.

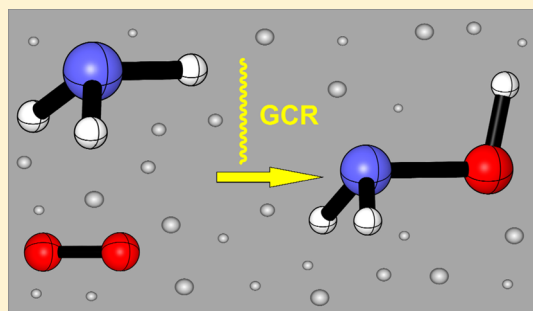
Yetsedaw A. Tsegaw,[†] Sándor Góbi,^{‡,§} Marko Förstel,^{‡,§,||} Pavlo Maksyutenko,^{‡,§,⊥} Wolfram Sander,^{*,†} and Ralf I. Kaiser^{*,‡,§,||}

[†]Lehrstuhl für Organische Chemie II, Ruhr-Universität Bochum, 44780 Bochum, Germany

[‡]Department of Chemistry and [§]W. M. Keck Research Laboratory in Astrochemistry, University of Hawaii at Manoa, 2545 McCarthy Mall, Honolulu 96822, Hawaii, United States

S Supporting Information

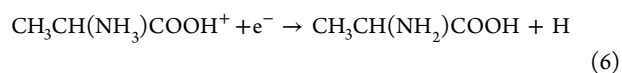
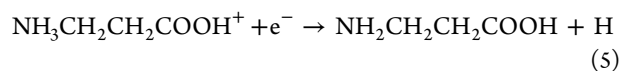
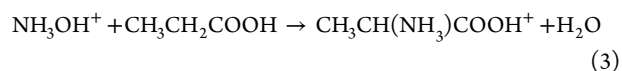
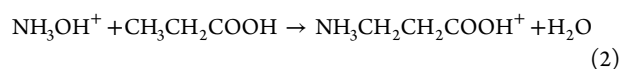
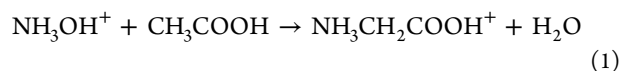
ABSTRACT: We irradiated binary ice mixtures of ammonia (NH₃) and oxygen (O₂) ices at astrophysically relevant temperatures of 5.5 K with energetic electrons to mimic the energy transfer process that occurs in the track of galactic cosmic rays. By monitoring the newly formed molecules *online* and *in situ* utilizing Fourier transform infrared spectroscopy complemented by temperature-programmed desorption studies with single-photon photoionization reflectron time-of-flight mass spectrometry, the synthesis of hydroxylamine (NH₂OH), water (H₂O), hydrogen peroxide (H₂O₂), nitrosyl hydride (HNO), and a series of nitrogen oxides (NO, N₂O, NO₂, N₂O₂, N₂O₃) was evident. The synthetic pathway of the newly formed species, along with their rate constants, is discussed exploiting the kinetic fitting of the coupled differential equations representing the decomposition steps in the irradiated ice mixtures. Our studies suggest the hydroxylamine is likely formed through an insertion mechanism of suprathreshold oxygen into the nitrogen–hydrogen bond of ammonia at such low temperatures. An isotope-labeled experiment examining the electron-irradiated D₃-ammonia–oxygen (ND₃–O₂) ices was also conducted, which confirmed our findings. This study provides clear, concise evidence of the formation of hydroxylamine by irradiation of interstellar analogue ices and can help explain the question how potential precursors to complex biorelevant molecules may form in the interstellar medium.



1. INTRODUCTION

During the last decades, the hydroxylamine molecule (NH₂OH) has received considerable attention from the astrochemistry and laboratory astrophysics communities due to its potential role as a precursor to biorelevant molecules like amino acids in the interstellar medium (ISM).^{1–3} Theoretical and laboratory studies suggest that protonated glycine (NH₃CH₂COOH⁺) (Reaction 1) and α -(NH₃CH₂CH₂COOH⁺) or β -alanine (CH₃CH(NH₃)COOH⁺) (Reactions 2 and 3) might be formed in the gas phase via the reaction of protonated hydroxylamine (NH₃OH⁺) with acetic acid (CH₃COOH) and propanoic acid (CH₃CH₂COOH), respectively.^{1,2} Dissociative recombination with an electron was proposed to yield amino acids (Reactions 4–6). While acetic acid is a well-known interstellar molecule^{4–6} and propanoic acid is a plausible species in the regions where acetic acid is found,⁷ hydroxylamine has not been observed so far in the ISM, although the stability of ionized and protonated hydroxylamine^{8,9} (Reactions 7 and 8) in the ISM was revealed computationally^{2,3} as well as experimentally.^{1,10} Thus, it would be of great interest for astrochemists and astrobiologists to untangle the formation mechanism of hydroxylamine under conditions relevant to the ISM eventually answering

the question how potential precursors to complex biorelevant molecules may form.



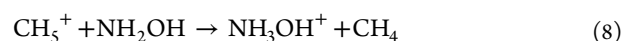
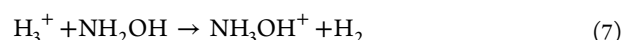
Received: July 28, 2017

Revised: September 8, 2017

Published: September 11, 2017

Table 1. Summary of CASINO Simulations on the Electron Irradiation Experiments of Ammonia (NH₃), D3-Ammonia (ND₃), Ammonia–Oxygen (NH₃–O₂), and D3-Ammonia–Oxygen (ND₃–O₂) Ices

ice	NH ₃	ND ₃	NH ₃ –O ₂	ND ₃ –O ₂
molar mass of molecules in the ice, <i>M</i> (g mol ^{−1})	17.03	20.05	17.03, ^a 32.00 ^b	20.05, ^a 32.00 ^b
average density of the ice, <i>ρ</i> (g cm ^{−3})	0.66 ± 0.03	0.94 ± 0.04	0.91 ± 0.03	1.14 ± 0.03
irradiated area, <i>A</i> (cm ²)	1.0 ± 0.1	1.0 ± 0.1	1.0 ± 0.1	1.0 ± 0.1
angle of incidence, <i>θ</i> (deg)	70	70	70	70
irradiation time, <i>t</i> (s)	3600 ± 2	3600 ± 2	3600 ± 2	3600 ± 2
applied electron current, <i>I</i> (nA)	15 ± 2	15 ± 2	15 ± 2	15 ± 2
total number of electrons (×10 ¹⁴)	3.4 ± 0.4	3.4 ± 0.4	3.4 ± 0.4	3.4 ± 0.4
initial kinetic energy of the electrons, <i>E</i> _{init} (keV)	5.0	5.0	5.0	5.0
average ^c kinetic energy of backscattered electrons, <i>E</i> _{bs} (keV)	3.2 ± 0.1	3.2 ± 0.1	3.3 ± 0.1	3.3 ± 0.1
fraction ^c of backscattered electrons, <i>f</i> _{bs} (%)	31 ± 3	31 ± 3	34 ± 3	34 ± 3
average ^c kinetic energy of transmitted electrons, <i>E</i> _{trans} (keV)	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0
fraction ^c of transmitted electrons, <i>f</i> _{trans} (%)	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0
simulated average ^c penetration depth, <i>l</i> (nm)	350 ± 30	350 ± 30	300 ± 20	300 ± 20
total number of molecules exposed (1 × 10 ¹⁷)	8.2 ± 1.1	6.9 ± 0.9	5.0 ± 0.7 ^a , 2.5 ± 0.3 ^b	4.6 ± 0.6 ^a , 2.3 ± 0.3 ^b
dose per molecule, <i>D</i> (eV)	1.7 ± 0.3	1.4 ± 0.3	1.4 ± 0.3 ^a , 2.6 ± 0.5 ^b	1.3 ± 0.2 ^a , 2.0 ± 0.4 ^b

^aNH₃/ND₃ molecules. ^bO₂ molecules. ^cValues from CASINO simulations.

However, the crucial question still under debate is whether the hydroxylamine synthesis takes place under collisionless conditions in the gas phase, via surface-mediated reactions, or in the “bulk” ices in condensed phase.¹¹ Recent laboratory studies focused on the formation of hydroxylamine in the condensed phase on ice-coated interstellar grains at temperatures as low as 10 K. Upon irradiation of a mixture of ammonia (NH₃) and water (H₂O) ices with ultraviolet (UV) photons,¹² electrons,¹³ and heavy ions of nickel and zinc,¹⁴ hydroxylamine was efficiently formed through radical–radical recombination involving amidogen (NH₂) and hydroxyl radical (OH) (Reaction 9). Via modeling, Charnley et al. proposed that hydroxylamine might also be formed through successive hydrogenation reaction of nitric oxide (NO) ice under dark cloud conditions (Reaction 10).¹⁵ This was confirmed experimentally.^{16–21} Recently, He et al. reported the formation of hydroxylamine on amorphous silicate surfaces via oxidation of ammonia at 70 K (Reaction 11), but mechanistical details are absent.²²



Astrochemical models propose that the formation of hydroxylamine involves radical–radical reactions *within* the ice-coated interstellar grains. The chemical models developed by Garrod et al.^{23,24} considered NH, NH₂, and OH radicals along with hydrogen atoms; these are produced by cosmic ray-induced dissociation of ammonia and water molecules in the ice. The model speculated that the radicals are not mobile at 10 K and only become mobile on the grain surface and eventually take part in successive radical reactions upon heating. These studies were expanded computationally revealing that hydroxylamine might be formed by radical–radical recombination such as reactions between the amidogen (NH₂) and the hydroxyl

radical (OH) (Reaction 9)²⁵ or via oxidation of ammonia (Reaction 11).²⁶

Although laboratory work and theoretical studies demonstrated the possibility of the formation of hydroxylamine (NH₂OH) in the ISM, it has not been detected in space. Several unsuccessful attempts were reported that struggled to detect the emission of NH₂OH toward a selection of bright sources including the galactic center hot-core source Sgr B2(N) using the NRAO²⁷ as well as toward the L1157-B1 and B2 shocked regions using CSO and CARMA.²⁸ Upper limits of NH₂OH column densities were estimated to be 1.4 × 10¹³ cm^{−2} and 1.5 × 10¹³ cm^{−2} toward the B1 and B2 shocks, respectively; upper limits of the relative abundances of N_{NH₂OH}/N_{H₂} were 1.4 × 10^{−8} and 1.5 × 10^{−8}, respectively. A recent experimental study suggested that the nondetection of hydroxylamine in space could be due to the high reactivity of the molecule.²⁹ They observed partial fragmentation of the molecule into nitrosyl hydride (HNO), ammonia (NH₃), and oxygen (O₂) close to 130 K, a temperature that is lower than the sublimation temperature of hydroxylamine (160–190 K).^{13,16}

Considering the fact that ammonia is present in ice mantles of interstellar grains at levels typically in the range of a few percent of water, in some rare cases at higher abundance,^{30–35} we probe the hypothesis to what extent hydroxylamine can be formed *inside* interstellar ices via reactions of ammonia (NH₃) with oxygen atoms (O). Suprathermal oxygen atoms, which are not in equilibrium with the surrounding ice, can be generated from oxygen-bearing molecules like water,^{36–39} carbon dioxide (CO₂),⁴⁰ and methanol (CH₃OH)⁴¹ (Reactions 12–14) at temperatures as low as 10 K. The newly formed hydroxylamine (NH₂OH) molecules along with their fully deuterated counterparts (ND₂OD) were probed via infrared spectroscopy *online* and *in situ* during the processing of astrophysically relevant ices by energetic electrons as a proxy for secondary electrons generated in the track of galactic cosmic rays (GCRs) penetrating ices on interstellar grains.^{42,43} Quantitatively, rate constants are calculated, and the formation mechanisms are discussed based on the kinetic profiles fit by solving a set of coupled differential equations.^{44,45} After irradiation, the newly formed molecules were allowed to sublime during the controlled

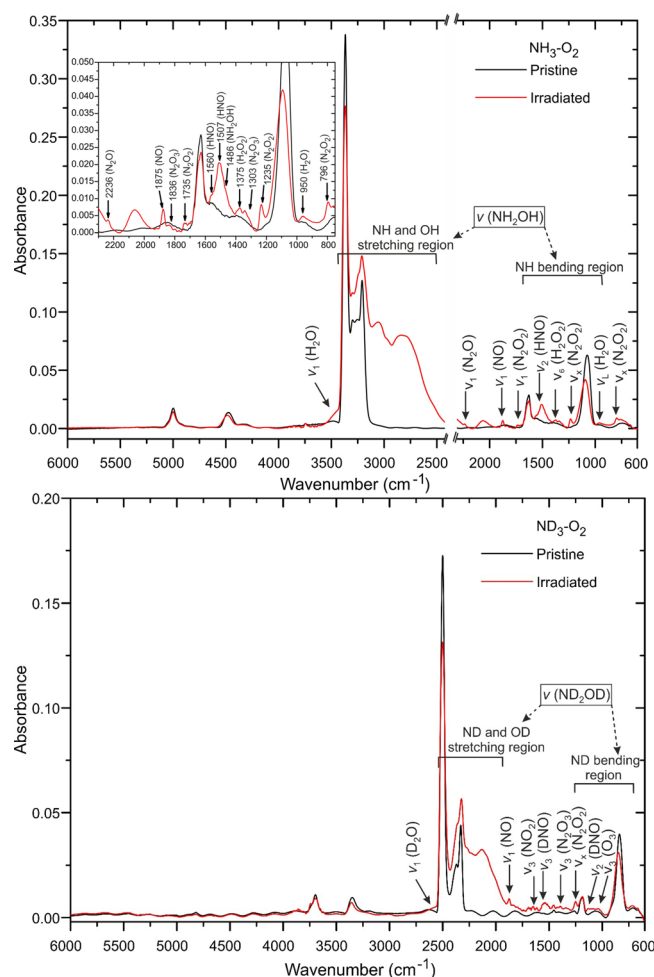


Figure 1. (a) Infrared spectrum of the ammonia–oxygen ($\text{NH}_3\text{--O}_2$) ices at 5.5 K before (black) and after (red) the electron irradiation. The infrared assignments are compiled in Table 2a. (inset) Details of the spectrum in the region of 770–2300 cm^{-1} . Deconvolution of the 2420–3550 cm^{-1} region to show features of hydroxylamine (NH_2OH), water (H_2O), and ammonia (NH_3) for selected temperatures are given in Figure 2. (b) Infrared spectrum of the D3-ammonia–oxygen ($\text{ND}_3\text{--O}_2$) ices at 5.5 K before (black) and after (red) 5 keV electron irradiation. The infrared assignments are compiled in Table 2b. Deconvolution of the 1930–2600 cm^{-1} region to show specific features of hydroxylamine (ND_2OD), D2-water (D_2O), and D3-ammonia (ND_3) for selected temperatures are given in Figure 2.

heating of the irradiated samples to 300 K (temperature-programmed desorption (TPD)). During this phase, the solid state (ices) was monitored spectroscopically in the infrared, while the gas phase was probed via single-photon photoionization reflectron time-of-flight mass spectroscopy (PI-ReTOF-MS).



