

Supplementary Information for

Detection of the elusive *cyclo*-1,2-dihydrotetrazete (N_4H_2) in the gas phase

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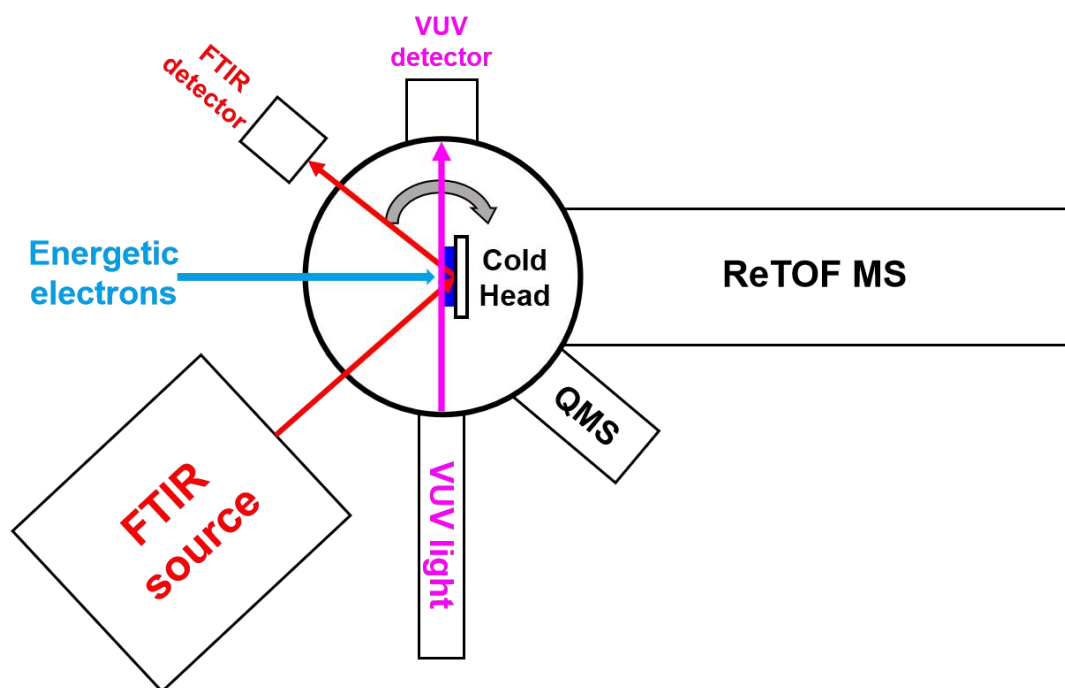
Experimental details

The experimental setup consists of a contamination-free stainless steel ultra-high vacuum chamber (UHV) evacuated to a base pressure of a few 10^{-11} Torr by magnetically levitated turbo molecular pumps coupled to oil-free scroll backing pumps. Within the chamber, a silver mirror substrate is interfaced to a cold finger, which is connected to a closed cycle helium compressor (Sumitomo Heavy Industries, SRDK-415E2). The temperature of the silver wafer was monitored by a silicon diode sensor (Lakeshore DT-670B-CO) and regulated in a range of 5 to 320 K with a precision of ± 0.1 K by a programmable temperature controller (Lakeshore 336). After the wafer reached 5.2 ± 0.1 K, ammonia (NH_3 , Air Liquide) (Supplementary Table 1) was deposited onto it via one glass capillary arrays to form an ice. The overall thickness of the ice was determined using laser interferometry¹ with a helium-neon laser (ThorLabs; HNLS008L-EC) operating at 632.8 nm. The laser light was reflected at an angle of 2.75° relative to the ice surface normal. Considering the refractive indexes of pure ices $n_{\text{NH}_3} = 1.38^2$, the ice thickness was calculated to be 1100 ± 60 nm.

