

Detection of the Elusive Triazane Molecule (N_3H_5) in the Gas Phase

Marko Förstel,^[a] Pavlo Maksyutenko,^[a] Brant M. Jones,^[a] Bing-Jian Sun,^[b] Shih-Hua Chen,^[b] Agnes. H.-H. Chang,^{*[b]} and Ralf I. Kaiser^{*[a]}

We report the detection of triazane (N_3H_5) in the gas phase. Triazane is a higher order nitrogen hydride of ammonia (NH_3) and hydrazine (N_2H_4) of fundamental importance for the understanding of the stability of single-bonded chains of nitrogen atoms and a potential key intermediate in hydrogen–nitrogen chemistry. The experimental results along with electronic-structure calculations reveal that triazane presents a stable molecule with a nitrogen–nitrogen bond length that is a few picometers shorter than that of hydrazine and has a lifetime exceeding $6 \pm 2 \mu s$ at a sublimation temperature of 170 K. Triazane was synthesized through irradiation of ammonia ice with energetic electrons and was detected in the gas phase upon sublimation of the ice through soft vacuum ultraviolet (VUV) photoionization coupled with a reflectron-time-of-flight mass spectrometer. Isotopic substitution experiments exploiting $[D_3]$ -ammonia ice confirmed the identification through the detection of its fully deuterated counterpart $[D_5]$ -triazane (N_3D_5).

The triazane molecule (N_3H_5) has been long postulated to be a key transient species in nitrogen–hydrogen chemistry and has received considerable interest from the viewpoint of chemical bonding theory and as a promising high-energy material.^[1] Unlike carbon chemistry, the nitrogen–nitrogen single bond is destabilized by the nonbonding electron pairs of the neighboring nitrogen atoms, resulting in significantly weaker nitrogen–nitrogen single bonds (157 – 168 kJ mol^{-1}) compared to their carbon–carbon counterparts (345 – 355 kJ mol^{-1}). Consequently, single-bonded hydrides of nitrogen are extremely rare and only the methane (CH_4) and ethane (C_2H_6) analogues of nitrogen—ammonia (NH_3) and hydrazine (N_2H_4)—have been isolated to date. The next higher homologue, triazane, was reported crystallographically in a zeolite, where it was stabilized by complexation to silver ions as $Ag_2(N_3H_5)_3^{2+}$.^[2] Attempts to isolate triazane from triazanium sulfite salts, $(N_3H_6)_2SO_3$, were unsuccessful

and only potential decomposition products of triazane (N_3H_5)—diazane ($HNNH$) and ammonia (NH_3)—could be sampled.^[1c] Finally, Fuji et al.^[1d] made an effort to detect free triazane in the microwave discharge of hydrazine, but only the lithium salt of triazane ($LiN_3H_5^+$) and the triazane cation ($N_3H_5^+$) could be identified. Therefore, whether free triazane (N_3H_5) can survive prompt dissociation in the gas phase has remained an unanswered question. This lack of experimental evidence on the stability of triazane has triggered substantial computational efforts.^[1a,b] An evaluation of the thermodynamic stability, accounting for hydrogen bonding as well as hyperconjugation effects, reveals three triazane conformers with C_1 and C_s symmetries, which range in stability within 24 kJ mol^{-1} .^[1a,b] Accounting for potential decomposition pathways, such as ammonia and diazene elimination, Schlegel and Skancke^[1b] concluded that “there appears to be no low energy channels for the unimolecular decomposition of triazane” and that triazane represents a “promising candidate(s) for synthesis.”

Here, we report the experimental detection of the hitherto elusive triazane molecule (N_3H_5) in the gas phase. Our experiments are combined with ab initio electronic-structure calculations to verify the stability of triazane in the gas phase. The experiments were carried out in an ultrahigh vacuum (UHV) surface science machine operated at a pressure of a 3×10^{-11} torr.^[3] Amorphous ices of ammonia (NH_3) and $[D_3]$ -ammonia (ND_3) were prepared in separate experiments with thicknesses of $500 \pm 50 \text{ nm}$ at $5.5 \pm 0.2 \text{ K}$. Nonequilibrium chemistry was induced by irradiating these ices with energetic electrons (5 keV) for one hour at an averaged dose of $1.9 \pm 0.2 \text{ eV}$ per molecule. After irradiation, the ices were heated at a rate of 0.5 K min^{-1} (temperature-programmed desorption; TPD). During the TPD process, the subliming neutral molecules were first ionized through single vacuum ultraviolet (VUV) photon ionization at 10.49 eV , then mass resolved in a reflectron time-of-flight mass spectrometer (Re-TOF), and eventually identified by their arrival times through a multichannel plate (see the Supporting Information).