2. EXPERIMENTAL SECTION

The experiments were conducted in a contamination-free ultrahigh vacuum (UHV) chamber evacuated to a base pressure of $(5 \pm 2) \times 10^{-11}$ torr.^{11,46} A rhodium-coated silver wafer located in the center of the chamber served as a substrate and was interfaced to a coldfinger made of oxygen-free

high-conductivity copper with a 0.2 mm sheet of indium foil to ensure thermal conductivity. The entire assembly is cooled to 5.5 ± 0.2 K by a closed-cycle helium refrigerator (Sumitomo Heavy Industries, RDK-415E). The ices were prepared by depositing the gas mixtures of ammonia (NH_3 , Matheson, 99.999%; ND_3 , Isotopes Inc., 99+% D) and oxygen (O_2 , BOC Gases, 99.999%) via a glass capillary array positioned 30 mm in front of the silver target. Deposition times range between 5 and 10 min. During the deposition, the main chamber pressure was increased to $(3 \pm 2) \times 10^{-8}$ torr; the thickness of the ices were measured online via in situ He–Ne laser interferometry (CVI Melles-Griot, 25-LHP-213) at $\lambda = 632.8$ nm striking the surface at an angle of incidence of $\theta = 4^\circ$.^{47–49} Given that the number of observed interference fringes (N_f) and the refractive indices of NH_3 ($n_{\text{NH}_3} = 1.36 \pm 0.03$)⁵⁰ and molecular oxygen ($n_{\text{O}_2} = 1.322$)⁵¹ are known, the thickness of the ices (d) can be extracted using eq E1 to be 500 ± 50 nm.^{49,50,52} With a modified Lambert–Beer relationship^{40,53,54} with the absorption coefficients of 3.11×10^{-17} cm molecule^{-1} of the ν_3 NH_3 band between 3700 and 3000 cm^{-1} based on the results of Sill et al.⁵⁵ and the total thickness of the ice, the ratio of ammonia to oxygen is determined to be $1.7 \pm 0.4:1$. Isotopically mixed ices of $\text{ND}_3\text{--O}_2$ (2:1) were also exposed to energetic electron radiation to confirm assignments via infrared frequency shifts and in the reflectron time-of-flight data via their shifts in mass-to-charge ratios.

$$d = \frac{N_f \lambda}{2\sqrt{n^2 - \sin^2 \theta}} \quad (\text{E1})$$

Each sample was then irradiated for 60 min with 5 keV electrons at a current of 0 nA (blank experiment) and at 15 ± 2 nA generated by a SPECS eq 22/35 electron gun measured by a Faraday cup mounted between the electron gun and the sample. With the Monte Carlo simulation program CASINO (v2.42)⁵⁶ averaging over 100 000 trajectories, the average dose per molecules (D) deposited was computed using eq E2, where I , t , M , e , N_A , ρ , A , and E_{init} are the irradiation current (C s^{-1}), irradiation time (s), molecular mass of the molecule (g mol^{-1}), the electron charge (C), Avogadro's constant (mol^{-1}), the density of the ice (g cm^{-3}), the irradiated area of the ice (cm^2), and the initial kinetic energy of the electrons (eV), respectively. The values f_{trans} , f_{bs} , E_{bs} , E_{trans} , and l denote the fraction of electrons transmitted through the ice, the fraction of electrons that are backscattered, the average kinetic energy of the backscattered electrons (eV), the average kinetic energy of the transmitted electrons (eV), and the average penetration depth of the electrons (cm), respectively. The simulation parameters are summarized in Table 1. These calculations yield average doses of 1.7 ± 0.3 eV per ammonia (NH_3) molecule and 2.0 ± 0.4 eV per D3-ammonia (ND_3) molecule. In the ammonia–oxygen mixed ices we determined a dose of 1.4 ± 0.3 eV per irradiated ammonia (NH_3) molecule and 2.6 ± 0.5 eV per irradiated oxygen molecule. Similarly, a dose of 1.6 ± 0.3 eV per irradiated D3-ammonia (ND_3) molecule and 2.6 ± 0.5 eV per irradiated oxygen molecule was calculated in the D3-ammonia–oxygen ices. The average penetration depth of the 5 keV electrons was also computed to be 300 ± 20 nm, which is less than the thickness of the deposited ice mixtures (500 ± 50 nm) ensuring that there is no interaction between the substrate and the electrons.

Table 2a. Infrared Absorption Features Recorded Before and After the Electron Irradiation of Ammonia–Oxygen (NH₃–O₂) Ices at 5.5 K

band position (cm ⁻¹)		ref	assignment ^a		
this work	literature value		species	vibration	characterization
before irradiation					
5000	4994	61	NH ₃	$\nu_3 + \nu_4$	combination
4477	4478	61	NH ₃	$\nu_3 + \nu_2$	combination
4345	4345	61	NH ₃	$\nu_1 + \nu_2$	combination
3488	3472	61	NH ₃	$\nu_1 + \nu_L$	combination
3369	3372	61	NH ₃	ν_3	antisymmetric stretch
3300	3290	61	NH ₃	$2\nu_4$	overtone
3211	3212	61	NH ₃	ν_1	symmetric stretch
1624, 1646	1628	61	NH ₃	ν_4	degenerated deformation
1550	1549	63	O ₂	ν_1	fundamental
1077	1097	61	NH ₃	ν_2	symmetric deformation
after irradiation					
3452	3452	37	H ₂ O	ν_1	symmetric stretch (out-of-phase)
3391	3317	13,17	NH ₂ OH	ν_1	O–H stretch
3336	3332	37	H ₂ O	ν_3	antisymmetric stretch (longitudinal)
3248	3261	13,17	NH ₂ OH	ν_7	N–H stretch (antisymmetric)
3213	3209	13,17	NH ₂ OH	ν_2	N–H stretch (symmetric)
3109	3107	37	H ₂ O	ν_1	symmetric stretch (in-phase)
3024	3074	13,17	NH ₂ OH	ν_2	N–H stretch (symmetric)
2963	2943–2507	13,17	NH ₂ OH	$\nu_3 + \nu_4$	combination
2916		13,17	NH ₂ OH	$2\nu_4$	overtone
2748		13,17	NH ₂ OH	$\nu_3 + \nu_5$	combination
2525		13,17	NH ₂ OH	$\nu_4 + \nu_8$	combination
2236	2235	17,20,67	N ₂ O	ν_3	N≡N stretch
1875	1875	17,20,64,65	NO	ν_1	fundamental
1836	1833–1851	17,20,64,68	N ₂ O ₃	ν_1	N=O stretch
1735	1737	17,20,64,65	(NO) ₂	ν_5	N=O stretch (antisymmetric)
1560	1561	17,69,70	HNO	ν_3	N=O stretch
1507	1507	17,69,70	HNO	ν_2	HNO bend
1486	1486	13,17	NH ₂ OH	ν_4	NOH bend
1375	1389	37	H ₂ O ₂	ν_6	antisymmetric bend
1342	1359	13,17	NH ₂ OH	ν_4	NOH bend
1303	1303	17,20,64,68	N ₂ O ₃	ν_3	NO ₂ stretch (symmetric)
1235	1240	66	N ₂ O ₂	ν_1	NO ₂ stretch (symmetric)
1145	1144	13,17	NH ₂ OH	ν_5	NH ₂ wag
950	941	37	H ₂ O	ν_L	libration
796	880	66	N ₂ O ₂	ν_2	N–N stretch

^aAssignment based on references.

$$D = \frac{ItM}{eN_A \rho A l} (E_{\text{init}} - f_{\text{trans}} E_{\text{trans}} - f_{\text{bs}} E_{\text{bs}}) \quad (\text{E2})$$

Before, during, and after irradiation, chemical modifications of the ices were recorded *online* and *in situ* using Fourier transform infrared spectroscopy (FTIR; Thermo Nicolet 6700), in the range of 6000 to 600 cm⁻¹ with a resolution of 4 cm⁻¹, and an EI-QMS device (Extrel 5221) to monitor molecules released into the gas phase (70 eV, 2 mA). One hour after the irradiation, TPD studies were conducted by heating the irradiated ices to 300 K at a constant rate of 0.5 K minute⁻¹. The spectra for selected temperatures were deconvoluted exploiting Gaussian fits utilizing the peak fitting using the least number of peaks resulting in a residual within the signal-to-noise ratio of the original spectra as described elsewhere.^{46,57}

After the ices were irradiated, molecules subliming into the gas phase were photoionized with 10.49 eV photons using soft vacuum ultraviolet (VUV) photoionization coupled with a reflectron time-of-flight mass spectrometer (ReTOF; Jordan

TOF Products, Inc.), which has been described in detail previously.^{11,46,49} The 10.49 eV photons were generated by frequency tripling of the third harmonic of an Nd:YAG (354.7 nm) (Spectra Physics, PRO-250, 30 Hz) laser in a jet of pulsed xenon (Xe) gas, as was reported earlier.⁴⁶ In the present setup, a flux of 5×10^{10} photons pulse⁻¹ were generated at 30 Hz.⁵⁸

3. RESULTS

3.1. FTIR Data. **3.1.1. Qualitative Analysis.** Figure 1 reveals the infrared (IR) spectra of the electron-irradiated ammonia–oxygen (NH₃–O₂) and D3-ammonia–oxygen (ND₃–O₂) ices before and after the irradiation. The newly formed species after the radiolysis are identified and compiled along with their vibrational assignments in Tables 2a and 2b, respectively. Before irradiating the sample, the absorption peaks of the reactant molecule (D3-)ammonia are observed, which nicely match the IR spectra of solid ammonia ices reported previously (Tables 2a and 2b).^{54,59–62} The fundamental O–O stretching of molecular oxygen can be seen at 1550 cm⁻¹ especially in the

Table 2b. Infrared Absorption Features Recorded Before and After the Electron Irradiation of D3-Ammonia–Oxygen (ND₃–O₂) Ices at 5.5 K

band position (cm ⁻¹)		ref	assignment ^a		
this work	literature value		species	vibration	characterization
before irradiation					
3700			ND ₃	$\nu_3 + \nu_4$	combination
3348			ND ₃	$\nu_3 + \nu_2$	combination
3178			ND ₃	$\nu_1 + \nu_2$	combination
2642			ND ₃	$\nu_1 + \nu_L$	combination
2500	2503	59	ND ₃	ν_3	antisymmetric stretch
2342			ND ₃	$2\nu_4$	overtone
2330	2326	59	ND ₃	ν_1	symmetric stretch
1550	1549	63	O ₂	ν_1	fundamental
1184, 1204	1185	59	ND ₃	ν_4	degenerated deformation
840	833	59	ND ₃	ν_2	symmetric deformation
after irradiation					
2567	2572	36	D ₂ O	ν_1	symmetric stretch (out-of-phase)
2522	2482	17	ND ₂ OD	ν_1	O—D stretch
2474	2470	36	D ₂ O	ν_3	antisymmetric stretch (longitudinal)
2358	2393	17	ND ₂ OD	ν_7	N—D stretch (antisymmetric)
2346		17	ND ₂ OD	ν_2	N—D stretch (symmetric)
2297	2305	36	D ₂ O	ν_1	symmetric stretch (in-phase)
2267		17	ND ₂ OD	ν_2	N—D stretch (symmetric)
2248	2184	17	ND ₂ OD	$\nu_3 + \nu_4$	combination
2131		17	ND ₂ OD	$2\nu_4$	overtone
2075	2045	17	ND ₂ OD	$\nu_3 + \nu_5$	combination
2027		17	ND ₂ OD	$\nu_4 + \nu_8$	combination
1875	1875	17,20,64,65	NO	ν_1	fundamental
1836	1833–1851	17,20,64,68	N ₂ O ₃	ν_1	N=O stretch
1735	1737	17,20,64,65	(NO) ₂	ν_5	N=O stretch (antisymmetric)
1616	1614	67	NO ₂	ν_3	N=O stretch (antisymmetric)
1543	1546	17,69	DNO	ν_3	N=O stretch
1303	1303	17,20,64,68	N ₂ O ₃	ν_3	NO ₂ stretch (symmetric)
1252	1240	66	N ₂ O ₂	ν_1	NO ₂ stretch (symmetric)
1135	1156	17,69	DNO	ν_2	DNO bend
1038	1037	63	O ₃	ν_3	antisymmetric stretch
881	920	17	ND ₂ OD	ν_5	ND ₂ wag
796	880	66	N ₂ O ₂	ν_2	N—N stretch
708	701	36	D ₂ O	ν_L	libration

^aAssignment based on references.

oxygen excess ammonia–oxygen (1:10) experiment (Figure S1 and Table S1 in the Supporting Information).⁶³ After the irradiation, the ammonia (NH₃) fundamentals at 3369 and 1077 cm⁻¹ and the D3-ammonia (ND₃) absorptions at 2500 and 840 cm⁻¹ decrease significantly in intensity. Nitrogen monoxide (NO) with its absorption band appears at 1875 cm⁻¹ and its dimer (NO)₂ at 1735 cm⁻¹ were evident in the electron-irradiated (D3-)ammonia–oxygen ices.^{17,20,64,65} The IR absorptions bands at 1235 and 796 cm⁻¹ in the irradiated ammonia–oxygen ices and at 1252 and 796 cm⁻¹ in the irradiated (D3-)ammonia–oxygen ices are assigned to dinitrogen dioxide (N₂O₂) based on its IR TPD profile, which was growing during the warm-up phase of the ice simultaneously with the decay of the NO band.⁶⁶ Further, a new band at 2236 cm⁻¹ from ammonia–oxygen ices was assigned to nitrous oxide (N₂O) in accordance with the literature value.^{17,20,67} A weak band at 1616 cm⁻¹ in the irradiated ND₃–O₂ sample is attributed to the antisymmetric stretch $\nu(\text{N}=\text{O})$ of nitrogen dioxide (NO₂) in agreement with the literature value at 1614 cm⁻¹.⁶⁷ However, this band is hidden in the irradiated ammonia–oxygen (NH₃–O₂) ice by the intense NH₃ fundamental. Small, but distinct,

levels of dinitrogen trioxide (N₂O₃) were observed in both irradiated ices at 1836 and 1303 cm⁻¹.^{17,20,64,68} Upon surface destruction of nitrogen dioxide (NO₂), Ioppolo et al. observed formation of a series of nitrogen oxides including nitrogen monoxide monomer (NO), dimer ((NO)₂), nitrous oxide (N₂O), dinitrogen trioxide (N₂O₃), and dinitrogen tetroxide (N₂O₄).²⁰ The formation of dinitrogen tetroxide (N₂O₄) is excluded in our experiments, as the calculated column density of the nitrogen dioxide (NO₂) is too small; therefore, it is not expected that its dimer is present in the sample with a concentration above detection limit.