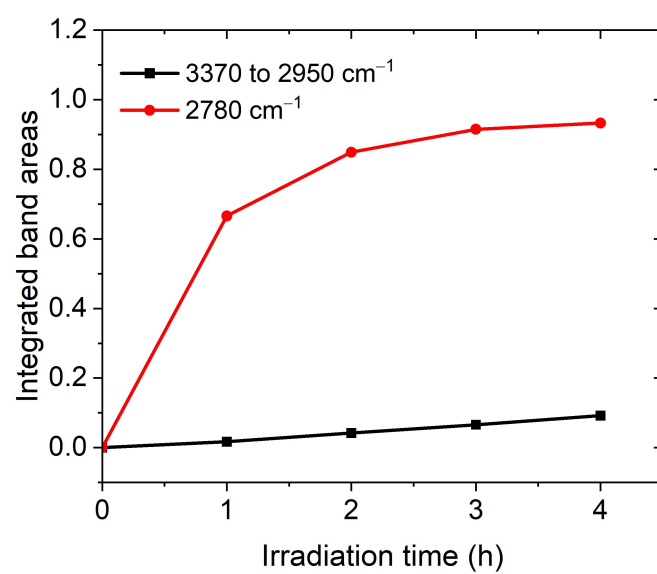
Mid-infrared (4000 to 600 cm^{-1}) spectra of the ices were recorded utilizing a Bruker Vertex 70 Fourier transform infrared (FTIR) spectrometer with 1 cm^{-1} spectral resolution. The FTIR spectra of the pristine ice is shown in Figure 3³. The ices were then irradiated at 5.2 ± 0.1 K with 120 nA electrons (ELG-2 electron source) perpendicular to the ice surface normal for 4 hours at currents of 0 nA (blank) and 120 nA (Supplementary Table 1). During the irradiation, in situ mid-infrared spectra of the ices were recorded every 2 minutes.

After the irradiation, the ices were heated to 300 K at a rate of 1 K min^{-1} (temperature programmed desorption (TPD)). During the TPD phase, any subliming molecules were detected using a reflectron time-of-flight (ReTOF) mass spectrometer with single photon ionization⁴. This photoionization process utilizes four-wave-mixing to produce vacuum ultraviolet light ($\omega_{\text{vuv}} = 2\omega_1 - \omega_2$). The experiments were performed with 10.49 eV, 9.9 eV, 9.2 eV, and 8.74 eV photoionization energies to distinguish the N_4H_2 isomers. To produce ω_1 , the second harmonic (355 nm) of a Nd:YAG laser was used to pump a Coumarin 450 dye

mixture (0.2 g L^{-1} ethanol) to obtain 445.132 nm (2.78 eV) (LIOP-TEC, Liopstar-E), which underwent a frequency doubling process to achieve $\omega_1 = 222.566 \text{ nm}$ (5.57 eV) (BaB_2O_4 (BBO) crystal, 220 nm to 320 nm). Creating $\omega_2 = 508 - 1000 \text{ nm}$ (2.44 - 1.24 eV) through a Nanosecond tunable optical parametric oscillator laser (INNOLAS, SpitLight 600 OPO). The VUV light was spatially separated from other wavelengths (due to multiple resonant and non-resonant processes ($2\omega_1 + \omega_2$; $3\omega_1$; $3\omega_2$)) using a lithium fluoride (LiF) biconvex lens (ISP Optics) and directed 2 mm above the sample to ionize subliming molecules. The ionized molecules were mass analyzed with the ReTOF mass spectrometer where the arrival time to a multichannel plate is based on mass-to-charge ratios, and recorded with a personal computer multichannel scalar (FAST ComTec), which is triggered via a pulse delay generator at 30 Hz. Here the ReTOF signal is the average of 3600 sweeps of the mass spectrum in 4 ns bin widths, which corresponds to an increase of the substrate temperature of 2 K.



Supplementary Figure 1. Schematics of the experimental setup. This figure is adapted from our previously published article “An experimental and theoretical study of the photoionization properties of polysulfanes (H_2S_n , $n = 2-4$)” in *Physical Chemistry Chemical Physics*⁵.



Supplementary Figure 2. The relationship between the integrated band area of the peaks at 3370 to 2950 cm^{-1} and 2780 cm^{-1} and the irradiation time.

Supplementary Table 1. List of experiments.

#	Precursors	Irradiation dose	Photoionization Energy (eV)
1	NH ₃	120 nA 4 hours	10.49
2	NH ₃	120 nA 4 hours	9.9
3	NH ₃	120 nA 4 hours	9.2
4	NH ₃	120 nA 4 hours	8.74
5	ND ₃	120 nA 4 hours	10.49
6	NH ₃	Blank	10.49

Supplementary Table 2. Data applied to calculate the average irradiation dose per molecule.