The mass spectra of the subliming molecules released from the irradiated ammonia ices are shown as a function of temperature in Figure 1. These spectra are dominated by the ammonia and $[D_3]$ -ammonia parent ions at $m/z = 17$ [NH_3^+ ; ionization energy (I_E) = $10.07 \pm 0.02 \text{ eV}$] in the irradiated ammonia ices shifted by 3 to $m/z = 20$ (ND_3^+) in the exposed $[D_3]$ -ammonia samples (Figure 2). As the temperature rises, hydrazine (N_2H_4) together with its deuterated counterpart (N_2D_4) are observable through their parent ions at $m/z = 32$ and 36 ($I_E =$

[a] Dr. M. Förstel, Dr. P. Maksyutenko, Dr. B. M. Jones, Prof. Dr. R. I. Kaiser
Department of Chemistry
University of Hawaii
2545 McCarthy Mall
Honolulu, HI 96822-2275 (USA)
E-mail: ralfk@hawaii.edu

[b] Dr. B.-J. Sun, Dr. S.-H. Chen, Prof. Dr. A. H.-H. Chang
Department of Chemistry
National Dong Hwa University
Shou-Feng, Hualien, 974 (Taiwan)
E-mail: hhchang@mail.ndhu.edu.tw

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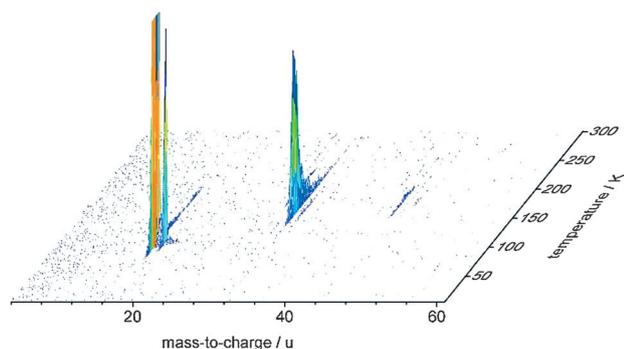


Figure 1. Reflectron time-of-flight (ReTOF) mass spectra as a function of the temperature of the newly formed products subliming into the gas phase from the irradiated ammonia ice measured at 10.49 eV. The signal of the most abundant species at 17 (ammonia) was truncated to allow for a better representation of the data.

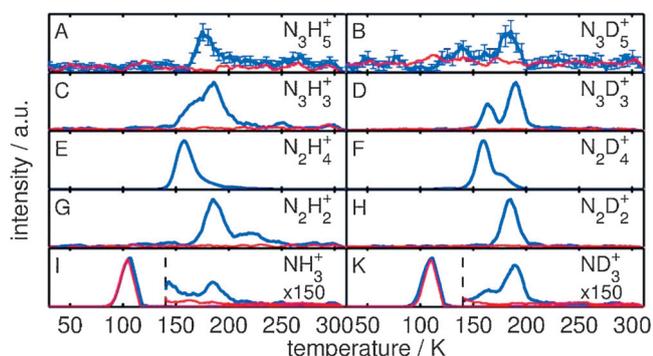


Figure 2. Temperature desorption profiles of key species subliming from the irradiated ammonia (left) and [D₃]-ammonia ices (right). Statistical error bars are included in Panels (A) and (B) for the newly identified triazane molecule. Traces in blue show the signal from the irradiated sample and traces in red are those measured for the nonirradiated sample.

8.10 ± 0.15 eV), respectively, as they are released into the gas phase with ion counts peaking at 160 K. With increasing temperature, we also observed signal at $m/z=30$ ($N_2H_2^+$), 45 ($N_3H_3^+$), and 47 ($N_3H_5^+$) along with their deuterated counterparts at $m/z=32$ ($N_2D_2^+$), 48 ($N_3D_3^+$), and 52 ($N_3D_5^+$) peaking at about 170 K. Signals at $m/z=30$ and 45 originate from ionized N_2H_2 ($IE=9.8 \pm 0.1$ eV) and N_3H_3 ($IE=9.6 \pm 0.1$ eV), respectively. No masses higher than 47 and 52 were observed for the irradiated ammonia and [D₃]-ammonia ices, respectively. It is important to stress that ion signals depicting identical TPD profiles indicate that fragmentation of the molecules with the highest mass may occur. Here, signals at $m/z=17$ (NH_3^+), 30 ($N_2H_2^+$), and 45 ($N_3H_3^+$), the TPD profiles of which peak at about 170 K, match the TPD profile of $m/z=47$ ($N_3H_5^+$), thus indicating that the lower masses are fragments from a molecule that contains nitrogen and hydrogen atoms with a molecular weight of 47, that is, triazane (N_3H_5). In case of [D₃]-ammonia ices, the fragment masses are shifted to $m/z=20$ (ND_3^+), 32 ($N_2D_2^+$), and 48 ($N_3D_3^+$), which, in turn, are fragments from [D₃]-triazane (N_3D_5) upon photoionization. Note that $m/z=47$ ($N_3H_5^+$) and 52 ($N_3D_5^+$) cannot originate from higher masses, as N_3H_5/N_3D_5 resembles the heaviest allowable fully hydrogen-