The next species observed in the irradiated ammonia–oxygen (NH₃–O₂) ices at 5.5 K is nitrosyl hydride (HNO) with its stretching and bending fundamental absorption bands appearing at 1560 and 1507 cm⁻¹, respectively, in agreement with literature values.^{17,69,70} Similarly, the fundamental absorption bands of deuterated nitrosyl hydride (DNO) at 1543 and 1135 cm⁻¹ were found in the irradiated D3-ammonia–oxygen (ND₃–O₂) ices at 5.5 K.^{17,69} Furthermore, water (H₂O) could be identified with its out-of-phase symmetric stretch appearing at 3452 cm⁻¹ and the libration band at 950 cm⁻¹ in the

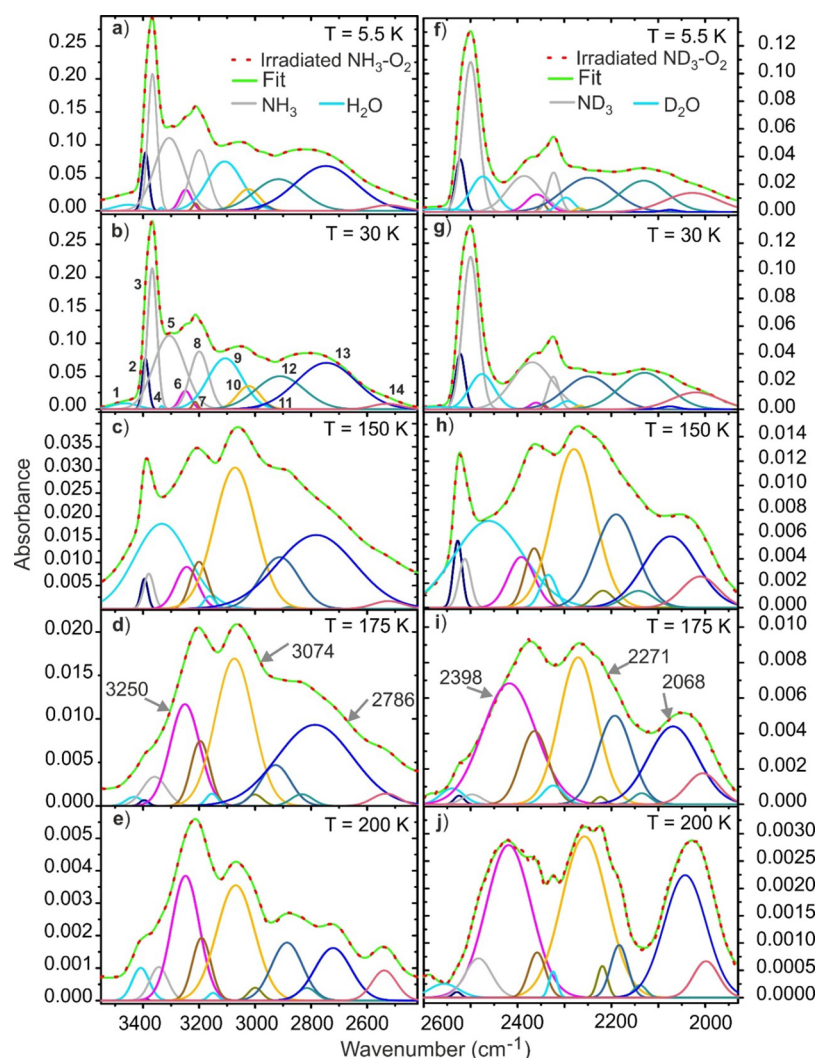


Figure 2. Deconvoluted infrared spectra of water, ammonia, and hydroxylamine from 2420–3550 cm^{-1} (left) and D2-water, D3-ammonia, and D3-hydroxylamine from 1930–2600 cm^{-1} (right) for selected temperatures corresponding to the sublimation temperatures of oxygen, (D3-)ammonia, and (D2-)water as observed via PI-ReTOF-MS and QMS. The individual band with particular color as marked 1–14 in (b) and their assignments are compiled in Tables 3a and 3b. The IR features of (D3-)hydroxylamine are increasing in intensity after most of the host molecule (D3-)ammonia (gray lines) and (D2-)water (sky blue lines) sublimed (see color version of this figure).

electron-irradiated $\text{NH}_3\text{-O}_2$ ices.³⁷ Note that assignments of other bands of water such as the in-phase symmetric stretch were difficult at 5.5 K due to overlying absorption of ammonia (NH_3) (Section 3.1.2). Similarly, the two bands in the energetic electron-irradiated $\text{ND}_3\text{-O}_2$ ices at 2567 and 708 cm^{-1} were assigned to deuterated water (D_2O), in agreement with the literature data at 2572 and 701 cm^{-1} .³⁶ Next, a weak band appearing at 1038 cm^{-1} in the irradiated $\text{ND}_3\text{-O}_2$ sample was assigned to the fundamental absorption band (ν_3) of ozone (O_3), in accordance with literature value at 1037 cm^{-1} .⁶³ This band could not be detected in the irradiated $\text{NH}_3\text{-O}_2$ ices due to overlapping absorption of ammonia (NH_3) and hydroxylamine (NH_2OH). Further, a new band at 1375 cm^{-1} in the irradiated $\text{NH}_3\text{-O}_2$ ices was tentatively assigned to antisymmetric bending (ν_6) vibration of hydrogen peroxide (H_2O_2), in agreement with the literature data at 1389 cm^{-1} .³⁷ However, the analogues D2-hydrogen peroxide (D_2O_2) could not be detected in the irradiated $\text{ND}_3\text{-O}_2$ ices due to overlying absorption of ozone (O_3).

Finally, a set of new bulk absorptions appeared at ~ 3213 , 3024, 2748, and 1145 cm^{-1} that raised during radiation exposure

of ammonia–oxygen ($\text{NH}_3\text{-O}_2$) ice at 5.5 K. These bands were persistent on the substrate up to ~ 200 K and were assigned to hydroxylamine (NH_2OH) in accordance with literature values.^{13,17} Although hydroxylamine (NH_2OH) was produced in the irradiated ice at 5.5 K (Figure 1), it was difficult to assign all absorptions at 5.5 K due to broadening and overlapping of peaks. In the NH bending region NH_2OH peaks were overlapping mainly with the aforementioned species, whereas in the NH and OH stretching region they were masked by the host molecule NH_3 as well as by H_2O peaks making the assignments difficult (Section 3.1.2). Similarly, broad bands centered at ~ 2346 , 2267, 2075, and 881 cm^{-1} in the irradiated (D3-)ammonia–oxygen ($\text{ND}_3\text{-O}_2$) ices are assigned to D3-hydroxylamine (ND_2OD).¹⁷ It is interesting to note, that the electron radiolysis of ammonium perchlorate (NH_4ClO_4) led to the formation of decomposition products similar to the ones listed above.⁷¹

3.1.2. Deconvolution of the Absorption Features in the OH(OD) and NH(ND) Stretching Region of Hydroxylamine. Since the main topic of this work is probing the formation of hydroxylamine under conditions relevant to astrochemical

environments, hereafter we focus on that formation during the oxidation of the NH_3 (ND_3) sample. First, IR spectra of the present work revealed the formation of NH_2OH (ND_2OD) in electron-irradiated $(\text{D}_3\text{-})\text{NH}_3\text{-O}_2$ ices at 5.5 K. However, as mentioned earlier, the absorptions of $(\text{D}_3\text{-})\text{NH}_3$ and $(\text{D}_2\text{-})\text{H}_2\text{O}$ made the $(\text{D}_3\text{-})\text{NH}_2\text{OH}$ assignments difficult at lower temperatures. In addition, absorptions were broad and not well-defined. Thus, it was necessary to perform their deconvolution to discriminate the peaks and probe which species were truly represented by these absorptions. The spectra for selected temperatures at 5.5, 30, 150, 175, and 200 K, corresponding to the sublimation temperatures of oxygen, $(\text{D}_3\text{-})$ ammonia, and $(\text{D}_2\text{-})$ water as observed via PI-ReTOF-MS and EI-QMS, were deconvoluted exploiting Gaussian fits utilizing the peak fitting application using the fewest number of fitting peaks to compute a fit that resulted in a residual within the signal-to-noise ratio of the original spectra (Figure 2, Tables 3a and 3b). Figure 2a–e exhibits the deconvoluted spectra of the NH and OH stretching region of NH_2OH in the region of 2420–3550 cm^{-1} , and their associated assignments are compiled in Table 3a. Likewise, Figure 2f–j exhibits the deconvoluted spectra of the ND and OD stretching region of ND_2OD in the region of 1930–2600 cm^{-1} , and their associated assignments are compiled in Table 3b.

The deconvolution identified three absorptions of NH_3 centered at 3366, 3307, and 3204 cm^{-1} and similarly ND_3 at 2500, 2350, and 2323 cm^{-1} in irradiated $(\text{D}_3\text{-})$ ammonia–oxygen ($\text{NH}_3/\text{ND}_3\text{-O}_2$) ices at 5.5 K, which are matching the absorption of NH_3 and ND_3 before irradiation, respectively (Tables 3a and 3b). Next, three bands centered at 3452, 3336, and 3109 cm^{-1} in the irradiated $\text{NH}_3\text{-O}_2$ ice at 5.5 K can be correlated to the out-of-phase symmetric stretch (ν_1), the antisymmetric stretch (longitudinal mode) (ν_3), and the in-phase symmetric stretch (ν_1) of H_2O , respectively, which are in agreement with the literature data at 3452, 3332, and 3107 cm^{-1} , respectively.³⁷ Similarly, three bands at 2567, 2474, and 2297 cm^{-1} in the irradiated $\text{ND}_3\text{-O}_2$ ice at 5.5 K are assigned to D_2O , in agreement with the literature data at 2572, 2470, and 2305 cm^{-1} , respectively.³⁶ Further, the band at 3163 cm^{-1} in the irradiated $\text{NH}_3\text{-O}_2$ ice at 150 K, that is, after most of the host molecule ammonia sublimed, are linked to the antisymmetric stretch (transversal mode) (ν_3) of H_2O (Table 3a). Note that this band is observed only after most of the NH_3 molecule sublimed. Likewise, the band centered at 2364 cm^{-1} in the irradiated $\text{ND}_3\text{-O}_2$ ice at 150 K is assigned to the antisymmetric stretch (transversal mode) (ν_3) of D_2O (Table 3b), in agreement with the literature value at 2370 cm^{-1} .³⁶

Concerning the hydroxylamine, the deconvolution revealed eight absorptions centered at 3391, 3248, 3213, 3024, 2963, 2916, 2748, and 2525 cm^{-1} in the irradiated $\text{NH}_3\text{-O}_2$ ice, and similarly at 2522, 2358, 2346, 2267, 2248, 2131, 2075, and 2027 cm^{-1} in the irradiated $\text{ND}_3\text{-O}_2$ ice at 5.5 K, which are close to the literature values of $(\text{D}_3\text{-})\text{NH}_2\text{OH}$.^{13,17,72,73} These IR bands are affected by the absorptions of the ammonia and water molecules at lower temperatures and are increasing in intensity once these molecules sublimed at higher temperatures as monitored via TPD IR study. In summary, deconvolution of the TPD IR spectra revealed three molecules in the region of 2420–3550 cm^{-1} in the irradiated $\text{NH}_3\text{-O}_2$ ices at 5.5 K: ammonia, water, and hydroxylamine, with ammonia dominating the IR spectra below 145 K, and then water overlaying the hydroxylamine up to 174 K. These findings were confirmed by the radiolysis of isotope-labeled $\text{ND}_3\text{-O}_2$ experiments as well.

Table 3a. Deconvoluted Peak Positions of Hydroxylamine (NH_2OH), Water (H_2O), and Ammonia (NH_3) Absorption Bands Observed in the Processed Ammonia–Oxygen ($\text{NH}_3\text{-O}_2$) Ices As Shown in Figure 2

band	this work (cm^{-1})					literature values (cm^{-1})				species	vibration	assignment ^a
	before irradiation	5.5 K	30 K	150 K	after irradiation	ref 13	ref 17	ref 61	ref 37			
1		3452	3457		3432				3452	H_2O	ν_1	symmetric stretch (out-of-phase)
2		3391	3391	3395	3395		3317			NH_2OH	ν_1	O–H stretch
3	3369	3366	3367	3379	3360			3372		NH_3	ν_3	antisymmetric stretch
4		3336	3333	3333					3332	H_2O	ν_3	antisymmetric stretch (longitudinal)
5	3300	3307	3306		3250			3290		NH_3	$2\nu_4$	overtone
6		3248	3249	3244	3196	3332	3261			NH_2OH	ν_7	N–H stretch (antisymmetric)
7		3213	3214	3200		3209	3194			NH_2OH	ν_2	N–H stretch (symmetric)
8	3211	3204	3207		3154			3212		NH_3	ν_1	symmetric stretch
9		3109	3107	3163	3154				3151, 3107	H_2O	ν_9	antisymmetric stretch (transversal), symmetric stretch (in-phase)
10		3024	3023	3072, 3004	3074, 3002	3074				NH_2OH	ν_2	N–H stretch (symmetric)
11		2963	2963	2917	2912	2943–2507	2899			NH_2OH	$\nu_3 + \nu_4$	combination
12		2916	2911	2879	2833					NH_2OH	$2\nu_4$	overtone
13		2748	2745	2782	2786		2716			NH_2OH	$\nu_3 + \nu_5$	combination
14		2525	2529	2524	2532					NH_2OH	$\nu_4 + \nu_8$	combination

^aAssignment based on references.

Table 3b. Deconvoluted Peak Positions of D3-Hydroxylamine (ND₂OD), D2-Water (D₂O), and D3-Ammonia (ND₃) Absorption Bands Observed in the Processed D3-Ammonia–Oxygen (ND₃–O₂) Ices As Shown in Figure 2

band	this work (cm ⁻¹)						literature values (cm ⁻¹)			assignment ^a		
	before irradiation	after irradiation								species	vibration	characterization
	5.5 K	5.5 K	30 K	150 K	175 K	200 K	ref 17	ref 59	ref 36			
1		2567	2559		2539	2557			2572	D ₂ O	ν_1	symmetric stretch (out-of-phase)
2		2522	2522	2527	2524	2529	2482			ND ₂ OD	ν_1	O–D stretch
3	2500	2500	2500	2512	2497	2487		2503		ND ₃	ν_3	antisymmetric stretch
4		2474	2476	2465					2470	D ₂ O	ν_3	antisymmetric stretch (longitudinal)
5	2342	2350	2352							ND ₃	$2\nu_4$	overtone
6		2358	2360	2392	2398	2409	2393			ND ₂ OD	ν_7	N–D stretch (antisymmetric)
7		2346	2342	2364	2364	2358				ND ₂ OD	ν_2	N–D stretch (symmetric)
8	2330	2323	2323					2326		ND ₃	ν_1	symmetric stretch
9		2297	2293	2364	2364	2361			2370, 2305	D ₂ O	ν_3, ν_1	antisymmetric stretch (transversal), symmetric stretch (in-phase)
10		2267	2267	2279, 2218	2271, 2223	2257, 2219				ND ₂ OD	ν_2	N–D stretch (symmetric)
11		2248	2249	2190	2192	2183	2184			ND ₂ OD	$\nu_3 + \nu_4$	combination
12		2131	2129	2142	2135	2139				ND ₂ OD	$2\nu_4$	overtone
13		2075	2075	2074	2068	2043	2045			ND ₂ OD	$\nu_3 + \nu_5$	combination
14		2027	2020	2011	2005	2003				ND ₂ OD	$\nu_4 + \nu_8$	combination

^aAssignment based on references.

Figure 3a,b shows the decay of absorption features of (D3-)hydroxylamine after (D3) ammonia and (D2-)water sublimed, with its vibrational mode frequencies compiled and compared with literature values in Tables 4a and 4b, respectively.^{13,17} The absorptions at 3395 cm⁻¹ in the irradiated ammonia–oxygen (NH₃–O₂) ices at 175 K correspond to the stretching mode of OH (ν_1); those at 3250 cm⁻¹ match the antisymmetric stretch vibration (ν_7) and at 3196 and 3074 cm⁻¹ originate from the symmetric stretch (ν_2) of N–H. The absorptions at 2833 and 1845 cm⁻¹ allotted to the NOH bending and N–O stretch overtones, respectively, and those at 2912, 2786, and 2532 cm⁻¹ results from combination bands. The bands at 1695 and 1580 cm⁻¹ results from the bending mode (ν_3) of NH₂ and at 1473 cm⁻¹ match to the NOH bending mode (ν_4). The absorptions at 1220 and 1145 cm⁻¹ assigned to the NH₂ rocking (ν_8) and wagging (ν_5) modes, respectively, and at 928 cm⁻¹ corresponds to the N–O stretching mode (ν_6). These patterns are similar to those ND₂OD absorption peaks observed in electron-irradiated deuterated ammonia–oxygen (ND₃–O₂) ices (Table 4b).

