

Supporting Information for

Abiotic Formation of Nitrile Precursors to Amino Acids and Nucleobases in Interstellar Ice Analogues

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Methods

Experimental. All experiments were carried out in an ultrahigh vacuum chamber maintained at base pressures of a few 10^{-11} Torr using magnetically suspended turbomolecular pumps (Osaka, TG1300MUCWB and TG420MCAB) backed by a dry scroll pump (XDS35i, BOC Edwards).¹ A closed-cycle helium cryostat (Sumitomo Heavy Industries, RDK415E) was used to cool a polished silver substrate to 5 K, which can be vertically translated and horizontally rotated via an adjustable bellows and a rotatable flange, respectively.¹ The samples consisted of hydrogen cyanide (HCN, 5% seeded in helium), ammonia (NH₃, 99.999%, Matheson), and phosphine (PH₃, 99.9995%, Sigma-Aldrich). After cooling the silver substrate to 5 K, HCN was deposited onto the substrate through a glass capillary array at a pressure of 1×10^{-7} Torr. For NH₃–HCN and PH₃–HCN ice mixtures, NH₃ or PH₃ gas was introduced independently from HCN via an additional capillary array, at partial pressures of 6×10^{-9} Torr (NH₃) and 5×10^{-9} Torr (PH₃). During deposition, the ice thickness was monitored *in situ* by laser interferometry using a helium-neon laser (632.8 nm, CVI Melles-Griot, 25-LHP-230), which measured the interference between reflections from the substrate and the ice surface.² The thicknesses of the HCN, NH₃–HCN, and PH₃–HCN ices were determined to be 540 ± 50 , 820 ± 50 , and 670 ± 80 nm, respectively, based on the refractive index of HCN ($n = 1.346$ at 18 K)³ and the average indices of NH₃–HCN ($n = 1.36 \pm 0.04$) and PH₃–HCN ($n = 1.43 \pm 0.12$) ice mixtures. Refractive indices of 1.38 ± 0.03 for NH₃ at 13 K⁴ and 1.51 ± 0.04 for PH₃ at 5.5 K² were used. Fourier transform infrared (FTIR) spectra of the ices were recorded using a Thermo Electron Nicolet 6700 spectrometer over the range of 6000–500 cm^{-1} with a spectral resolution of 4 cm^{-1} (Fig. 2, Figs. S2–S3, Tables S1–S2).

After deposition, HCN ices were irradiated with energetic electrons (5 keV; SPECS, EQ PU-22) to simulate secondary electrons generated by galactic cosmic rays (GCRs) in interstellar ices,⁵ at an incidence angle of 70° and a current of 104 nA for 60 minutes (Table S3). The irradiation doses was calculated to be 8.2 ± 1.3 eV per HCN molecule using Monte Carlo simulations with the CASINO software suite,⁶ corresponding to GCR exposure in cold molecular clouds over timescales of $(3.0 \pm 0.5) \times 10^7$ years.⁷ The average electron penetration depth in HCN ice was determined to be 345 ± 40 nm; the simulations indicate that 99% of the incident electron energy was deposited within the upper 430 ± 20 nm of the ice—well below the total ice thickness of 540 ± 50 , thereby minimizing contributions from the underlying substrate. FTIR spectra of the ices were collected *in situ* before, during, and after irradiation. Subsequently, the irradiated ices were