ated, closed-shell nitrogen hydride. The molecular ions at $m/z=47$ ($N_3H_5^+$) and 52 ($N_3D_5^+$) are stable in the ReTOF depicting—based on the time-of-flight—life times of at least 30 ± 1 μ s; the stability of the molecular ion is consistent with the study of Fuji et al. that identified the triazane cation in the microwave discharge of hydrazine. Finally, we would like to outline that the second ion peak and the shoulder of the TPD at $m/z=48$ ($N_3D_3^+$) and 45 ($N_3H_3^+$), respectively, emerging at about 160 K might originate from N_3D_3/N_3H_3 isomers triazene (H_2NNNH) and/or cyclotriazane ($c-N_3H_3$) together with their deuterated counterparts.

It is important to stress that we also conducted control experiments, that is, experiments under identical conditions, but without irradiating the ices with energetic electrons. In these control studies, only ion signals derived from ammonia and [D₃]-ammonia were observable. This demonstrates that the abovementioned products and the triazane molecule in particular are a result of the radiolysis of the ammonia ices, and not an artifact from the photolysis and/or ion–molecule reactions of the subliming ammonia. Therefore, our data provide compelling evidence that a molecule with the molecular formulae N_3H_5 (ammonia ice) and N_3D_5 ([D₃]-ammonia ice) have been formed in the ices upon exposure to energetic electrons; these species were released into the gas phase upon sublimation and then ionized by single-photon ionization. The calculated adiabatic IE of triazane was computed to be 7.7 ± 0.1 eV, which is well below the energy of the vacuum ultraviolet photon of 10.49 eV exploited to ionize the subliming molecules (see the Supporting Information). Considering the root-mean-square velocity of 310 ms^{-1} of a triazane molecule subliming at 170 K and the distance between the ice and the photoionization laser of 2 mm, we determined a lifetime of the subliming triazane and [D₃]-triazane molecules of at least 6 ± 2 and 7 ± 2 μ s, respectively, and possibly much longer.

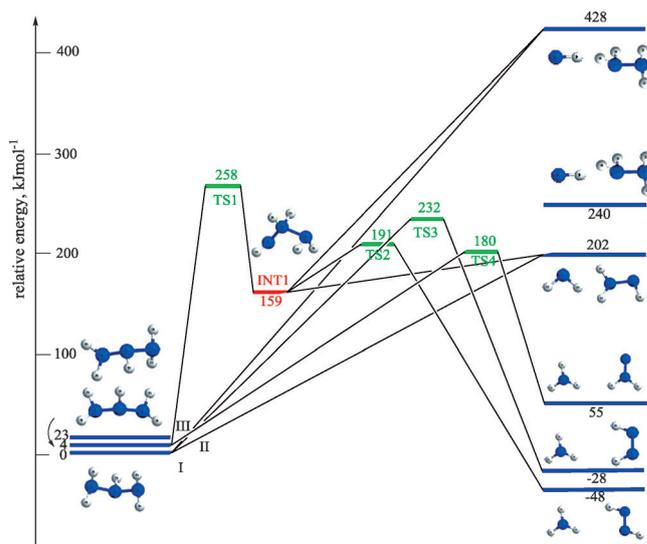


Figure 3. Structures of three conformers of triazane, I–III, together with their computed decomposition pathways of triazane. All energies are given in $kJ\ mol^{-1}$. The molecular structures of the reactants, intermediates, products, and transition states are shown in Figure 4.