3.1.3. Quantitative Analysis of Hydroxylamine Formation, Mass Balances. The number of reactant molecules decomposed during the radiolysis in the ammonia (NH₃)–oxygen (O₂) ices can be calculated if the decrease in their integrated infrared areas and their absorption coefficients are known; these are summarized in Table 5 (and in Table S2 in the Supporting Information for the 1:10 mixture). When comparing the number of destroyed ammonia molecules ($(4.8 \pm 0.7) \times 10^{17}$ cm⁻²) to the exposed reactants ($(5.0 \pm 0.7) \times 10^{17}$ cm⁻², Table 1), it can be concluded that $95 \pm 5\%$ of them are destroyed within the penetration depth of the electrons. The same values for molecular oxygen (O₂) are $(1.6 \pm 0.3) \times 10^{17}$ cm⁻² and $(2.5 \pm 0.3) \times 10^{17}$ cm⁻² meaning that $66 \pm 15\%$ of the irradiated molecules decomposed. To calculate the number of molecules degraded, the integrated absorption coefficients of

3.11×10^{-17} cm molecule⁻¹ of the ν_3 NH₃ band between 3700–3000 cm⁻¹ based on the results of Sill et al.⁵⁵ and 5.00×10^{-21} cm molecule⁻¹ (ν_1 O₂ band at 1550 cm⁻¹)⁷⁴ were used, respectively.

The integrated band areas can also be determined for the radiolysis products, and if their absorption coefficients are known, it allows for the calculation of their concentration in the sample. On the basis of the absorption coefficient of 4.16×10^{-18} cm molecule⁻¹ for the vibrational band of the hydroxylamine (ν_4 NH₂OH) at 1486 cm⁻¹ (utilizing the findings of Saldyka & Mielke),⁷⁵ its column density is found to be $(1.6 \pm 0.2) \times 10^{17}$ cm⁻². The same value for nitrogen monoxide (ν_1 NO at 1875 cm⁻¹) equals to $(1.6 \pm 0.3) \times 10^{16}$ cm⁻² when the absorption coefficient of 6.80×10^{-18} cm molecule⁻¹ is used.⁶⁵ An absorption coefficient of 1.66×10^{-17} cm molecule⁻¹ can be used for the vibrational band of the nitrosyl hydride (ν_3 HNO) at 1560 cm⁻¹ corresponding to $(6.0 \pm 4.1) \times 10^{13}$ cm⁻²; the estimation is based on the absorption coefficients obtained for its isomer isonitrosyl hydride (HON).⁷⁶ The column density of dinitrogen dioxide (N₂O₂) was calculated to be $(3.2 \pm 0.1) \times 10^{15}$ cm⁻² based on the integrated area of its vibrational band at 1235 cm⁻¹ (O–N–O symmetric stretching); for this, the absorption coefficient (5.00×10^{-17} cm molecule⁻¹) had to be estimated as well. This was conducted by using the absorption coefficients of the same vibrational mode of similar dinitrogen oxides (N₂O_x, $x = 3-5$).⁶⁵ The number of nitrogen monoxide dimer ((NO)₂) molecules are determined to be $(2.15 \pm 0.03) \times 10^{15}$ cm⁻² if its absorption coefficient of 2.72×10^{-17} cm molecule⁻¹ for its ν_1 vibrational band (at 1735 cm⁻¹) is utilized.⁷⁷ The column density of water molecules formed upon irradiation can also be determined $((2.1 \pm 0.2) \times 10^{15}$ cm⁻²) through the integrated area of its vibrational band at 950 cm⁻¹ (ν_L H₂O, 3.10×10^{-17} cm molecule⁻¹).⁷⁸ The vibrational bands of ozone are completely hidden by the more intense ammonia (NH₃)

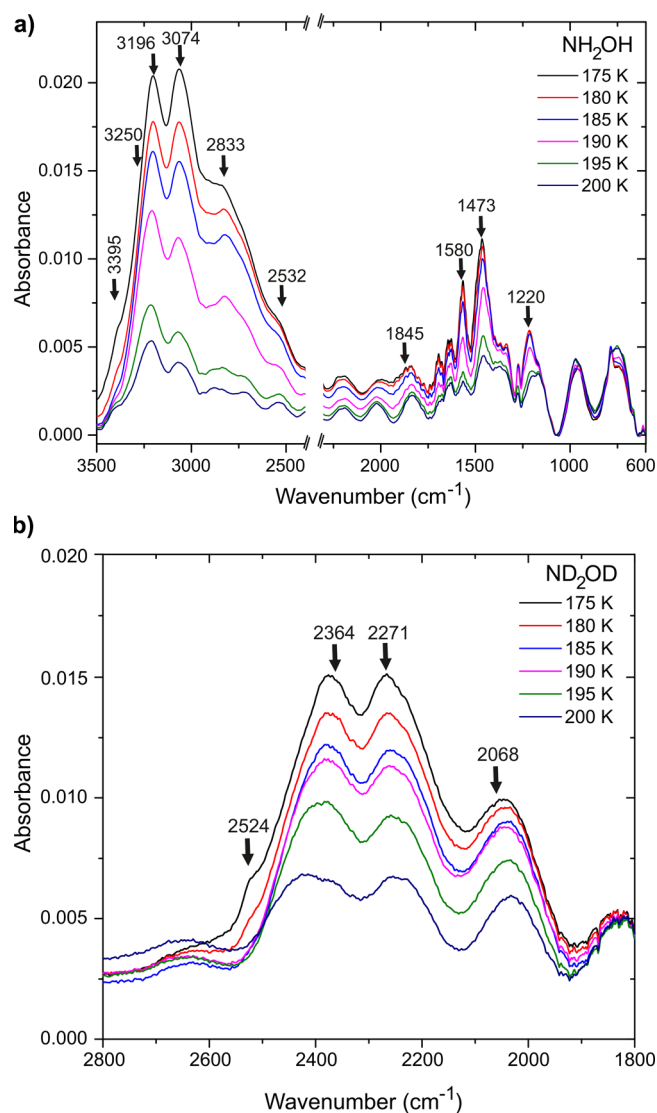


Figure 3. (a) Infrared absorption features of the hydroxylamine (NH_2OH) species at 175, 180, 185, 190, 195, and 200 K after most of the host molecules ammonia (NH_3) and oxygen (O_2) as well as accompanying byproducts such as water (H_2O) sublimed. The deconvoluted absorption features of the NH_2OH at 5.5, 30, 150, 175, and 200 K are shown in Figure 2 and Table 3a. The individual band assignments are compiled in Table 4a. (b) Infrared absorption features of the D3-hydroxylamine (ND_2OD) species at 175, 180, 185, 190, 195, and 200 K after most of the host molecules D3-ammonia (ND_3) and oxygen (O_2) as well as computing byproducts such as water (D_2O) sublimed. The deconvoluted absorption features of the ND_2OD at 5.5, 30, 150, 175, and 200 K are shown in Figure 2 and Table 3b. The individual band assignments are compiled in Table 4b. Atmospheric carbon dioxide has been traced out.

and hydroxylamine (NH_2OH) signals at 1038 cm^{-1} ($\nu_3 \text{ O}_3$, $1.53 \times 10^{-17}\text{ cm molecule}^{-1}$) in the irradiated $\text{NH}_3\text{--O}_2$ 2:1 ices.⁷⁹ However, it can be observed in the deuterated sample ($\text{ND}_3\text{--O}_2$ 2:1), and its column density can then be estimated ($(7.9 \pm 1.4) \times 10^{14}\text{ cm}^{-2}$). Tentatively, hydrogen peroxide is also produced upon irradiation; the integrated area of its band at 1375 cm^{-1} ($\nu_6 \text{ H}_2\text{O}_2$) with an estimated absorption coefficient of $6.00 \times 10^{-17}\text{ cm molecule}^{-1}$ can be used to obtain its column density ($(5.5 \pm 0.2) \times 10^{14}\text{ cm}^{-2}$). It is worth noting that the absorption coefficient was obtained based on the known one of the combinational bands close to 2900 cm^{-1}

($\nu_2 + \nu_6 \text{ H}_2\text{O}_2$).⁸⁰ The number of nitrous oxide ($\nu_1 \text{ N}_2\text{O}$ at 2236 cm^{-1}) with an absorption coefficient of $5.20 \times 10^{-17}\text{ cm molecule}^{-1}$,⁸¹ and nitrogen dioxide ($\nu_3 \text{ NO}_2$ at 1616 cm^{-1} , $6.36 \times 10^{-17}\text{ cm molecule}^{-1}$)⁶⁵ could also be determined; these values are $(3.7 \pm 0.1) \times 10^{14}\text{ cm}^{-2}$ and $(3.5 \pm 0.2) \times 10^{14}\text{ cm}^{-2}$, respectively. Note that the signal of nitrogen dioxide—similarly to that of the ozone (O_3) molecule—is hidden in the normal ice; it can be determined by using the results of the deuterated $\text{ND}_3\text{--O}_2$ 2:1 ice mixture. The last species that could be detected in the radiolyzed ice is dinitrogen trioxide (N_2O_3) having an absorption coefficient of $6.43 \times 10^{-17}\text{ cm molecule}^{-1}$ for the vibrational band at 1836 cm^{-1} ($\nu_1 \text{ N}_2\text{O}_3$)⁶⁵ meaning its column density corresponds to $(5.7 \pm 1.3) \times 10^{13}\text{ cm}^{-2}$.

If the number of nitrogen and oxygen atoms that can be found in the irradiation products is added up, the values obtained can be compared to the number of these elements originated from the destruction of ammonia (NH_3) and oxygen (O_2). Their total number required for the formation of the aforementioned species are found to be $(1.9 \pm 0.2) \times 10^{17}\text{ cm}^{-2}$ and $(9.6 \pm 1.2) \times 10^{16}\text{ cm}^{-2}$, whereas $(4.8 \pm 0.7) \times 10^{17}\text{ cm}^{-2}$ and $(3.3 \pm 0.6) \times 10^{17}\text{ cm}^{-2}$ nitrogen and oxygen atoms were formed when the two parent molecules were destroyed. This means that they account for the $39 \pm 8\%$ and $29 \pm 4\%$ of the total number of nitrogen and oxygen atoms formed upon the irradiation. Some of the oxygen that cannot be accounted for combines with another one recycling molecular oxygen (O_2),⁸² which sublimates from the irradiated sample upon TPD at $\sim 35\text{ K}$, and its signal at $m/z = 32$ can be detected via the EI-QMS instrument.^{83,84} The missing nitrogen is likely present as molecular nitrogen (N_2) formed via the radiolysis of ammonia.⁸⁵

3.2. PI-ReTOF-MS Data Analysis. It is of interest to correlate the infrared observation with a highly sensitive mass spectrometric analysis of the molecules subliming into the gas phase. The PI-ReTOF-MS data of the subliming molecules taken at the photoionization energy of 10.49 eV are compiled in Figure 4. The TPD profiles are dominated by the signal of the host matrix molecule ammonia (NH_3) at mass-to-charge ratio (m/z) = 17 ($\text{IE} = 10.07 \pm 0.01\text{ eV}$)⁸⁶ and, respectively at $m/z = 20$ from D3-ammonia (ND_3) ($\text{IE} = 10.08 \pm 0.01\text{ eV}$).⁸⁶ The TPD profile suggests two sublimation events for this species from ~ 75 and 145 K with a maximum peak at $\sim 125\text{ K}$ and from ~ 170 and 220 K with maximum peak at 190 K .⁸⁷ The next highest contribution found in the 10.49 eV probed (D3)–ammonia–oxygen samples is that of the nitrogen monoxide (NO) ($\text{IE} = 9.2643 \pm 0.0002\text{ eV}$)⁸⁸ with its mass-to-charge-ratio at 30 peaking at $165 \pm 2\text{ K}$ and second sublimation event maximum at $\sim 191 \pm 2\text{ K}$. Further, nitrosyl hydride (HNO) ($m/z = 31$ and $\text{IE} = 10.18 \pm 0.01$)⁸⁹ with its counterpart deuterated nitrosyl hydride (DNO) ($m/z = 32$ and $\text{IE} = 10.29 \pm 0.14$)⁹⁰ were observed in the 10.49 eV probed (D3)–ammonia–oxygen sample peaking at $187 \pm 5\text{ K}$. Finally NH_2OH ($\text{IE} = 10.00\text{ eV}$)⁸ at $m/z = 33$ and ND_2OD at $m/z = 36$ were detected with 10.49 eV photolyzed $\text{NH}_3\text{--O}_2$ and $\text{ND}_3\text{--O}_2$ samples, respectively. The TPD profiles found for NH_2OH and ND_2OD molecules are essentially identical peaking at 191 ± 2 and $196 \pm 1\text{ K}$, respectively. Note that the formation of a series of nitrogen oxides evident in the FTIR experiment such as nitrous oxide (N_2O) ($\text{IE} = 12.880 \pm 0.005\text{ eV}$)⁹¹ were unable to be detected using the PI-ReTOF-MS, as their ionization energy is higher than the energy of the photons applied in our experiments (10.49 eV). For the same

Table 4a. Assignment of the Hydroxylamine (NH₂OH) Absorption Bands (cm⁻¹) at 175 K Compared to Reference Values

this work (NH ₃ -O ₂ ice)	ref 1 ^{a,b,13} (NH ₃ -H ₂ O ice)	ref 2 ^{a,c,17} (NO + H ice)	assignment ^a
3395		3317	ν_1 (a') O-H stretch
3250	3332	3261	ν_7 (a'') N-H stretch (antisymmetric)
3196, 3074	3209–3074	3194	ν_2 (a') N-H stretch (symmetric)
2912	2943–2507	2899	$\nu_3 + \nu_4$ combination
2833			$2\nu_4$ overtone
2786		2716	$\nu_3 + \nu_5$ combination
2532			$\nu_4 + \nu_8$ combination
1845	1886		$2\nu_6$ (a') overtone
1695		1608	ν_3 (a') NH ₂ bend
1580	1616	1592, 1514	ν_3 (a') NH ₂ bend, ν_4 (a') NOH bend
1473	1486	1359	ν_4 (a') NOH bend
1220	1201	1203	ν_8 (a'') NH ₂ rock
1145	1107	1144	ν_5 (a') NH ₂ wag
928	921	919, 889	ν_6 (a') N-O stretch

^aAssignment based on references. ^bat 175 K. ^cat 15 K.

Table 4b. Assignment of the D3-Hydroxylamine (ND₂OD) Absorption Bands (cm⁻¹) at 175 K Compared to Reference Values

this work (ND ₃ -O ₂ ice)	ref 1 ^{a,b,17} (NO+D ice)	assignment ^a
2524	2482	ν_1 (a') O-D stretch
2398	2393	ν_7 (a'') N-D stretch (antisymmetric)
2364, 2271		ν_2 (a') N-D stretch (symmetric)
2192	2184	$\nu_3 + \nu_4$ combination
2135		$2\nu_4$ overtone
2068	2045	$\nu_3 + \nu_5$ combination
2005		$\nu_4 + \nu_8$ combination
1267–1230		$2\nu_6$ (a') overtone
	1185	ν_3 (a') ND ₂ bend
1216–1170	1175, 1126	ν_3 (a') ND ₂ bend, ν_4 (a') NOD bend
988–1107	1026	ν_4 (a') NOD bend
952	946	ν_8 (a'') ND ₂ rock
	920	ν_5 (a') ND ₂ wag
819–933	878, 825	ν_6 (a') N-O stretch

^aAssignment based on reference. ^bAt 15 K.

reason, water (H₂O) (IE = 12.6188 ± 0.0009 eV),⁹² D₂-water (D₂O) (IE = 12.6398 ± 0.0009 eV),⁹² hydrogen peroxide (H₂O₂) (IE = 10.92 ± 0.05 eV),⁹³ and ozone (O₃) (IE = 12.519 ± 0.004 eV)⁹⁴ were not detected in our PI-ReTOF-MS experiments (Table 6).

