This file includes:

Materials and Methods
SupplementaryText
Tables S1 to S2

Materials and Methods

Experimental Approach: Layers of 500 ± 50 nm of amorphous NH_3 (Matheson; 99.999 %) and D3-ammonia (Isotopes Inc; 99+ % D) were deposited in separate experiments on a silver substrate interfaced to a cold finger at a temperature of 5.5 ± 0.2 K in a vacuum chamber with a base pressure of a few 10^{-11} torr via gas phase deposition using a glass capillary array [1]. The deposition time was 3 min at a pressure of (4 ± 2) × 10^{-8} torr. The ice thicknesses were determined using in situ helium-neon (He-Ne) laser interferometry [2] with a laser wavelength λ of 632.8 nm and a refractive index *n* of the ammonia ice at 5.5 K of 1.35 ± 0.05 [3] via equation (1), where d is the ice thickness and Θ is the angle of incidence of the laser with respect to the surface normal (4°).

$$(1) \qquad d = \frac{N_f \lambda}{2\sqrt{n^2 - \sin^2\theta}}$$

Each sample was then irradiated for 60 min with 5 keV electrons at a current of 15 ± 2 nA by scanning the electron beam over the target surface of 1.0 ± 0.1 cm^2 at an angle of 70° with respect to the surface normal of the substrate. The average deposited dose *D* per ammonia molecule can be calculated using equation (2), where I, t, m, e, N_A, ρ and A and E_{init} are the irradiation current, irradiation time, molecular mass of the molecule, the electron charge, Avogadro's constant, the density of the ice, the irradiated area of the ice, and the initial kinetic energy of the electrons, respectively.

$$(2) \qquad D = \frac{I\ t\ m}{e\ N_A\ \rho\ A\ l}(E_{init} - f_{trans}E_{trans} - f_{bs}E_{bs}),$$

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 which are backscattered, the average kinetic energy of the backscattered electrons, the average kinetic energy of the transmitted electrons, and the average penetration depth of the electrons. These values are determined exploiting the Monte-Carlo simulation program CASINO [4] averaging over 20,000 trajectories. The deposited energy per ammonia molecule in this experiments is determined to be 1.9 ± 0.2 eV with the simulation parameters summarized in Table S1. After the irradiation, the ice was kept at 5.5 K for one hour. During the irradiation and the equilibration phase, infrared spectra (FTIR, Nicolet6700) were recorded from 6000 to 500 cm^{-1} with a resolution of 4 cm^{-1}. The substrate was then warmed up with a constant rate of 0.5 $Kmin^{-1}$ to 300 K. Molecules subliming into the gas phase were photo ionized at 10.49 eV and detected using a reflectron time-of-flight mass spectrometer (ReTOF)[1]. Vacuum ultraviolet (VUV) light at 10.49 eV was produced by non-resonant four wave mixing of

the third harmonic of a Nd:YAG laser at 30 Hz resulting in a pulse width of 10 ± 4 ns and (4 ± 2) × 10^{12} photons cm^{-2} s^{-1}. The VUV beam had a diameter of 1.0 ± 0.1 mm and was directed over the substrate parallel to its surface at a distance of 2.0 ± 0.1 mm. Molecules which were ionized above the substrate were accelerated into the ReTOF and detected using microchannel plates.

The infrared spectra are in line with an earlier study[5] and show mainly a decrease in the ammonia bands and an emerging signal of the hydrazine molecule (N_2H_4) at 900, 1151 and 3185 cm^{-1}. This earlier study also exploited a residual gas analyzer (quadrupole mass spectrometer; QMS) with electron impact (EI) ionization (100 eV). The dominant products subliming into the gas phase were identified to be molecular hydrogen (H_2), molecular nitrogen (N_2), at least one isomer of diimide/trans diazene (N_2H_2), and hydrazine (N_2H_4). A comparison between the earlier QMS-EI [6] setup and the present Re-TOF-PI [7] study suggests that the Re-TOF coupled with VUV photo ionization at 10.49 eV not only significantly reduces the background counts, but also increases the signal-to-noise of the experiments essentially improving the sensitivity of the detection scheme by a factor of at least 30. The triazane molecule (N_3H_5) as detected via Re-TOF is formed at levels of about 10 % of hydrazine (N_2H_4). At these levels, triazane could not have been observed in the earlier experiment exploiting QMS-EI, where hydrazine (N_2H_4) was barely above the detection threshold of the system. Similarly, accounting for the computed infrared absorption coefficient of the most intense fundamental of triazane at 1007 cm^{-1} suggests that triazane is below the detection levels via infrared spectroscopy.