subjected to temperature-programmed desorption (TPD), during which the temperature was heated from 5 to 320 K at a rate of 1 K min⁻¹. After reaching 320 K, the wafer was maintained at this temperature for 90 minutes. Molecules released into the gas phase were photoionized by pulsed vacuum ultraviolet (VUV) light (30 Hz) generated through four-wave mixing in krypton/xenon gas jets. Photon energies of 11.10 eV ($2\omega_1 + \omega_2$), 10.49 eV ($3\omega_1$), 9.61–9.79 eV, 9.82–9.93 eV, 9.34 eV, and 7.60 eV ($2\omega_1 - \omega_2$) were produced using two tunable dye lasers (Cobra-Stretch, Sirah Lasertechnik) pumped by Nd:YAG lasers (Spectra-Physics Quanta Ray, PRO 270-30/250-30). In the xenon gas jet, 10.49 eV photons were generated via frequency tripling of the third harmonic (355 nm) of the Nd: YAG laser fundamental. Photons at 11.10 eV and 7.60 eV were obtained using $\omega_1 = 249.628$ nm in combination with $\omega_2 = 1064$ and 532 nm, respectively. Photons in the ranges of 9.61–9.79 eV and 9.82–9.93 eV, as well as at 9.34 eV, were produced from $\omega_1 = 212.556$ nm in krypton gas. Detailed photon generation parameters are listed in Table S4. The VUV light was separated from the laser beams (ω_1, ω_2) using a biconvex lithium fluoride lens (Korth Kristalle, $R_1 = R_2 = 131$ mm) operated in an off-axis configuration. The VUV photons were then directed 2.0 ± 0.5 mm above the substrate to photoionize the subliming molecules in the gas phase. The resulting photoionized species were extracted into a reflectron time-of-flight mass spectrometer (ReToF-MS; Jordan TOF Products) and detected with a dual microchannel plate detector. Ion signals were recorded using a multichannel scaler (FAST ComTec, MCS6A) with a temporal resolution of 3.2 ns, and each mass spectrum was accumulated over 2 minutes (3600 sweeps). The species desorbing during TPD were monitored using an electron impact quadrupole mass spectrometer (QMS; Extrel, model 5221) operated at 70 eV electron energy and an emission current of 2 mA. In addition, resonance-enhanced multiphoton ionization (REMPI) spectroscopy of nitrogen monoxide (NO, 99.95%, Sigma Aldrich) were used to verify the proper operation of the REMPI detection system; the REMPI measurements were conducted either in the gas phase via a leak valve or from NO ice at 50 K (Fig. S8).

Computational. All computations of CH₂N₂, CH₄N₂, C₂H₂N₂, and C₂H₄N₂ isomers were performed using Gaussian 16, Revision C.01.⁸ The density functional theory (DFT) B3LYP functional⁹⁻¹¹ was employed for geometry optimizations and vibrational frequencies calculations, utilizing the Dunning correlation consistent split valence basis set aug-cc-pVTZ.¹² Based on these geometries, the corresponding frozen-core coupled cluster¹³⁻¹⁶ CCSD(T)/cc-pVTZ and CCSD(T)/cc-pVQZ single point energies were computed with the built-in extrapolation routine in

ORCA 5.0.3,¹⁷ and extrapolated to complete basis set limit CCSD(T)/CBS with B3LYP/aug-cc-pVTZ zero-point vibrational energy (ZPVE) corrections.¹⁸ Adiabatic ionization energies (IEs) were calculated by taking the ZPVE corrected energy difference between the neutral and ionic species corresponding to the similar conformations. The uncertainty analysis in the IEs was corrected for a combined error of $-0.05/+0.05$ eV, along with an additional -0.03 eV correction for thermal and Stark effects (Tables S5–S8). Franck-Condon factors for the $C_2H_4N_2$ isomer were computed at the B3LYP/aug-cc-pVTZ level of theory. The optimized Cartesian coordinates, electronic energies, harmonic vibrational frequencies, and infrared intensities of the CH_2N_2 , CH_4N_2 , $C_2H_2N_2$, and $C_2H_4N_2$ isomers are compiled in Tables S9–S12.