Special attention is paid to the detection of hydroxylamine utilizing the highly sensitive PI-ReTOF-MS technique based on its mass-to-charge ratio, the sublimation temperature, and how the mass-to-charge ratios shift upon isotope labeling. Here, because of the simplicity of the host ice, made up of only three elements (H, N, and O), the identification of the observed mass-to-charge ratios are straightforward (Figure 5). Thus, the signal at $m/z = 33$ must stem from molecule(s) with a chemical formula N₂H₅, HO₂, NH₃O, and/or NH₂OH. First we ruled out the formation of the hydroperoxyl radical (HO₂), as its ionization energy (IE = 11.35 ± 0.01 eV)⁹⁵ resides well-above the energy of our photons (10.49 eV). Next, although N₂H₅ is claimed to exist as intermediate,⁹⁶ it has never been isolated in pure form, and the ionization energy is not known as a result. Also, no signal was observed for N₂D₅ in the deuterated ammonia-oxygen samples. This suggests that the signal at $m/z = 33$ can only arise from NH₂OH and/or its zwitterionic

Table 5. Mass Balance of the Ammonia-Oxygen (NH₃-O₂) Ice as well as that of the Irradiation Products Determined from Their Experimental IR Decay/Growth Curves

process	decay product	number of molecules produced/decomposed during irradiation
NH ₃ → X		(4.8 ± 0.7) × 10 ¹⁷
fraction of NH ₃ degraded		95 ± 5%
O ₂ → O	O	(1.6 ± 0.3) × 10 ¹⁷
fraction of O ₂ degraded		66 ± 15%
number of molecules in sample after irradiation	NH ₂ OH	(1.6 ± 0.2) × 10 ¹⁷
	NO ^c	(1.6 ± 0.3) × 10 ¹⁶
	N ₂ O ₂	(3.2 ± 0.1) × 10 ¹⁵
	(NO) ₂ ^c	(2.15 ± 0.03) × 10 ¹⁵
	H ₂ O	(2.1 ± 0.2) × 10 ¹⁵
	O ₃ ^d	(7.9 ± 1.4) × 10 ¹⁴
	H ₂ O ₂	(5.5 ± 0.2) × 10 ¹⁴
	N ₂ O	(3.7 ± 0.1) × 10 ¹⁴
	NO ₂ ^d	(3.5 ± 0.2) × 10 ¹⁴
	HNO	(6.0 ± 4.1) × 10 ¹³
	N ₂ O ₃	(5.7 ± 1.3) × 10 ¹³
nitrogen balance ^a		39 ± 8%
oxygen balance ^b		29 ± 4%

^aFraction of nitrogen atoms originating from ammonia destruction that is needed for the formation of the irradiation products. ^bFraction of oxygen atoms originating from molecular oxygen destruction that is needed for the formation of the irradiation products. ^cThe NO monomer and dimer were treated together during the simulations. ^dDetermined by using the integrated band areas of the ND₃-O₂ ice sample.

form NH₃O. However, a recent study at the CCSD(T)/BSIII//MP2/BSIII level of theory (Reaction 15) suggests that the normal hydroxylamine isomer NH₂OH is more stable than the zwitterionic form NH₃O by ~1 eV.⁹⁷ Hydroxylamine was detected between 160 and 220 K peaking at 191 ± 2 K, in agreement with literature values (Table 7).^{13,16,19,20,22,29} Moreover, the TPD profile reveals that NH₂OH peaks at the same temperature (191 ± 2 K) as the signals of mass-to-charge ratio $m/z = 31$ (HNO) and $m/z = 30$ (NO) (Figure 5). This is consistent with the findings of Congiu et al.¹⁶ who performed the hydrogenation of NO and observed NH₂OH in the TPD along with its thermal degradation in the region of 160–200 K peaking at 190 K. These findings are also consistent with the isotope-labeled experiment, namely, the electron irradiation of

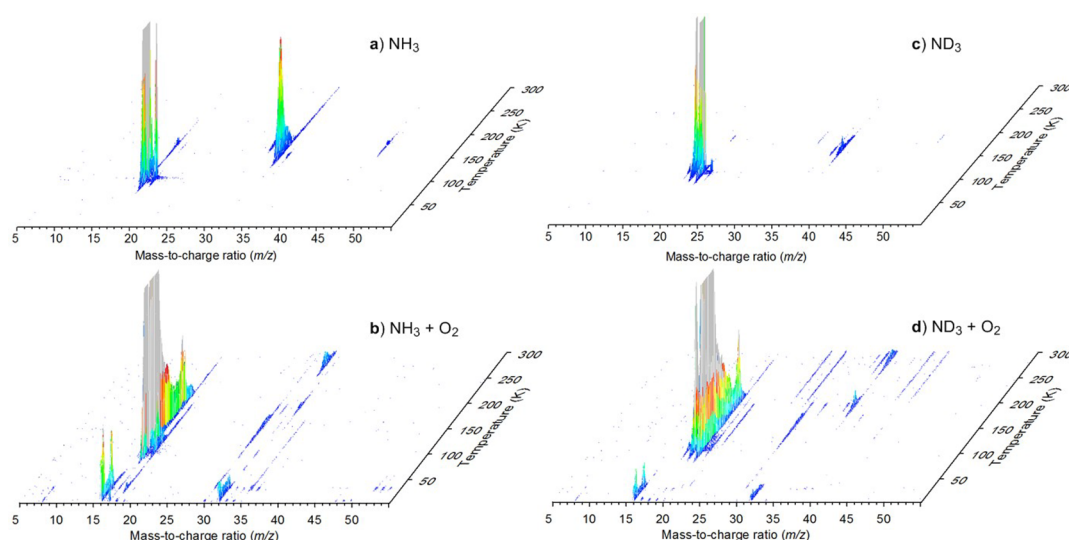


Figure 4. Three-dimensional visualization of the PI-ReTOF-MS data of the irradiated (a) ammonia, (b) ammonia–oxygen, (c) D3-ammonia, and (d) D3-ammonia–oxygen ices at a photon energy of 10.49 eV collected during the TPD of the reactants and products subliming into the gas phase.

Table 6. Ionization Energies of the Species under Discussion

<i>m/z</i>	species ^a	ionization energy (eV)	references
17	<i>NH₃</i>	10.07	86
	OH	13.017	98
18	H ₂ O	12.6188	92
	ND ₂	11.14 ^b	99
	OD	13.029	98
20	ND ₃	10.08	86
	D ₂ O	12.6398	92
28	N ₂	15.581	100
30	NO	9.2643	88
31	HNO	10.18	89
32	DNO	10.29	90
	O ₂	12.0697	101
33	<i>NH₂OH</i>	10.00	8
	HO ₂	11.35	95
34	DO ₂	11.35 ^b	95
	H ₂ O ₂	10.92	93
35	<i>NH₃-H₂O</i>		
36	ND ₂ OD	10.00 ^b	8
	D ₂ O ₂	10.92 ^b	93
44	N ₂ O	12.880	91
46	NO ₂ ^c	9.586	102
48	O ₃	12.519	94
60	N ₂ O ₂		
62	NO ₃	12.57	103
76	N ₂ O ₃		
92	N ₂ O ₄	10.8	104
108	N ₂ O ₅	11.90	103

^aItalic font indicates species detected by PI-ReTOF-MS, as their ionization energy (IE) is less than the photon source applied in our experiments (10.49 eV). ^bIE is not known, but it can be assumed to be similar to the IE of the isotopologues containing H atoms. ^cBelow detection limit.

ND₃–O₂ ices. As can be seen in the right panel of Figure 5, signals are recorded at mass-to-charge ratio *m/z* = 36 (ND₂OD), *m/z* = 32 (DNO), and *m/z* = 30 (NO) after exposing the ND₃–O₂ ices to 10.49 eV photons.



4. DISCUSSION

Having already assigned the (D3-)hydroxylamine formed after energetic electron irradiation of (D3-)ammonia–oxygen ices (Tables 3a and 4a, Figures 1–5), we are now proposing the possible formation pathway exploiting the IR and ReTOF data. For the infrared data, we fit the temporal profiles of the reactants and of the newly formed molecules with a system of coupled differential equations (R1–R12). These are visualized by the kinetic scheme in Figure 6 and listed in Table 8; the fitting curves resulting from the numerical solution of the set of equations are plotted on the experimental column densities in Figure 7, whereas Table 8 also summarizes the kinetic rate constants obtained as a result of the kinetic fitting. First, upon exposure to energetic electron, the ammonia (NH₃) molecule is known to undergo decomposition to form atomic hydrogen (H) and amidogen (NH₂) via reaction (16a) as well as a spin-forbidden molecular decomposition to molecular hydrogen (H₂) and the triplet amino hydride (NH) via reaction 16b.^{85,87} The amidogen radical can undergo barrierless recombination with a second amidogen radical forming hydrazine (N₂H₄) followed by stepwise radiolysis via diimide (N₂H₂) to form eventually molecular nitrogen (N₂) (Reactions 17–19).⁸⁵ In the present system, this scheme is expressed with the overall equation R3 and rate constant *k*₃ (Rice-Herzfeld chain, Δ_r*H*_{0K} = +77.9 kJ ± 0.5 mol^{–1}). Likewise, molecular oxygen was shown to decompose to two oxygen atoms⁶³ (R1, Δ_r*H*_{0K} = +683.2 kJ mol^{–1}) thus supplying a highly oxidizing environment and a reactant to form ozone (O₃, R12, Δ_r*H*_{0K} = +391.3 ± 2.0 kJ mol^{–1}). The energy needed for these endoergic reactions to take place and therefore for the formation of the energetic oxygen atoms are covered by the 5 keV electrons used for irradiating the sample.



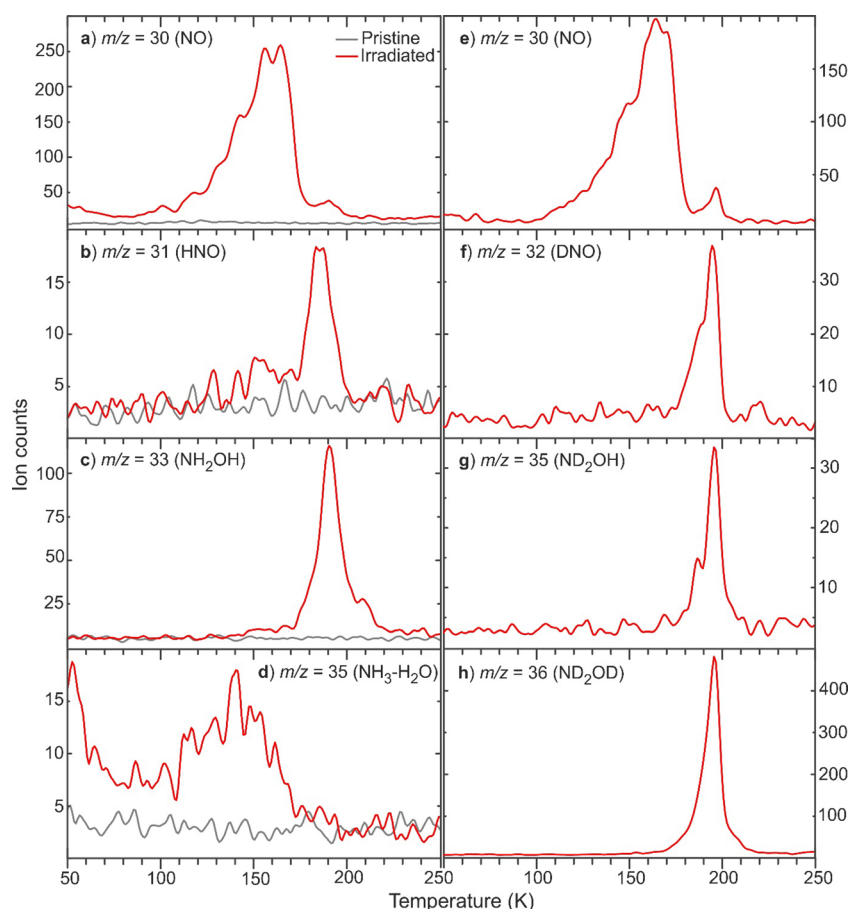


Figure 5. Selected TPD profiles extracted from the PI-ReTOF-MS spectra shown in Figure 4. TPD profiles of (a) $m/z = 30$ (NO^+), (b) $m/z = 31$ (HNO^+), (c) $m/z = 33$ (NH_2OH^+), and (d) $m/z = 35$ ($\text{NH}_3\text{-H}_2\text{O}^+$) subliming from the irradiated ammonia–oxygen ($\text{NH}_3\text{-O}_2$) ices (left) and TPD profiles of (e) $m/z = 30$ (NO^+), (f) $m/z = 32$ (DNO^+), (g) $m/z = 35$ (ND_2OH^+) and (h) $m/z = 36$ (ND_2OD^+) subliming from the irradiated D3-ammonia–oxygen ($\text{ND}_3\text{-O}_2$) ices (right) recorded at photoionization energies of 10.49 eV.

Table 7. Compilation of the Desorption Temperatures of (D3-)Hydroxylamine N=O stretch (antisymmetric)

sample	conditions	detection techniques	temperature (K)		ref
			range	peaking at approximately	
$\text{NH}_3 + \text{O}_2$	electron irradiation at 5.5 K	QMS, IR, PI-ReTOF-MS	160–220	191 ± 2	this work
$\text{ND}_3 + \text{O}_2$	electron irradiation at 5.5 K	QMS, IR, PI-ReTOF-MS	160–220	196 ± 1	this work
$\text{NH}_3 + \text{O}$	oxidation of NH_3 at 70 K	QMS	160–200	180	22
$\text{NH}_3 + \text{H}_2\text{O}$	electron irradiation at 10 K	QMS, IR	160–200	190	13
$\text{NO} + \text{H}$	hydrogenation at 10 K	QMS, IR	160–200	190	16,19
$\text{NO} + \text{D}$	deuteration at 10 K	QMS, IR	160–200	190	19
$\text{NO}_2 + \text{H}$	hydrogenation at 10 K	QMS, IR	225–265	245	20
$(\text{NH}_2\text{OH})_3\text{H}_3\text{PO}_4$	thermal decomposition then condensation at 3 K	QMS, IR	130–220	180	29



Ammonia was found to be oxidized via two pathways leading eventually to nitrosyl hydride (HNO): the oxidation via reaction with two oxygen atoms and water (H_2O) elimination (R4, $\Delta_r H_{0\text{K}} = -583.6 \text{ kJ} \pm 0.4 \text{ mol}^{-1}$) and in one step to hydroxylamine (NH_2OH , R2, $\Delta_r H_{0\text{K}} = -430.1 \text{ kJ mol}^{-1}$), which itself can be oxidized to nitrosyl hydride (HNO , R5, $\Delta_r H_{0\text{K}} = -335.9 \text{ kJ} \pm 10.0 \text{ mol}^{-1}$). Note that the oxidation of ammonia to hydroxylamine is, by a factor of ~ 5 , faster than the oxidation to nitrosyl hydride (HNO). As evident from Figure 7, nitrosyl hydride (HNO) builds very rapidly within the

first few minutes of the experiments reaching then a steady concentration. This can only be accounted for by a destruction pathway of nitrosyl hydride (HNO , R6, $\Delta_r H_{0\text{K}} = +196.6 \text{ kJ} \pm 0.3 \text{ mol}^{-1}$) to nitrogen monoxide (NO). The latter can either form dinitrogen dioxide (N_2O_2 , R7) or is oxidized to nitrogen dioxide (NO_2 , R8, $\Delta_r H_{0\text{K}} = -300.6 \text{ kJ} \pm 0.1 \text{ mol}^{-1}$). Both processes are barrierless, since they involve a recombination of radicals/atoms. A second production pathway of dinitrogen dioxide (N_2O_2) proceeds through oxidation of nitrogen to dinitrogen monoxide (N_2O , R10, $\Delta_r H_{0\text{K}} = -161.8 \text{ kJ} \pm 0.5 \text{ mol}^{-1}$),⁶⁷ which itself can be oxidized to form dinitrogen dioxide (N_2O_2 , R11). To avoid overproduction, an additional oxidation route to dinitrogen trioxide (N_2O_3 , R9) was incorporated.