Initial kinetic energy of the electrons, E_{init} (keV)	2
Ice	NH ₃
Thickness of ice, nm	1100 ± 60
Irradiation current, I (nA)	120 ± 10
Total number of electrons	$(1.1 \pm 0.1) \times 10^{16}$
Average penetration depth, l_{ave} (nm) ^a	110 ± 10
Average kinetic energy of backscattered electrons, E_{bs} (keV) ^a	1.0 ± 0.1
Fraction of backscattered electrons, f_{bs} ^a	0.06 ± 0.01
Average kinetic energy of transmitted electrons, E_{trans} (keV) ^a	0
Fraction of transmitted electrons, f_{trans} ^a	0
Irradiated area, A (cm ²)	1.0 ± 0.1
Dose (eV/molecule)	69 ± 6

Note.

^a Parameters obtained from CASINO software v2.42.

Supplementary Table 3. Infrared absorption peaks (cm^{-1}) before irradiation for ammonia ice.

NH ₃	ND ₃	Assignment
Pristine ice, before irradiation (5 K)		
3382	2513	ν_3
3298	2391	$2\nu_4/\nu_1$
3213	2322	ν_1
1626	1180	ν_4
1057	822	ν_2

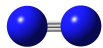
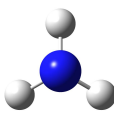
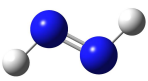
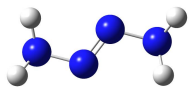
Supplementary Table 4. Observed newly formed infrared frequencies (cm^{-1}) from irradiated ammonia ices and calculated frequencies (cm^{-1} , collected from Source data) for potentially relevant N_4H_2 isomers.

Experimental results			Assignments	Possible related N_4H_2 isomers		
NH_3 ice	ND_3 ice	Isotopic shift	Functional group	Calculated N_4H_2 isomers	Calculated N_4D_2 isomers	Isotopic shift
3370 to 3090	2500 to 2290	−870 to −800	N–H stretching mode ($\nu_{\text{N-H}}$) and/or overtones of NH_2 scissoring mode	3334 to 2970 (2a to 6b)	2480 to 2013 (2a to 6b)	−854 to −957
2780	2110	−670	$\text{N}=\text{NH}_2(\nu_5)$ and/or combinations of newly formed NH_2 scissoring + twisting modes			
2090	2085	−5	asymmetric stretching mode of the $-\text{N}=\text{N}=\text{N}$ group	2087 (5a)	2062 (5a)	−25
1515	1135	−380	ν_2 of the $\cdot\text{NH}_2$ radical and/or NH_2 scissoring mode			
1153	877	−276	NH_2 twisting	1206 (5a) 1121 (5b)	868 (5a) 870 (5b)	−338 (5a) −251 (5b)

Supplementary Table 5. The species detected in the experiment.

Precursors		Precursors	
NH ₃		ND ₃	
<i>m</i> / <i>z</i>	Ion	<i>m</i> / <i>z</i>	Ion
17	NH ₃ ⁺	20	ND ₃ ⁺
30	N ₂ H ₂ ⁺	32	N ₂ D ₂ ⁺
32	N ₂ H ₄ ⁺	36	N ₂ D ₄ ⁺
45	N ₃ H ₃ ⁺	48	N ₃ D ₃ ⁺
58	N ₄ H ₂ ⁺	60	N ₄ D ₂ ⁺
60	N ₄ H ₄ ⁺	64	N ₄ D ₄ ⁺

Supplementary Table 6. Comparison of experimental to computed ionization energies (CCSD(T)/CBS//CCSD(T)/cc-pVTZ + zero-point vibrational energy (ZPVE) corrections) of nitrogen, ammonia, diimide and (E)-2-tetrazene with average deviations computed from the error limits. Combined error limits are used to obtain the corrected computed ionization energies.

Structure	Name	Experimental IE (eV)	References	Computed IE (eV)	Computed IE – Experimental IE (max) (eV)	Computed IE – Experimental IE (min) (eV)
	Nitrogen	15.581 ± 0.008	6	15.59	0.001	0.017
	Ammonia	10.070 ± 0.020	6	10.17	0.08	0.12
	Diimide	9.589 ± 0.007	7	9.59	– 0.006	0.008
	(E)-2-Tetrazene	8.15 ± 0.03	8	8.13	– 0.05	0.01
					Average 0.03 ± 0.05	Average 0.04 ± 0.05
					Error Limits – 0.02 to + 0.09	Error Limits – 0.01 to + 0.09
					Combined Error Limits – 0.02 to + 0.09	

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