Additional mass channels and their tentative assignments

The TPD profile of $m/z = 29$ exhibits a broad sublimation event centered at 286 K at 10.49 eV (Fig. S7), which disappears when the photon energy is reduced to 9.34 eV. This sublimation event could be attributed to methanimine (H_2CNH , $\text{IE} = 9.88 \pm 0.07$ eV).¹⁹ However, a small sublimation event is also observed in the blank experiment between 125 K and 320 K, suggesting that the ion signal of $m/z = 29$ at 10.49 eV can only be tentatively assigned to methanimine. The TPD profile of the ion signal at $m/z = 68$ from the irradiated HCN ice at 10.49 eV exhibits a broad sublimation event spanning 180–320 K (Fig. S9a). This event remains at 9.34 eV but disappears at 7.60 eV, which may be attributed to $\text{C}_3\text{H}_4\text{N}_2$ isomers such as 1H-pyrazole ($\text{IE} = 9.27 \pm 0.05$ eV)²⁰ and 1H-imidazole ($\text{IE} = 8.81 \pm 0.01$ eV).²¹ For $m/z = 69$, a broad sublimation event centered around 305 K is observed at 10.49 eV (Fig. S9b), which vanishes at 9.34 eV. This feature may arise from $\text{C}_4\text{H}_7\text{N}$ and/or $\text{C}_2\text{H}_3\text{N}_3$ isomers, such as 1H-1,2,4-triazole ($\text{IE} = 9.80$ eV)²² and 1-pyrroline ($\text{IE} = 9.71$ eV).²³ The ion signal of $m/z = 81$ at 10.49 eV reveals two prominent sublimation events: a low-intensity peak at 194 K and a higher intensity event at 297 K (Fig. S9c). No ion signal is detected in the blank experiment, confirming that these events originate from electron irradiation. The sublimation event vanishes at 9.34 eV. These events are likely associated with $\text{C}_3\text{H}_3\text{N}_3$ isomers such as aminomalononitrile (**6**) and 1,3,5-triazine (*c*- $\text{C}_3\text{H}_3\text{N}_3$, $\text{IE} = 10.01 \pm 0.01$ eV).²⁴ The trimerization of HCN to form 1,3,5-triazine is calculated to be exergonic by 123 kJ mol^{-1} , with a reaction barrier of 219 kJ mol^{-1} at the B3LYP/6-311G(d,p) level of theory.²⁵ To further investigate this assignment, a one-color [1 + 1] REMPI experiment was conducted with irradiated HCN ice by scanning ultraviolet (UV) photon energy from 31526 to 31606 cm^{-1} , corresponding to the 6_0^1 transition of 1,3,5-triazine.²⁶ However, no ion signal of $m/z = 81$ was observed, providing no evidence for the formation of 1,3,5-triazine under the current experimental conditions.

Additional ion signal at $m/z = 83, 93, 108, 121, 135$, and 150 at 10.49 eV exhibit broad sublimation events between 180 K and 320 K (Figs. S10). These signals may correspond to $\text{C}_3\text{H}_5\text{N}_3$, $\text{C}_4\text{H}_3\text{N}_3$, $\text{C}_4\text{H}_4\text{N}_4$, $\text{C}_4\text{H}_3\text{N}_5$, $\text{C}_5\text{H}_5\text{N}_5$, and $\text{C}_5\text{H}_6\text{N}_6$ isomers, respectively. All sublimation events remain at 9.34 eV but are absent at 7.60 eV. Possible isomers include diaminomaleonitrile (**7**), diaminofumaronitrile (**8**), and 4-aminoimidazole-5-carbonitrile (**9**) for $\text{C}_4\text{H}_4\text{N}_4$; and 2,6-diaminopurine ($\text{C}_5\text{H}_6\text{N}_6$, **12**) for $\text{C}_5\text{H}_6\text{N}_6$ isomers. Notably, the $\text{C}_5\text{H}_5\text{N}_5$ isomers may be linked to adenine (**3**, $\text{IE} = 8.267 \pm 0.005$ eV)²⁷ and/or 2-aminopurine (**12**, $\text{IE} = 7.87$ eV).²⁸ To probe adenine (**3**) and 2-aminopurine, one-color [1 + 1] REMPI experiments were performed over 36088 – 36127

cm^{-1} and $32347 - 32389 \text{ cm}^{-1}$, corresponding to the 0–0 band of the $\pi\pi^*$ state of adenine (**3**)²⁹ and 2-aminopurine,³⁰ respectively. However, no ion signal at $m/z = 135$ was detected, providing no evidence of the formation of either adenine (**3**) or 2-aminopurine from the irradiated HCN ice under the current experimental conditions.