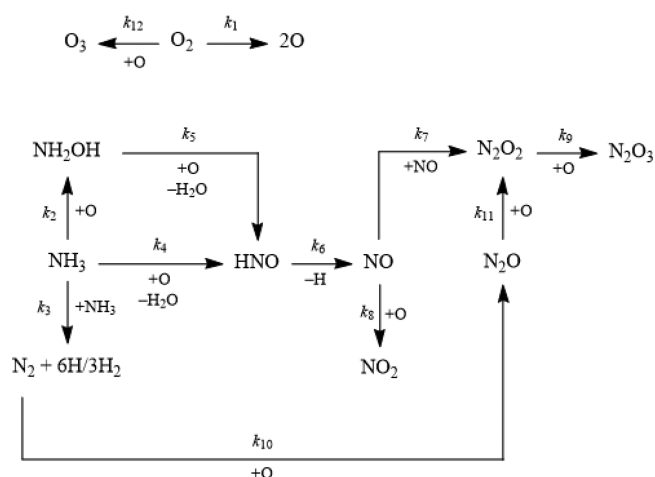


Figure 6. Reaction scheme exploited for the kinetics fits of the temporal profiles of the newly formed molecules during photolysis of ammonia–oxygen ices as compiled in Table 8.

Table 8. Decay Rate Constants of the Ammonia–Oxygen ($\text{NH}_3\text{--O}_2$) Ice as well as the Formation Rates of the Irradiation Products Based on their Experimental IR Decay/Growth Curves

reaction		rate constant	(pseudo) first-order value
number	equation		
R1	$\text{O}_2 \rightarrow (^1\text{D})\text{O} + (^3\text{P})\text{O}$	k_1	$(3.4 \pm 0.5) \times 10^{-4}$
R2	$\text{NH}_3 + (^1\text{D})\text{O} \rightarrow \text{NH}_2\text{OH}$	k_2^a	$(2.5 \pm 0.7) \times 10^{-4}$
R3	$\text{NH}_3 + \text{NH}_3 \rightarrow \text{N}_2 + 6\text{H}/3\text{H}_2$	k_3^a	$(8.6 \pm 1.4) \times 10^{-5}$
R4	$\text{NH}_3 + 2\text{O} \rightarrow \text{HNO} + \text{H}_2\text{O}$	k_4^a	$(4.6 \pm 1.7) \times 10^{-5}$
R5	$\text{NH}_2\text{OH} + \text{O} \rightarrow \text{HNO} + \text{H}_2\text{O}$	k_5^a	$(6.0 \pm 1.7) \times 10^{-6}$
R6	$\text{HNO} \rightarrow \text{NO} + \text{H}$	k_6	$(2.0 \pm 0.2) \times 10^{-1}$
R7	$\text{NO} + \text{NO} \rightarrow \text{N}_2\text{O}_2$	k_7^a	$(1.5 \pm 0.2) \times 10^{-4}$
R8	$\text{NO} + \text{O} \rightarrow \text{NO}_2$	k_8^a	$(7.8 \pm 0.6) \times 10^{-6}$
R9	$\text{N}_2\text{O}_2 + \text{O} \rightarrow \text{N}_2\text{O}_3$	k_9^a	$(4.9 \pm 1.5) \times 10^{-6}$
R10	$\text{N}_2 + \text{O} \rightarrow \text{N}_2\text{O}$	k_{10}^a	$(2.1 \pm 0.1) \times 10^{-6}$
R11	$\text{N}_2\text{O} + \text{O} \rightarrow \text{N}_2\text{O}_2$	k_{11}^a	$(2.7 \pm 0.2) \times 10^{-4}$
R12	$\text{O}_2 + \text{O}_2 \rightarrow \text{O}_3 + \text{O}$	k_{12}^a	$(1.0 \pm 0.3) \times 10^{-6}$

^aHigher-order reaction rate, its corresponding pseudo-first-order rate can be obtained by multiplying it by the average number of the reactant(s) during the irradiation. These are the following species depending on the reaction equation: NH_3 ($[\text{NH}_3]_{\text{av}} = ((2.1 \pm 1.3) \times 10^{17})$), O_2 ($[\text{O}_2]_{\text{av}} = ((1.5 \pm 0.5) \times 10^{17})$), NO ($[\text{NO}]_{\text{av}} = (1.4 \pm 0.6) \times 10^{16}$), and O ($[\text{O}]_{\text{av}} = ((6.6 \pm 1.7) \times 10^{13})$).

Considering the formation of hydroxylamine (NH_2OH), recall that three possible formation routes were proposed in the interstellar medium. These are the synthesis of hydroxylamine (NH_2OH) via an exoergic reaction ($\Delta H_{\text{r},298}^\circ = -270.2 \text{ kJ mol}^{-1}$)¹⁰⁵ involving radical recombination between amidogen (NH_2) and hydroxyl radical (OH) (Reaction 9)^{13,23,25} and/or through a barrierless successive hydrogenation of nitrogen monoxide (NO) (Reaction 10)^{15,16} at low temperatures. However, our kinetics scheme reveals that these two reaction pathways are insignificant to the synthesis of hydroxylamine (NH_2OH) in our experiments. The third and the most likely reaction route for the formation of hydroxylamine (NH_2OH) in our experiment is via the insertion of a suprathermal singlet or a triplet atomic oxygen (O) into the N–H bond of ammonia (NH_3), with the latter being followed by intersystem crossing (ISC) to the singlet surface. Recall that both are among the most

abundant species in our system of interest. These reaction pathways are further verified by kinetically fitting the temporal evolution of the column densities of all species formed during irradiation (Figures 6 and 7, Table 8).

5. CONCLUSIONS

Since its first detection in 1968 in the center of our galaxy,¹⁰⁶ ammonia has been known to be one of the most common species adsorbed onto the colder interstellar dust icy-grain surface, with an abundance of $\approx 5\%$ relative to water ice.^{34,35} Oxygen is also the third most abundant element in the universe^{107,108} and has been detected in recent comets with local abundances ranging from 1 to 10% with respect to water.^{109,110} Thus, significant experimental and theoretical work to understand the energetic radiation effect on the oxygen and ammonia ices is crucial to accurately model the chemistry of the ISM. On the one hand, in cold dense molecular clouds where the temperatures are lower than the desorption temperature of oxygen, that is, below 20–25 K in our experimental conditions, ammonia and oxygen ices could be exposed to different forms of energetic irradiation and thus be responsible for the formation of various nitrogen- and oxygen-bearing building blocks of prebiotic species such as hydroxylamine (NH_2OH) through insertion or radical–radical combination mechanisms. On the other hand, at temperatures near or higher than 25 K, oxygen could start to diffuse and would be able to collide with ammonia ices to form the same species. In the present study, we have shown the formation of hydroxylamine from energetic electron-irradiated ammonia–oxygen interstellar model ices under UHV conditions and cryogenic temperatures at 5.5 K, using infrared spectroscopic analysis complemented by TPD studies utilizing highly sensitive PI-ReTOF-MS at photoionization energies of 10.49 eV. According to our kinetic studies, the major reaction pathway for the formation of hydroxylamine is found to occur via insertion of a suprathermal singlet oxygen into ammonia or by insertion of triplet oxygen followed by ISC.

To date, and to the best of our knowledge, hydroxylamine has not been detected in the ISM either in solid state in dark molecular clouds or in gas phase in the star-forming regions. Our experimental results show that hydroxylamine may be present both in condensed phase on ice-coated interstellar grains as well as in gas phase in the so-called “hot-core” proto-star regions. Our study also suggests that hydroxylamine can be easily oxidized to HNO, with the latter detected in the ISM as early as 1977.¹¹¹ Accordingly, it might be difficult to detect hydroxylamine, if it is formed in strongly oxidizing environments. However, we expect hydroxylamine to be detected in the near future by ALMA at a temperature at which hydroxylamine might be sublimed into the gas phase prior to excessive oxidation ($\sim 160 \text{ K}$ according to our experiments). Finally, a route for linking our findings to the synthesis of amino acids under interstellar environments starting from gas-phase hydroxylamine has been proposed by Bohme and his group.^{1,2} They have shown the formation of glycine from gas-phase reaction of hydroxylamine and acetic acid; the latter—a well-known interstellar molecule^{4–6}—has been successfully prepared in our laboratory from energetic electron-irradiation of methane (CH_4) and carbon dioxide (CO_2) ices under the same experimental conditions to the present study.¹¹² Moreover, Förstel et al. pointed out that radiolysis of ammonia–methane ices mixtures can lead to the formation of potential precursors of amino acids.⁵⁸ Thus, it would be of a great desire to synthesize

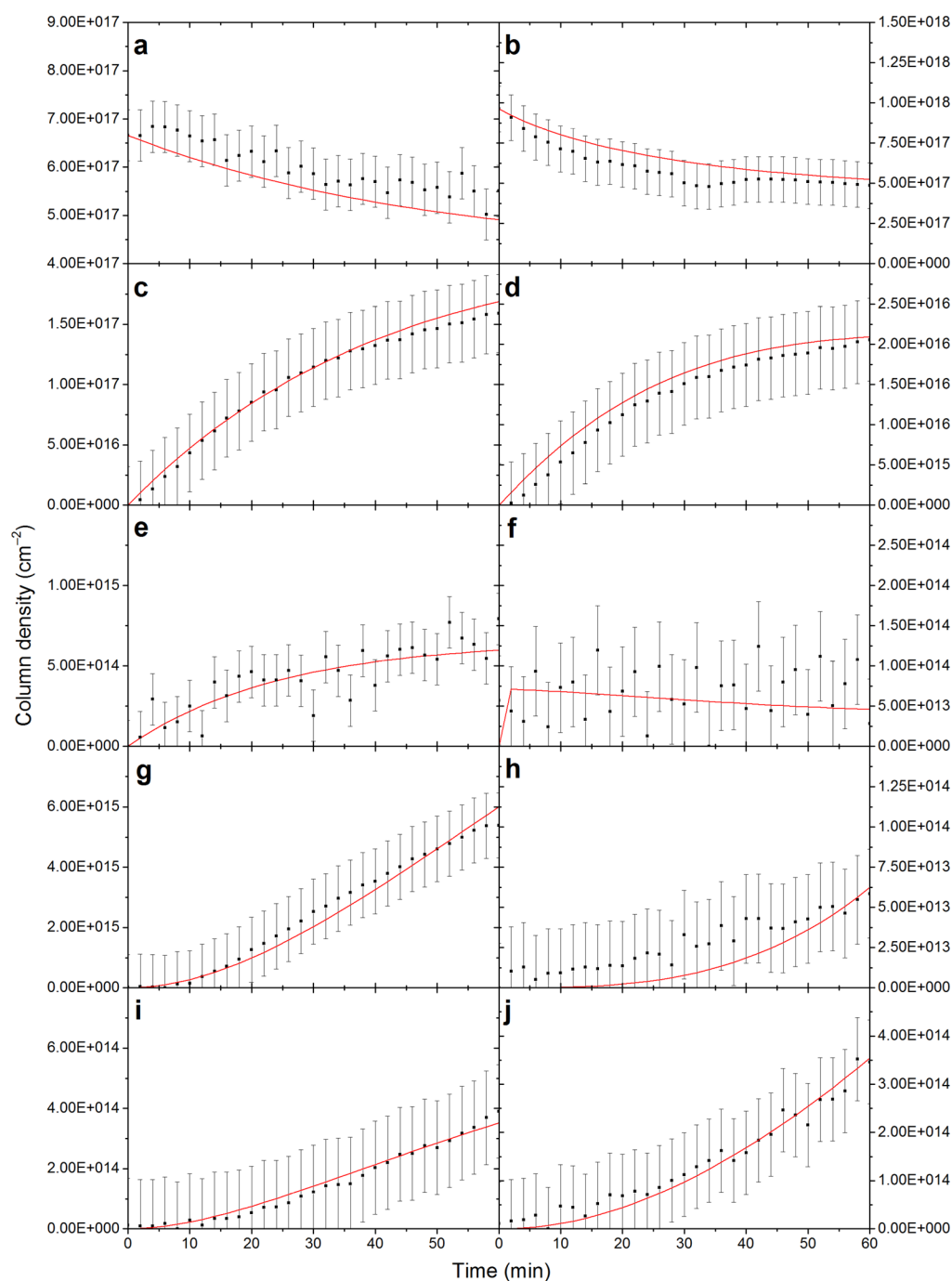


Figure 7. Decay curves of the IR bands of the $\text{NH}_3\text{--O}_2$ mixture sample upon energetic electron irradiation (a) at 1550 cm^{-1} ($\nu_1\text{ O}_2$) and (b) at 3369 cm^{-1} ($\nu_3\text{ NH}_3$), respectively. Growth curves of the IR bands of the same sample (c) at 1486 cm^{-1} ($\nu_4\text{ NH}_2\text{OH}$), (d) 1875 cm^{-1} ($\nu_1\text{ NO}$), (e) 1038 cm^{-1} ($\nu_3\text{ O}_3$), (f) 1560 cm^{-1} ($\nu_3\text{ HNO}$), (g) 1235 cm^{-1} ($\nu\text{ N}_2\text{O}_2$), (h) 1836 cm^{-1} ($\nu_1\text{ N}_2\text{O}_3$), (i) 2236 cm^{-1} ($\nu_1\text{ N}_2\text{O}$), and (j) 1616 cm^{-1} ($\nu_3\text{ NO}_2$), respectively.

glycine from ice mixtures analogous to the ones that can be found in the ISM in the future.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpca.7b07500.

Infrared absorption features, mass balance and TPD profiles of the irradiated ammonia–oxygen ($\text{NH}_3\text{--O}_2$) (1:10) experiments (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: wolfram.sander@rub.de. (W.S.)

*E-mail: ralfk@hawaii.edu. (R.I.K.)

ORCID

Ralf I. Kaiser: 0000-0002-7233-7206

Present Addresses

^{||}Berlin Institute of Technology, IOAP Hardenbergstrasse 36, 10623 Berlin, Germany.

[†]Harvard-Smithsonian Center for Astrophysics, 60 Garden Street, Cambridge MA, United States.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The Hawaii group would like to thank the U.S. National Science Foundation (AST-1505502) for support to conduct the present experiments. The authors also acknowledge the W. M. Keck Foundation for financing the experimental setup. M.F. acknowledges funding from the DFG (FO 941/1). The Bochum team (Y.A.T. and W.S.) thanks the Cluster of Excellence RESOLV (EXC 1069), funded by the Deutsche Forschungsgemeinschaft, for support.