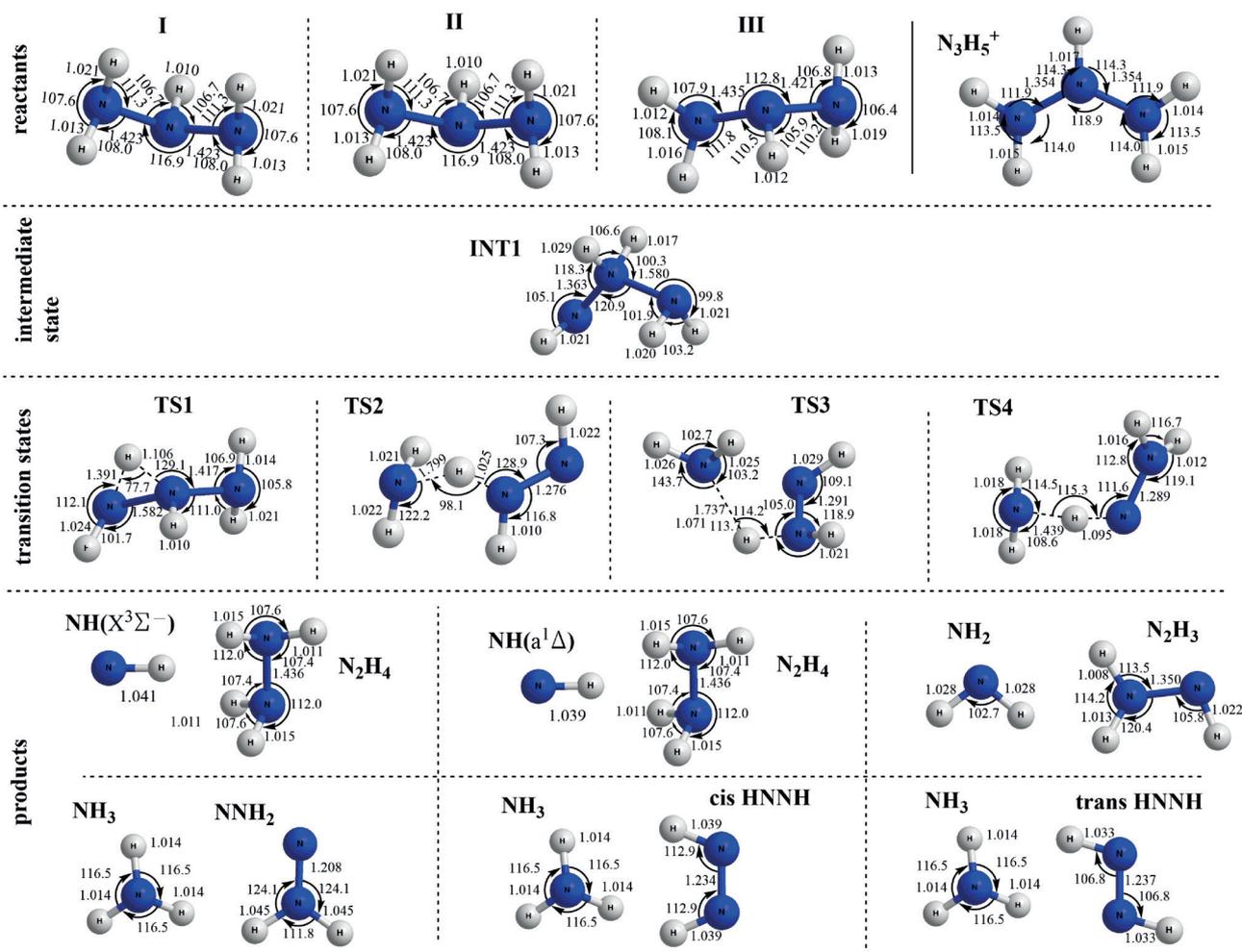


Figure 4. Structures of reactant conformers (I–III), the intermediate (INT1), products, and transition states (TS1–TS4); bond lengths and angles are defined in pm and degrees, respectively. Also shown is the structure of the triazane ion. Calculation details and the corresponding energies are given in Table S2 in the Supporting Information.

Having provided experimental evidence on the formation, identification, and stability of the previously elusive gas-phase triazane (N_3H_5) molecule together with its deuterated counterpart, we turned our attention to the underlying N_3H_5 potential energy surface so that we could merge the experimental findings with theory (see the Supporting Information). Our computations identified three triazane Conformers I (0 kJ mol^{-1}), II (4 kJ mol^{-1}), and III (23 kJ mol^{-1}) with the relative energetics given in parentheses (Figures 3 and 4). This stability sequence agrees well with previous computations,^[1a,b] and predict Conformer II to be 3–4 kJ mol^{-1} higher in energy than Conformer I; with Conformer III determined to present the highest energy structure ranging from 21 to 22 kJ mol^{-1} above Conformer I. The computed bond lengths and bond angles agree, within the error limits, with the ones found crystallographically.^[2] Furthermore, our computations identified six potential decomposition pathways of the triazane molecule (N_3H_5) in the gas phase. First, triazane (N_3H_5) can undergo unimolecular decomposition through elimination of electronically excited nitrene, $\text{NH}(^3\Sigma^-)$; the reversed reaction resembles an insertion of nitrene into a nitrogen–hydrogen bond of hydrazine (N_2H_4); the