Alkane	Alkene		Alkyne		Cyclic		Other		
 Cyanomethylene HCCN	 Vinyl cyanide CH ₂ CHCN	 Methacrylonitrile CH ₂ C(CH ₃)CN	 Methylcyanoacetylene CH ₃ C ₃ N	 1-Cyanocyclopentadiene C ₆ H ₅ CN	 1-Cyanopyrene C ₁₆ H ₉ CN	 Cyano radical CN	 Hydrogen cyanide HCN	 Sodium cyanide NaCN	
 Cyanomethyl CH ₂ CN	 Cyanoallene CH ₂ CCHCN	 g-Allyl cyanide g-CH ₂ CHCH ₂ CN	 3-Butynenitrile HC ₃ H ₂ CN	 Cyanoacetylene HC ₃ N	 2-Cyanocyclopentadiene C ₆ H ₅ CN	 5-Cyanoacenaphthalene C ₁₂ H ₇ CN	 Isocyanogen CNCN	 Magnesium cyanide MgCN	
 Methylcyanide CH ₃ CN	 1-Cyanopropargyl HC ₃ HCN	 c-Allyl cyanide c-CH ₂ CHCH ₂ CN	 t-Cyanovinylacetylene HC ₃ CHCHCN	 Cyanoethynylmethylene HC ₄ N	 Benzonitrile C ₆ H ₅ CN	 2-Cyanopyrene C ₁₆ H ₉ CN	 Cyanomethylidyne CCN	 Cyanamide NH ₂ CN	 Cyanosilicone SiCN
 Ethylcyanide C ₂ H ₅ CN	 3-Cyanopropargyl CH ₂ C ₃ N	 Z-Maleonitrile CH ₂ CHCHCHCN	 Vinylcyanoacetylene CH ₂ CHC ₃ N	 Cyanodiacetylene HC ₅ N	 1-Cyanonaphthalene C ₁₀ H ₇ CN	 2-Cyanopyrene C ₁₆ H ₉ CN	 Z-Cyanomethanimine Z-NHCHCN	 Aminoacetonitrile NH ₂ CH ₂ CN	 Thiocyanic acid HSCN
 n-Propylcyanide C ₃ H ₇ CN	 t-Crotononitrile t-CNCHCHCH ₃	 E-1-cyanobutadiene CH ₂ CHCHCHCN	 Methylcyanodiacetylene CH ₃ C ₆ N	 2-Cyanonaphthalene C ₁₀ H ₇ CN	 4-Cyanopyrene C ₁₆ H ₉ CN	 E-Cyanomethanimine NHCHCN	 Cyanoformaldehyde HOCCN	 Potassium cyanide KCN	
 i-Propylcyanide (CH ₃) ₂ CHCN	 Cyanovinyl H ₂ CCCN	 2-Cyanobutadiene CH ₂ CHC(CN)CH ₂	 Cyanotriacetylene HC ₇ N	 2-Cyanoindene C ₉ H ₇ CN	 Cyanocoronene C ₂₄ H ₁₁ (CN)	 N-Cyanomethanimine H ₂ CNCN	 Glycolonitrile HOCH ₂ CN	 Silyl cyanide Si ₃ CN	
 Malononitrile NCCH ₂ CN	 cis-Crotononitrile cis-CNCHCHCH ₃		 Methylcyanotriacetylene CH ₂ C ₇ N	 1-Cyanoacenaphthalene C ₁₂ H ₇ CN		 Cyanoacetyleneallene CH ₂ C ₂ HC ₃ N	 Cyanoformamide NCCONH ₂	 Hydrido magnesium cyanoacetylidyne HMgCCCN	
			 Cyanotetraacetylene HC ₈ N	 Cyanopentaacetylene HC ₁₁ N			 Cyanic acid HOCN	 Sodium cyanoacetylidyne NaCCCN	

Figure S1. Known interstellar C $\equiv$ N-containing molecules. Atoms are color-coded as follows: hydrogen (white), carbon (gray), nitrogen (blue), oxygen (red), sodium (purple), magnesium (green), potassium (orange), silicon (silver), and sulfur (yellow). Tentative identified molecules are shown in *italics*.