REFERENCES

- (1) Blagojevic, V.; Petrie, S.; Bohme, D. K. Gas-Phase Syntheses for Interstellar Carboxylic and Amino Acids. *Mon. Not. R. Astron. Soc.* **2003**, *339*, L7–L11.
- (2) Snow, J. L.; Orlova, G.; Blagojevic, V.; Bohme, D. K. Gas-Phase Ionic Syntheses of Amino Acids: β versus α . *J. Am. Chem. Soc.* **2007**, *129*, 9910–9917.
- (3) Largo, L.; Rayón, V. M.; Barrientos, C.; Largo, A.; Redondo, P. Stability of Protonated and Ionized Hydroxylamine in the Interstellar Medium. *Chem. Phys. Lett.* **2009**, *476*, 174–177.
- (4) Mehringer, D. M.; Snyder, L. E.; Miao, Y.; Lovas, F. J. Detection and Confirmation of Interstellar Acetic Acid. *Astrophys. J.* **1997**, *480*, L71–L74.
- (5) Remijan, A.; Snyder, L. E.; Friedel, D. N.; Liu, S. Y.; Shah, R. Y. A Survey of Acetic Acid toward Hot Molecular Cores. *Astrophys. J.* **2003**, *590*, 314–332.
- (6) Shiao, Y. S. J.; Looney, L. W.; Remijan, A. J.; Snyder, L. E.; Friedel, D. N. First Acetic Acid Survey with CARMA in Hot Molecular Cores. *Astrophys. J.* **2010**, *716*, 286–298.
- (7) Karton, A.; Talbi, D. Pinning the most Stable $H_xC_yO_z$ Isomers in Space by means of High-Level Theoretical Procedures. *Chem. Phys.* **2014**, *436–437*, 22–28.
- (8) Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. Gas-Phase ion and Neutral Thermochemistry. *J. Phys. Chem. Ref. Data, Suppl.* **1988**, *17*, 1–861.
- (9) Boulet, P.; Gilardoni, F.; Weber, J.; Chermette, H.; Ellinger, Y. Theoretical Study of Interstellar Hydroxylamine Chemistry: Protonation and Proton Transfer Mediated by H_3^+ . *Chem. Phys.* **1999**, *244*, 163–174.
- (10) Øiestad, E. L.; Uggerud, E. The Unimolecular Chemistry of Protonated Hydroxylamine. *Int. J. Mass Spectrom.* **1999**, *185–187*, 231–240.
- (11) Abplanalp, M. J.; Gozem, S.; Krylov, A. I.; Shingledecker, C. N.; Herbst, E.; Kaiser, R. I. A Study of Interstellar Aldehydes and Enols as Tracers of a Cosmic Ray-Driven Nonequilibrium Synthesis of Complex Organic Molecules. *Proc. Natl. Acad. Sci. U. S. A.* **2016**, *113*, 7727–7732.
- (12) Nishi, N.; Shinohara, H.; Okuyama, T. Photodetachment, Photodissociation, and Photochemistry of Surface Molecules of Icy Solids Containing NH_3 and Pure H_2O Ices. *J. Chem. Phys.* **1984**, *80*, 3898–3910.
- (13) Zheng, W.; Kaiser, R. I. Formation of Hydroxylamine (NH_2OH) in Electron-Irradiated Ammonia–Water Ices. *J. Phys. Chem. A* **2010**, *114*, S251–S255.
- (14) Bordalo, V.; da Silva, E. F.; Lv, X. Y.; Domaracka, A.; Rothard, H.; Duarte, E. S.; Boduch, P. Chemical Processing of Pure Ammonia and Ammonia–Water Ices Induced by Heavy Ions. *Astrophys. J.* **2013**, *774*, 105.
- (15) Charnley, S. B.; Rodgers, S. D.; Ehrenfreund, P. Gas-Grain Chemical Models of Star-Forming Molecular Clouds as Constrained by ISO and SWAS Observations. *Astron. Astrophys.* **2001**, *378*, 1024–1036.
- (16) Congiu, E.; Fedoseev, G.; Ioppolo, S.; Dulieu, F.; Chaabouni, H.; Baouche, S.; Lemaire, J. L.; Laffon, C.; Parent, P.; Lamberts, T.; et al. NO Ice Hydrogenation: A Solid Pathway to NH_2OH Formation in Space. *Astrophys. J.* **2012**, *750*, L12.
- (17) Fedoseev, G.; Ioppolo, S.; Lamberts, T.; Zhen, J. F.; Cuppen, H. M.; Linnartz, H. Efficient Surface Formation Route of Interstellar Hydroxylamine Through NO Hydrogenation. II. The Multilayer Regime in Interstellar Relevant Ices. *J. Chem. Phys.* **2012**, *137*, 054714.
- (18) Fedoseev, G.; Chuang, K.-J.; van Dishoeck, E. F.; Ioppolo, S.; Linnartz, H. Simultaneous Hydrogenation and UV-photolysis Experiments of NO in CO-rich Interstellar Ice Analogues; Linking HNCO, OCN^- , NH_2CHO , and NH_2OH . *Mon. Not. R. Astron. Soc.* **2016**, *460*, 4297–4309.
- (19) Congiu, E.; Chaabouni, H.; Laffon, C.; Parent, P.; Baouche, S.; Dulieu, F. Efficient Surface Formation Route of Interstellar Hydroxylamine Through NO Hydrogenation. I. The Submonolayer Regime on Interstellar Relevant Substrates. *J. Chem. Phys.* **2012**, *137*, 054713.
- (20) Ioppolo, S.; Fedoseev, G.; Minissale, M.; Congiu, E.; Dulieu, F.; Linnartz, H. Solid State Chemistry of Nitrogen Oxides – Part II: Surface Consumption of NO_2 . *Phys. Chem. Chem. Phys.* **2014**, *16*, 8270–8282.
- (21) Minissale, M.; Fedoseev, G.; Congiu, E.; Ioppolo, S.; Dulieu, F.; Linnartz, H. Solid State Chemistry of Nitrogen Oxides – Part I: Surface Consumption of NO. *Phys. Chem. Chem. Phys.* **2014**, *16*, 8257–8269.
- (22) He, J.; Vidali, G.; Lemaire, J.-L.; Garrod, R. T. Formation of Hydroxylamine on Dust Grains via Ammonia Oxidation. *Astrophys. J.* **2015**, *799*, 49.
- (23) Garrod, R. T. A Three-phase Chemical Model of Hot Cores: The Formation of Glycine. *Astrophys. J.* **2013**, *765*, 60.
- (24) Garrod, R. T.; Weaver, S. L. W.; Herbst, E. Complex Chemistry in Star-forming Regions: An Expanded Gas-Grain Warm-up Chemical Model. *Astrophys. J.* **2008**, *682*, 283.
- (25) Mousavipour, S. H.; Pirhadi, F.; Habibagahi, A. A Theoretical Investigation on the Kinetics and Mechanism of the Reaction of Amidogen with Hydroxyl Radical. *J. Phys. Chem. A* **2009**, *113*, 12961–12971.
- (26) Wang, L.; Mebel, A. M.; Yang, X.; Wang, X. Ab Initio/RRKM Study of the $O(^1D) + NH_3$ Reaction: Prediction of Product Branching Ratios. *J. Phys. Chem. A* **2004**, *108*, 11644–11650.
- (27) Pulliam, R. L.; McGuire, B. A.; Remijan, A. J. A Search for Hydroxylamine (NH_2OH) toward Select Astronomical Sources. *Astrophys. J.* **2012**, *751*, 1.
- (28) McGuire, B. A.; Carroll, P. B.; Dollhopf, N. M.; Crockett, N. R.; Corby, J. F.; Loomis, R. A.; Burkhardt, A. M.; Shingledecker, C.; Blake, G. A.; Remijan, A. J. CSO and CARMA Observations of L1157. I. A Deep Search for Hydroxylamine (NH_2OH). *Astrophys. J.* **2015**, *812*, 76.
- (29) Jonusas, M.; Krim, L. A Possible Answer to the Mysterious Non-detection of Hydroxylamine in Space: the Thermal Desorption Mechanism. *Mon. Not. R. Astron. Soc.* **2016**, *459*, 1977–1984.
- (30) Bottinelli, S.; Boogert, A. C. A.; Bouwman, J.; Beckwith, M.; van Dishoeck, E. F.; Öberg, K. I.; Pontoppidan, K. M.; Linnartz, H.; Blake, G. A.; Evans, N. J., II; et al. The c2d *Spitzer* Spectroscopic Survey of Ices Around Low-mass Young Stellar Objects. IV. NH_3 and CH_3OH . *Astrophys. J.* **2010**, *718*, 1100–1117.
- (31) Di Francesco, J.; Hogerheijde, M. R.; Welch, W. J.; Bergin, E. A. Abundances of Molecular Species in Barnard 68. *Astron. J.* **2002**, *124*, 2749–2755.
- (32) Gibb, E. L.; Whittet, D. C. B.; Boogert, A. C. A.; Tielens, A. G. M. Interstellar Ice: The Infrared Space Observatory Legacy. *Astrophys. J., Suppl. Ser.* **2004**, *151*, 35–73.
- (33) Öberg, K. I.; Boogert, A. C. A.; Pontoppidan, K. M.; van den Broek, S.; van Dishoeck, E. F.; Bottinelli, S.; Blake, G. A.; Evans, N. J., II. The *Spitzer* Ice Legacy: Ice Evolution from Cores to Protostars. *Astrophys. J.* **2011**, *740*, 109.
- (34) Chiar, J. E.; Tielens, A. G. G. M.; Whittet, D. C. B.; Schutte, W. A.; Boogert, A. C. A.; Lutz, D.; van Dishoeck, E. F.; Bernstein, M. P.

The Composition and Distribution of Dust along the Line of Sight toward the Galactic Center. *Astrophys. J.* **2000**, *537*, 749–762.

(35) Lacy, J. H.; Faraji, H.; Sandford, S. A.; Allamandola, L. J. Unraveling the 10 Micron “Silicate” Feature of Protostars: The Detection of Frozen Interstellar Ammonia. *Astrophys. J.* **1998**, *501*, L105–L109.

(36) Zheng, W.; Jewitt, D.; Kaiser, R. I. Electron Irradiation of Crystalline and Amorphous D₂O Ice. *Chem. Phys. Lett.* **2007**, *435*, 289–294.

(37) Zheng, W.; Jewitt, D.; Kaiser, R. I. Formation of Hydrogen, Oxygen, and Hydrogen Peroxide in Electron-irradiated Crystalline Water Ice. *Astrophys. J.* **2006**, *639*, 534–548.

(38) Zheng, W.; Kim, Y. S.; Kaiser, R. I. Formation of Nitric Oxide and Nitrous Oxide in Electron-Irradiated H₂¹⁸O/N₂ Ice Mixtures—Evidence for the Existence of Free Oxygen Atoms in Interstellar and Solar System Analog Ices. *Phys. Chem. Chem. Phys.* **2011**, *13*, 15749–15754.

(39) Zheng, W.; Jewitt, D.; Kaiser, R. I. Temperature Dependence of the Formation of Hydrogen, Oxygen, and Hydrogen Peroxide in Electron-Irradiated Crystalline Water Ice. *Astrophys. J.* **2006**, *648*, 753–761.

(40) Bennett, C. J.; Jamieson, C.; Mebel, A. M.; Kaiser, R. I. Untangling the Formation of the Cyclic Carbon Trioxide Isomer in Low Temperature Carbon Dioxide Ices. *Phys. Chem. Chem. Phys.* **2004**, *6*, 735–746.

(41) Bennett, C. J.; Chen, S.-H.; Sun, B.-J.; Chang, A. H. H.; Kaiser, R. I. Mechanistical Studies on the Irradiation of Methanol in Extraterrestrial Ices. *Astrophys. J.* **2007**, *660*, 1588–1608.

(42) Zheng, W.; Kaiser, R. I. On the Formation of Carbonic Acid (H₂CO₃) in Solar System Ices. *Chem. Phys. Lett.* **2007**, *450*, 55–60.

(43) Kaiser, R. I.; Eich, G.; Gabrysch, A.; Roessler, K. Theoretical and Laboratory Studies on the Interaction of Cosmic-Ray Particles with Interstellar Ices. II. Formation of Atomic and Molecular Hydrogen in Frozen Organic Molecules. *Astrophys. J.* **1997**, *484*, 487–498.

(44) Jamieson, C. S.; Mebel, A. M.; Kaiser, R. I. Identification of the D_{3h} Isomer of Carbon Trioxide (CO₃) and its Implications for Atmospheric Chemistry. *ChemPhysChem* **2006**, *7*, 2508–2513.

(45) Bennett, C. J.; Hama, T.; Kim, Y. S.; Kawasaki, M.; Kaiser, R. I. Laboratory Studies on the Formation of Formic Acid (HCOOH) in Interstellar and Cometary Ices. *Astrophys. J.* **2011**, *727*, 27.

(46) Maity, S.; Kaiser, R. I.; Jones, B. M. Infrared and Reflectron Time-of-flight Mass Spectroscopic Study on the Synthesis of Glycolaldehyde in Methanol (CH₃OH) and Methanol–Carbon Monoxide (CH₃OH–CO) Ices Exposed to Ionization Radiation. *Faraday Discuss.* **2014**, *168*, 485–516.

(47) Westley, M. S.; Baratta, G. A.; Baragiola, R. A. Density and Index of Refraction of Water Ice Films Vapor Deposited at Low Temperatures. *J. Chem. Phys.* **1998**, *108*, 3321–3326.

(48) Zhou, L.; Maity, S.; Abplanalp, M.; Turner, A.; Kaiser, R. I. On the Radiolysis of Ethylene Ices by Energetic Electrons and Implications to the Extraterrestrial Hydrocarbon Chemistry. *Astrophys. J.* **2014**, *790*, 38.

(49) Turner, A. M.; Abplanalp, M. J.; Chen, S. Y.; Chen, Y. T.; Chang, A. H. H.; Kaiser, R. I. A Photoionization Mass Spectroscopic Study on the Formation of Phosphanes in Low Temperature Phosphine Ices. *Phys. Chem. Chem. Phys.* **2015**, *17*, 27281–27291.

(50) Satorre, M. A.; Leliwa-Kopystynski, J.; Santonja, C.; Luna, R. Refractive Index and Density of Ammonia Ice at Different Temperatures of Deposition. *Icarus* **2013**, *225*, 703–708.

(51) Fulvio, D.; Sivaraman, B.; Baratta, G. A.; Palumbo, M. E.; Mason, N. J. Novel Measurements of Refractive Index, Density and Mid-Infrared Integrated Band Strengths for Solid O₂, N₂O and NO₂:N₂O₂ Mixtures. *Spectrochim. Acta, Part A* **2009**, *72*, 1007–1013.

(52) Brunetto, R.; Caniglia, G.; Baratta, G. A.; Palumbo, M. E. Integrated Near-Infrared Band Strengths of Solid CH₄ and Its Mixtures with N₂. *Astrophys. J.* **2008**, *686*, 1480–1485.

(53) Turner, A. M.; Abplanalp, M. J.; Kaiser, R. I. Probing the Carbon-phosphorus Bond Coupling in Low-temperature Phosphine

(PH₃)—Methane (CH₄) Interstellar Ice Analogues. *Astrophys. J.* **2016**, *819*, 97.

(54) Moore, M. H.; Ferrante, R. F.; Hudson, R. L.; Stone, J. N. Ammonia–Water Ice Laboratory Studies Relevant to Outer Solar System Surfaces. *Icarus* **2007**, *190*, 260–273.