We would like to comment briefly on potential reaction pathways to form triazane (N_3H_5). Due to the lack of intensity in the infrared spectrum, no temporal profiles and hence no kinetic information on synthetic pathways to triazane can be obtained. Therefore, the following considerations shall be taken as *feasible* reaction pathways. Upon interaction of ionizing radiation with the energetic electrons, ammonia was found to fragment via a predominant atomic hydrogen channel and to a lesser extent via molecular hydrogen loss (reactions (1) - (2)) [8]

$$(1)\ NH_3 \rightarrow NH_2 + H$$
$$(2)\ NH_3 \rightarrow NH + H_2$$

Hydrazine (N_2H_4), which in turn is formed via radical-radical recombination of two amidogen radicals (NH_2) (reaction (3)) or via insertion of nitrene (NH) into the nitrogen – hydrogen bond of ammonia (NH_3) [5], can react with nitrene (NH) yielding triazane (N_3H_5) (reaction (5)). Alternatively, hydrazine (N_2H_4) can be radiolyzed to the hydrazinyl radical (N_2H_3), which in turn undergoes radical-radical recombination with the amidogen radical (NH_2) (reactions ((6) and (7)) yielding triazane.

$$(3)\ NH_2 + NH_2 \rightarrow N_2H_4$$
$$(4)\ NH + NH_3 \rightarrow N_2H_4$$
$$(5)\ NH + N_2H_4 \rightarrow N_3H_5$$
$$(6)\ N_2H_4 \rightarrow N_2H_3 + H$$
$$(7)\ N_2H_3 + NH_2 \rightarrow N_3H_5$$

Theoretical Methods: The triazane decomposition channels are investigated by *ab initio* electronic structure calculations. The optimized geometries and harmonic frequencies of reactant (and its cation), intermediate, transition states, and products are predicted by the hybrid density functional B3LYP [9] level of theory with the cc-pVTZ basis set. The energies of these species were refined employing the CCSD(T)/cc-pVTZ with B3LYP/cc-pVTZ zero-point energy corrections.[10] The GAUSSIAN09 program [11] was utilized in the electronic structure calculations. The energy computation is expected to have accuracy of 10 kJ mol^{-1}. The adiabatic ionization energy was then calculated by taking the energy difference between the ionic and the lowest lying neutral state (I) calculated by CCSD(T)/cc-pVTZ with B3LYP/cc-pVTZ zero-point energy correction. Previous computations at this level compared with experimentally derived ionization energies suggests that the ionization energies derived from the CCSD(T)/cc-pVTZ with B3LYP/cc-pVTZ zero-point energy correction method are accurate within ± 0.2 eV[12].

Table S1. Data applied to calculate the irradiation dose per molecule. * marks values from CASINO simulations.

initial kinetic energy of the electrons, E_{init}	5 keV
irradiation current, I	15 ± 2 nA
total number of electrons	$(3.4 \pm 0.3) \times 10^{14}$
average kinetic energy of backscattered electrons, E_{bs}^*	3.2 ± 0.9 keV
fraction of backscattered electrons, f_{bs}^*	0.3 ± 0.1
average kinetic energy of transmitted electrons, E_{trans}^*,	1.0 ± 0.5 keV
fraction of transmitted electrons, f_{trans}^*	0.16 ± 0.05
average penetration depth, l^*	350 ± 80 nm
density of the ice, ρ	0.66 ± 0.05 g cm^{-3}
irradiated area, A	1.0 ± 0.1 cm^2
total number of molecules processed	$(8 \pm 2) \times 10^{17}$
dose per molecule, D	1.9 ± 0.2 eV

Table S2. Energies of the reactants, intermediates, products, and transition states.