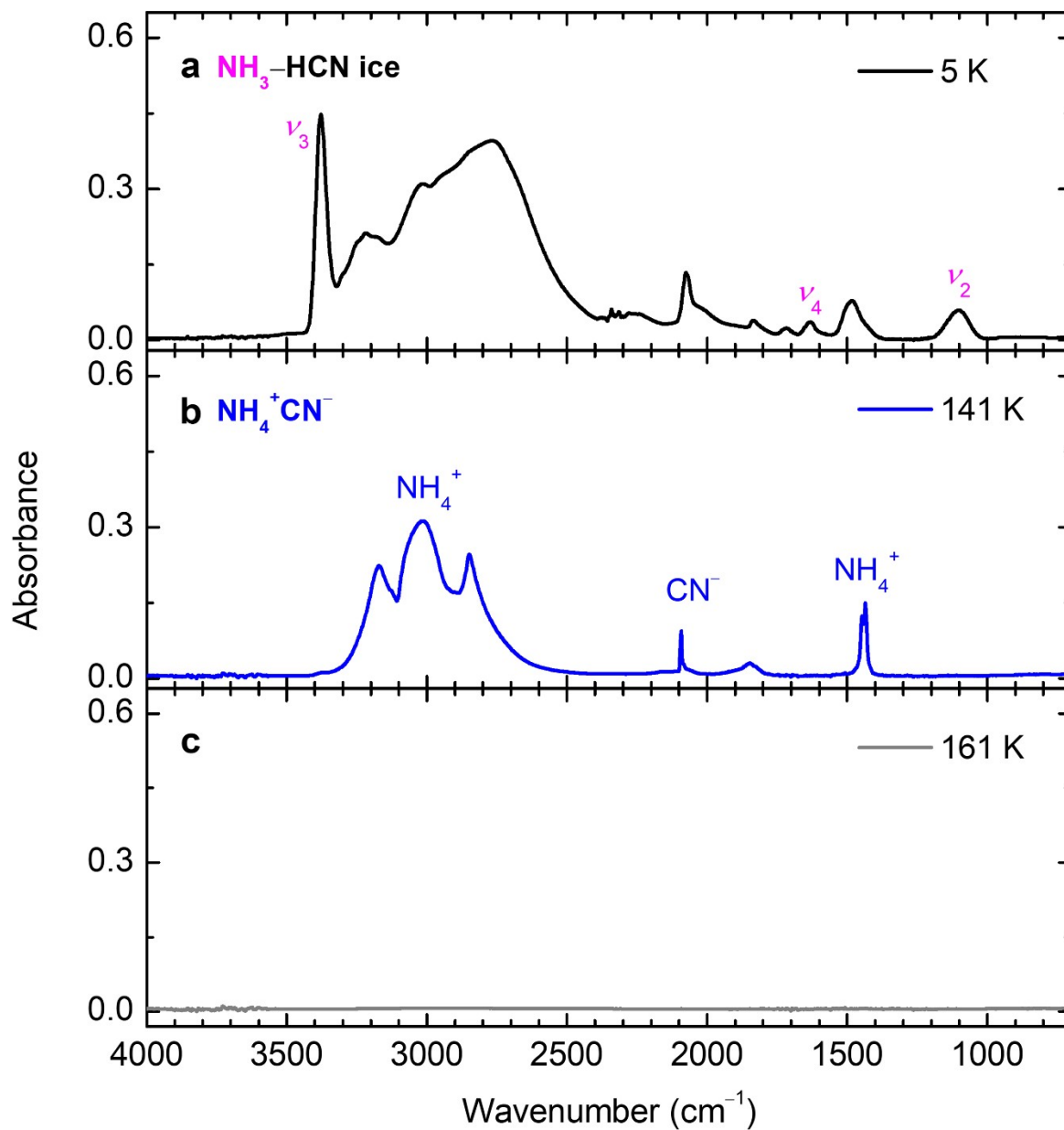


Figure S2. Infrared spectra of $\text{NH}_3\text{-HCN}$ ice with a thickness of 820 ± 50 nm recorded at 5 K (a), 141 K (b), and 161 K (c). After deposition at 5 K, the ice was heated to 320 K at 1 K min^{-1} . At 141 K, NH_3 and HCN sublime, leaving only NH_4CN , which remains until 161 K. The NH_4CN spectrum matches well with previous measurements.³¹