(55) Sill, G.; Fink, U.; Ferraro, J. R. Absorption Coefficients of Solid NH₃ from 50 to 7000 cm^{−1}. *J. Opt. Soc. Am.* **1980**, *70*, 724–739.

(56) Drouin, D.; Couture, A. R.; Joly, D.; Tastet, X.; Aimez, V.; Gauvin, R. CASINO V2.42—A Fast and Easy-to-use Modeling Tool for Scanning Electron Microscopy and Microanalysis Users. *Scanning* **2007**, *29*, 92–101.

(57) McMurtry, B. M.; Turner, A. M.; Saito, S. E. J.; Kaiser, R. I. On the Formation of Niacin (Vitamin B3) and Pyridine Carboxylic Acids in Interstellar Model Ices. *Chem. Phys.* **2016**, *472*, 173–184.

(58) Förstel, M.; Bergantini, A.; Maksyutenko, P.; Góbi, S.; Kaiser, R. I. Formation of Methylamine and Ethylamine in Extraterrestrial Ices and Their Role as Fundamental Building Blocks of Proteinogenic α -amino Acids. *Astrophys. J.* **2017**, *845*, 83.

(59) Holt, J. S.; Sadoskas, D.; Pursell, C. J. Infrared spectroscopy of the Solid Phases of Ammonia. *J. Chem. Phys.* **2004**, *120*, 7153–7157.

(60) Zheng, W.; Jewitt, D.; Kaiser, R. I. Infrared Spectra of Ammonia–Water Ices. *Astrophys. J., Suppl. Ser.* **2009**, *181*, 53–61.

(61) Zheng, W.; Kaiser, R. I. An Infrared Spectroscopy Study of the Phase Transition in Solid Ammonia. *Chem. Phys. Lett.* **2007**, *440*, 229–234.

(62) Kim, Y. S.; Kaiser, R. I. On the Formation of Amines (RNH₂) and the Cyanide Anion (CN[−]) in Electron-irradiated Ammonia–hydrocarbon Interstellar Model Ices. *Astrophys. J.* **2011**, *729*, 68.

(63) Bennett, C. J.; Kaiser, R. I. Laboratory Studies on the Formation of Ozone (O₃) on Icy Satellites and on Interstellar and Cometary Ices. *Astrophys. J.* **2005**, *635*, 1362–1369.

(64) Fateley, W. G.; Bent, H. A.; Crawford, B., Jr. Infrared Spectra of the Frozen Oxides of Nitrogen. *J. Chem. Phys.* **1959**, *31*, 204–217.

(65) Stirling, A.; Pápai, I.; Mink, J.; Salahub, D. R. Density Functional Study of Nitrogen-Oxides. *J. Chem. Phys.* **1994**, *100*, 2910–2923.

(66) Arnold, D. W.; Neumark, D. M. Study of N₂O₂ by Photoelectron Spectroscopy of N₂O₂[−]. *J. Chem. Phys.* **1995**, *102*, 7035–7045.

(67) Jamieson, C. S.; Bennett, C. J.; Mebel, A. M.; Kaiser, R. I. Investigating the Mechanism for the Formation of Nitrous Oxide [N₂O(X¹Σ⁺)] in Extraterrestrial Ices. *Astrophys. J.* **2005**, *624*, 436–447.

(68) Sluys, E. J.; Van der Veken, B. J. On the Behaviour of Nitrogen Oxides in Liquefied Argon and Krypton. Dimerisation of Nitric Oxide. *J. Mol. Struct.* **1994**, *320*, 249–267.

(69) Jacox, M. E.; Milligan, D. E. Matrix-Isolation Study of the Reaction of H Atoms with NO: The Infrared Spectrum of HNO. *J. Mol. Spectrosc.* **1973**, *48*, 536–559.

(70) Ruzi, M.; Anderson, D. T. Quantum Diffusion-Controlled Chemistry: Reactions of Atomic Hydrogen with Nitric Oxide in Solid Parahydrogen. *J. Phys. Chem. A* **2015**, *119*, 12270–12283.

(71) Góbi, S.; Bergantini, A.; Turner, A. M.; Kaiser, R. I. Electron Radiolysis of Ammonium Perchlorate: A Reflectron Time-of-Flight Mass Spectrometric Study. *J. Phys. Chem. A* **2017**, *121*, 3879–3890.

(72) Nightingale, R. E.; Wagner, E. L. The Vibrational Spectra and Structure of Solid Hydroxylamine and Deutero-Hydroxylamine. *J. Chem. Phys.* **1954**, *22*, 203–208.

(73) Kowal, A. T. Anharmonic Vibrational Spectra of Hydroxylamine and its ¹⁵N, ¹⁸O, and Deuterium Substituted Analogs. *Spectrochim. Acta, Part A* **2002**, *58*, 1055–1067.

(74) Vandenbussche, B.; Ehrenfreund, P.; Boogert, A. C. A.; van Dishoeck, E. F.; Schutte, W. A.; Gerakines, P. A.; Chiar, J.; Tielens, A. G. G. M.; Keane, J.; Whittet, D. C. B.; et al. Constraints on the Abundance of Solid O₂ in Dense Clouds from ISO-SWS and Ground-Based Observations. *Astron. Astrophys.* **1999**, *346*, L57–L60.

(75) Saldyka, M.; Mielke, Z. Photodecomposition of Formohydroxamic Acid. Matrix Isolation FTIR and DFT Studies. *Phys. Chem. Chem. Phys.* **2003**, *5*, 4790–4797.

- (76) Maier, G.; Reisenauer, H. P.; De Marco, M. Isonitroso Hydrogen (Hydroxy Nitrene, HON). *Angew. Chem., Int. Ed.* **1999**, *38*, 108–110.
- (77) Krim, L. The NO dimer, ^{14}N and ^{15}N Isotopomers Isolated in Nitrogen Matrix: A Near, Mid and Far Infrared Study. *J. Mol. Struct.* **1998**, *471*, 267–273.
- (78) Gerakines, P.; Schutte, W. A.; Greenberg, J. M.; van Dishoeck, E. F. The Infrared Band Strengths of H_2O , CO and CO_2 in Laboratory Simulations of Astrophysical Ice Mixtures. *Astron. Astrophys.* **1995**, *296*, 810–818.
- (79) Adler-Golden, S. M.; Langhoff, S. R.; Bauschlicher, C. W., Jr; Carney, G. D. Theoretical Calculation of Ozone Vibrational Infrared Intensities. *J. Chem. Phys.* **1985**, *83*, 255–264.
- (80) Moore, M. H.; Hudson, R. L. IR Detection of H_2O_2 at 80 K in Ion-Irradiated Laboratory Ices Relevant to Europa. *Icarus* **2000**, *145*, 282–288.
- (81) Wang, F.; Larkins, F. P.; Brunger, M. J.; Michalewicz, M. T.; Winkler, D. A. Core Molecular Orbital Contribution to N_2O Isomerization as Studied Using Theoretical Electron Momentum. *Spectrochim. Acta, Part A* **2001**, *57*, 9–15.
- (82) Turner, A. M.; Abplanalp, M. J.; Kaiser, R. I. Mechanistic Studies on the Radiolytic Decomposition of Perchlorates on the Martian Surface. *Astrophys. J.* **2016**, *820*, 127.
- (83) Bennett, C. J.; Ennis, C. P.; Kaiser, R. I. Experimental Studies on the Formation of D_2O and D_2O_2 by Implantation of Energetic D⁺ Ions into Oxygen Ices. *Astrophys. J.* **2014**, *782*, 63.
- (84) Góbi, S.; Bergantini, A.; Kaiser, R. I. In Situ Detection of Chlorine Dioxide (ClO_2) in the Radiolysis of Perchlorates and Implications for the Stability of Organics on Mars. *Astrophys. J.* **2016**, *832*, 164.
- (85) Zheng, W.; Jewitt, D.; Osamura, Y.; Kaiser, R. I. Formation of Nitrogen and Hydrogen-bearing Molecules in Solid Ammonia and Implications for Solar System and Interstellar Ices. *Astrophys. J.* **2008**, *674*, 1242–1250.
- (86) Loch, R.; Leyh, B.; Denzer, W.; Hagenow, G.; Baumgärtel, H. The Photoionization of Ammonia revisited. The Vibrational Autoionization of NH_3 and its Three Isotopomers in the 10–12 eV Photon Energy Range. *Chem. Phys.* **1991**, *155*, 407–422.
- (87) Förstel, M.; Tsegaw, Y. A.; Maksyutenko, P.; Mebel, A. M.; Sander, W.; Kaiser, R. I. On the Formation of N_3H_3 Isomers in Irradiated Ammonia Bearing Ices: Triazene (H_2NNNH) or Triimide (HNHNNH). *ChemPhysChem* **2016**, *17*, 2726–2735.
- (88) Ebata, T.; Anezaki, Y.; Fujii, M.; Mikami, N.; Ito, M. High Rydberg States of Nitric Oxide Studied by Two-color Multiphoton Spectroscopy. *J. Phys. Chem.* **1983**, *87*, 4773–4776.
- (89) Kuo, S.-C.; Zhang, Z.; Ross, S. K.; Klemm, R. B.; Johnson, R. D.; Monks, P. S.; Thorn, R. P.; Stief, L. J. Discharge Flow-Photoionization Mass Spectrometric Study of HNO: Photoionization Efficiency Spectrum and Ionization Energy and Proton Affinity of NO. *J. Phys. Chem. A* **1997**, *101*, 4035–4041.
- (90) Kohout, F. C.; Lampe, F. W. Ionization Potential of the Nitroxyl Molecule. *J. Chem. Phys.* **1966**, *45*, 1074–1075.
- (91) Coppens, P.; Smets, J.; Fishel, M. G.; Drowart, J. Mass Spectrometric Study of the Photoionization of Nitrous Oxide in the Wavelength Interval 1000–600 Å. *Int. J. Mass Spectrom. Ion Phys.* **1974**, *14*, 57–74.
- (92) Page, R. H.; Larkin, R. J.; Shen, Y. R.; Lee, Y. T. High-resolution Photoionization Spectrum of Water Molecules in a Supersonic Beam. *J. Chem. Phys.* **1988**, *88*, 2249–2263.
- (93) Foner, S. N.; Hudson, R. L. Ionization and Dissociation of Hydrogen Peroxide by Electron Impact. *J. Chem. Phys.* **1962**, *36*, 2676–2680.
- (94) Weiss, M. J.; Berkowitz, J.; Appelman, E. H. Photoionization of Ozone: Formation of O_4^+ and O_5^+ . *J. Chem. Phys.* **1977**, *66*, 2049–2053.
- (95) Dyke, J. M.; Jonathan, N. B. H.; Morris, A.; Winter, M. J. Vacuum Ultraviolet Photoelectron Spectroscopy of Transient Species. *Mol. Phys.* **1981**, *44*, 1059–1066.
- (96) Pelegrini, M.; Parreira, R. L. T.; Ferrão, L. F. A.; Caramori, G. F.; Ortolan, A. O.; da Silva, E. H.; Roberto-Neto, O.; Rocco, J. A. F. F.; Machado, F. B. C. Hydrazine Decomposition on a Small Platinum Cluster: the role of N_2H_5 Intermediate. *Theor. Chem. Acc.* **2016**, *135*, 58.
- (97) Wang, Q.; Wei, C.; Perez, L. M.; Rogers, W. J.; Hall, M. B.; Mannan, M. S. Thermal Decomposition Pathways of Hydroxylamine: Theoretical Investigation on the Initial Steps. *J. Phys. Chem. A* **2010**, *114*, 9262–9269.
- (98) Wiedmann, R. T.; Tonkyn, R. G.; White, M. G.; Wang, K.; McKoy, V. Rotationally Resolved Threshold Photoelectron Spectra of OH and OD. *J. Chem. Phys.* **1992**, *97*, 768–772.
- (99) Gibson, S. T.; Greene, J. P.; Berkowitz, J. Photoionization of the Amidogen Radical. *J. Chem. Phys.* **1985**, *83*, 4319–4328.
- (100) Trickl, T.; Cromwell, E. F.; Lee, Y. T.; Kung, A. H. State-Selective Ionization of Nitrogen in the $X_2\Sigma^+g v_+=0$ and $v_+=1$ States by Two-color (1+1) Photon Excitation Near Threshold. *J. Chem. Phys.* **1989**, *91*, 6006–6012.
- (101) Tonkyn, R. G.; Winniczek, J. W.; White, M. G. Rotationally Resolved Photoionization of O_2^+ Near Threshold. *Chem. Phys. Lett.* **1989**, *164*, 137–142.
- (102) Clemmer, D. E.; Armentrout, P. B. Direct Determination of the Adiabatic Ionization Energy of NO_2 as Measured by Guided Ion-Beam Mass Spectrometry. *J. Chem. Phys.* **1992**, *97*, 2451–2458.
- (103) Joshipura, K. N.; Gangopadhyay, S.; Vaishnav, B. G. Electron Scattering and Ionization of NO, N_2O , NO_2 , NO_3 and N_2O_5 Molecules: Theoretical Cross Sections. *J. Phys. B: At., Mol. Opt. Phys.* **2007**, *40*, 199–210.
- (104) Frost, D. C.; McDowell, C. A.; Westwood, N. P. C. The Photoelectron Spectrum of Dinitrogen Tetroxide. *J. Electron Spectrosc. Relat. Phenom.* **1977**, *10*, 293–303.
- (105) Fagerström, K.; Jodkowski, J. T.; Lund, A.; Ratajczak, E. Kinetics of the Self-reaction and the Reaction with OH of the Amidogen Radical. *Chem. Phys. Lett.* **1995**, *236*, 103–110.
- (106) Cheung, A. C.; Rank, D. M.; Townes, C. H.; Thornton, D. D.; Welch, W. J. Detection of NH_3 Molecules in the Interstellar Medium by Their Microwave Emission. *Phys. Rev. Lett.* **1968**, *21*, 1701–1705.
- (107) Goldsmith, P. F.; Liseau, R.; Bell, T. A.; Black, J. H.; Chen, J.-H.; Hollenbach, D.; Kaufman, M. J.; Li, D.; Lis, D. C.; Melnick, G.; et al. Herschel Measurements of Molecular Oxygen in Orion. *Astrophys. J.* **2011**, *737*, 96.
- (108) Pagani, L.; Olofsson, A. O. H.; Bergman, P.; Bernath, P.; Black, J. H.; Booth, R. S.; Buat, V.; Crovisier, J.; Curry, C. L.; Encrenaz, P. J.; et al. Low Upper Limits on the O_2 Abundance from the Odin Satellite. *Astron. Astrophys.* **2003**, *402*, L77–L81.
- (109) Bieler, A.; Altwegg, K.; Balsiger, H.; Bar-Nun, A.; Berthelier, J.-J.; Bochsler, P.; Briois, C.; Calmonte, U.; Combi, M.; De Keyser, J.; et al. Abundant Molecular Oxygen in the Coma of Comet 67P/Churyumov-Gerasimenko. *Nature* **2015**, *526*, 678–681.
- (110) Rubin, M.; Altwegg, K.; van Dishoeck, E. F.; Schwehm, G. Molecular Oxygen in Oort Cloud Comet 1P/Halley. *Astrophys. J.* **2015**, *815*, L11.
- (111) Ulich, B. L.; Hollis, J. M.; Snyder, L. E. Radio Detection of Nitroxyl (HNO): The First Interstellar NO Bond. *Astrophys. J.* **1977**, *217*, L105–L108.
- (112) Bennett, C. J.; Kaiser, R. I. The Formation of Acetic Acid (CH_3COOH) in Interstellar Ice Analogs. *Astrophys. J.* **2007**, *660*, 1289.