	B3LYP/ cc-pVTZ[a]	E_{zpc} [b]	CCSD(T)/ cc-pVTZ	IP(eV)[c]	IP(eV)[d]
$NH_2NHNH_2(^1A)$	-167.192258	0.070471	-166.940565	0.00	0.00
$NH_2NHNH_2^+(^2A')$	-166.915139	0.069796	-166.656608	7.54	7.71
	B3LYP/ cc-pVTZ[a]	E_{zpc} [b]	CCSD(T)/ cc-pVTZ	E(kJ/mol) [e]	E(kJ/mol) [f]
$NH_2NHNH_2(X^1A')$	-167.192258	0.070471	-166.940565	0	0
$NH_2NHNH_2^+(X^2A')$	-166.915139	0.069796	-166.656608	728	744
$NH_2NHNH_2'(X^1A)$	-167.190756	0.070288	-166.938882	4	4
$NH_2NHNH_2''(X^1A)$	-167.184014	0.069754	-166.931014	22	23
$INT(X^1A)$	-167.132931	0.069478	-166.877622	152	159
$N_2H_4(X^1A)$	-111.862641	0.053219	-111.698545		
$NH_3(X^1A_1)$	-56.550474	0.034252	-56.473157		
trans $HNNH(X^1A_g)$	-110.657077	0.028316	-110.477660		
cis $HNNH(X^1A_1)$	-110.649782	0.027625	-110.469421		
$H_2NN(X^1A_1)$	-110.624527	0.026519	-110.436759		
TS3	-167.103201	0.062952	-166.844662	234	232
TS4	-167.129837	0.062446	-166.863852	164	180
TS1	-167.093493	0.064313	-166.834452	259	258
TS2	-167.123036	0.064377	-166.861913	182	191
$^1NH + N_2H_4$	-167.016683	0.060720	-166.768164	461	428
$^3NH + N_2H_4$	-167.098047	0.060623	-166.839231	247	240
$NH_2 + NHNH_2$	-167.122421	0.058366	-166.851544	183	202
NH_3 + trans HNNH	-167.207551	0.062568	-166.950817	-40	-48
NH_3 + cis HNNH	-167.200256	0.061877	-166.942578	-21	-28
$NH_3 + NNH_2$	-167.175001	0.060771	-166.909916	45	55

[a] B3LYP/cc-pVTZ energy with zero-point energy correction in hartree.
[b] zero-point energy by B3LYP/cc-pVTZ in hartree.
[c] ionization potential by B3LYP/cc-pVTZ with zero-point energy correction.
[d] ionization potential by CCSD(T)/cc-pVTZ with B3LYP/cc-pVTZ zero-point energy correction.
[e] relative energy by B3LYP/cc-pVTZ with zero-point energy correction.
[f] relative energy by CCSD(T)/cc-pVTZ with B3LYP/cc-pVTZ zero-point energy correction.

[1] B. M. Jones, R. I. Kaiser, *JPhChL* **2013**, *4*, 1965-1971.
[2] a) O. S. Heavens, *Optical Properties of Thin Solid Films*, Butterworhts Scientific Publications, London, **1955**; b) M. S. Westley, G. A. Baratta, R. A. Baragiola, *JChPh* **1998**, *108*, 3321-3326.
[3] M. Á. Satorre, J. Leliwa-Kopystynski, C. Santonja, R. Luna, *Icar* **2013**, *225*, 703-708.
[4] D. Drouin, A. R. Couture, D. Joly, X. Tastet, V. Aimez, R. Gauvin, *Scanning* **2007**, *29*, 92-101.
[5] W. Zheng, D. Jewitt, Y. Osamura, R. I. Kaiser, *ApJ* **2008**, *674*, 1242-1250.
[6] C. J. Bennett, C. S. Jamieson, Y. Osamura, R. I. Kaiser, *ApJ* **2005**, *624*, 1097-1115.
[7] R. I. Kaiser, S. Maity, B. M. Jones, *PCCP* **2014**, *16*, 3399-3424.
[8] C. J. Bennett, B. Jones, J. E. Knox, J. Perry, Y. S. Kim, R. I. Kaiser, *ApJ* **2010**, *723*, 641-648.
[9] a) A. D. Becke, *JChPh* **1993**, *98*, 5648-5652; b) A. D. Becke, *JChPh* **1992**, *96*, 2155-2160; c) A. D. Becke, *JChPh* **1992**, *97*, 9173-9177; d) C. Lee, W. Yang, R. G. Parr, *Physical Review B* **1988**, *37*, 785-789.
[10] a) G. D. Purvis, R. J. Bartlett, *JChPh* **1982**, *76*, 1910-1918; b) C. Hampel, K. A. Peterson, H.-J. Werner, *Chemical Physics Letters* **1992**, *190*, 1-12; c) P. J. Knowles, C. Hampel, H. J. Werner, *JChPh* **1993**, *99*, 5219-5227; d) M. J. O. Deegan, P. J. Knowles, *Chemical Physics Letters* **1994**, *227*, 321-326.
[11] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, N. J. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian, Inc., Wallingford, CT, USA, **2009**.
[12] a) O. Kostko, J. Zhou, B. J. Sun, J. S. Lie, A. H. Chang, R. I. Kaiser, M. Ahmed, *ApJ* **2010**, *717*, 674; b) I. K. Ralf, P. K. Sergey, M. M. Alexander, K. Oleg, A. Musahid, *ApJ* **2012**, *761*, 178.