decomposition pathway is endoergic by 428 kJ mol^{-1} . Note that nitrene has a $^3\Sigma^-$ electronic ground state, which lies 188 kJ mol^{-1} below the excited singlet state. Even if intersystem crossing occurs, the overall reaction, which yields ground-state nitrene plus hydrazine, is still endoergic by 240 kJ mol^{-1} . The computed singlet–triplet splitting of 188 kJ mol^{-1} agrees well within 12 kJ mol^{-1} with the experimentally determined value of 176 kJ mol^{-1} .^[14] Second, the triazane II conformer (N_3H_5) can isomerize through a transition state located 258 kJ mol^{-1} above the reactant through a [1,2]-hydrogen shift to INT1 (Figure 4); the latter represents a highly unstable intermediate that is 159 kJ mol^{-1} less favorable than the triazane isomer and fragments into singlet nitrene plus hydrazine (N_2H_4) in an overall endoergic reaction ($+428 \text{ kJ mol}^{-1}$). Third, triazane (N_3H_5) was predicted to undergo unimolecular decomposition forming ammonia (NH_3) plus *cis*-diazene (HNNH) in an overall exoergic reaction (-28 kJ mol^{-1}) after passing a transition state located 232 kJ mol^{-1} above triazane. Fourth, INT1 was predicted to decompose through ammonia (NH_3) loss to form *trans*-diazene (HNNH) in an overall exoergic reaction (-48 kJ mol^{-1}). Fifth, triazane (N_3H_5) was found to eliminate ammonia (NH_3) along

with diimide (H_2NN) in an overall endoergic reaction ($+55 \text{ kJ mol}^{-1}$). Finally, a unimolecular decomposition of triazane through a simple nitrogen–nitrogen bond rupture process leads to the amino radical (NH_2) together with the hydrazinyl radical (N_2H_3) with the overall reaction being endoergic by 202 kJ mol^{-1} . Based on the overall reaction energies and the location of the transition states involved, our electronic-structure calculations predict that although triazane is thermodynamically less stable compared to ammonia (NH_3) plus *cis*-/*trans*-diazene (HNNH), triazane is kinetically stable, as the associated transition state located 258 (*trans*-diazene) and 232 kJ mol^{-1} (*cis*-diazene) above triazane cannot be overcome under our experimental conditions. Considering a temperature of the subliming triazane molecules of 170 K holding a Maxwell–Boltzmann distribution, less than 1 part per billion of triazane is expected to decompose. Consequently, our electronic-structure calculations confirm that gas-phase triazane (N_3H_5) is stable under our experimental conditions.

In conclusion, our combined experimental and computational study, exploiting soft vacuum ultraviolet (VUV) photoionization coupled with a reflectron-time-of-flight mass spectroscopy, provides convincing evidence of gas-phase triazane (N_3H_5) together with its deuterated counterpart (N_3D_5). Triazane is a higher order nitrogen hydride of ammonia (NH_3) and hydrazine (N_2H_4) of fundamental importance for the understanding of the stability of single-bonded chains of nitrogen atoms and a potential key intermediate in hydrogen–nitrogen chemistry. With a nitrogen–nitrogen bond length that is slightly shorter (by a few picometers) than that in hydrazine, free triazane presents an astonishingly stable molecule with a lifetime exceeding $6 \pm 2 \mu\text{s}$ at 170 K. Although triazane was predicted computationally to be thermodynamically unstable with respect to unimolecular decomposition to ammonia (NH_3) and *cis*-/*trans*-diazene (HNNH), the energetically unfavorable transition state cannot be overcome, thus making triazane kinetically stable toward fragmentation. The identification of triazane

from electron-irradiated ammonia ices might, in future experimental studies, even lead to the synthesis of more-complex nitrogen–hydrogen compounds; for example, isoalent molecules of the well-known higher order phosphanes, which have been identified up to octaphosphane (P_8H_{10}),^[5] thus eventually transferring Langmuir's concept of isovalency to main group V hydrides nearly a century after its foundation.^[6]

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