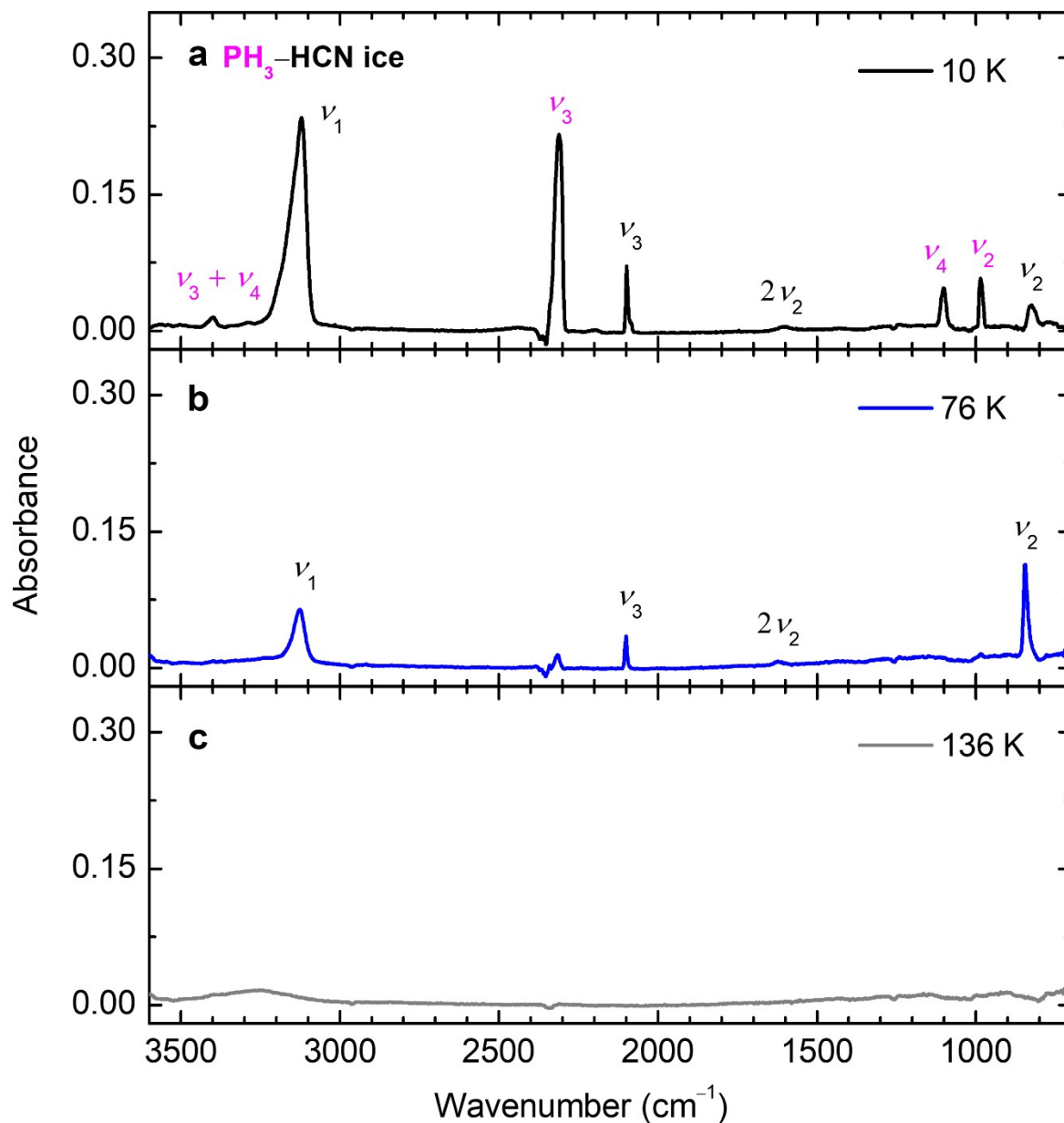
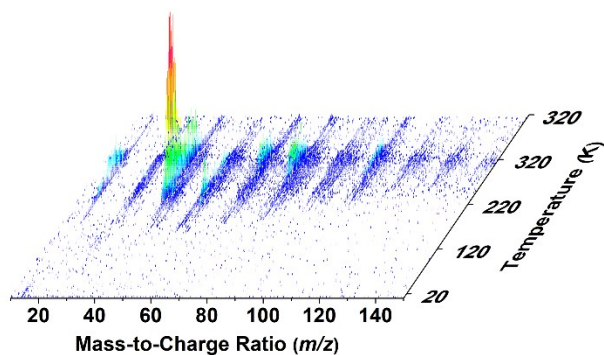
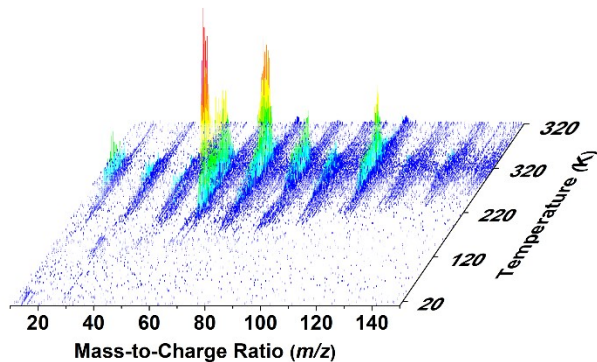


Figure S3. Infrared spectra of $\text{PH}_3\text{-HCN}$ ice with a thickness of 670 ± 80 nm recorded at 10 K (a), 76 K (b), and 136 K (c). After deposition at 10 K, the $\text{PH}_3\text{-HCN}$ ice was heated to 320 K at 1 K min^{-1} . At 76 K, PH_3 sublimates and only HCN remains; at 136 K both reactant sublime. Absorptions of PH_3 and HCN are labeled in magenta and black, respectively. Detailed band assignments are provided in Table S2.

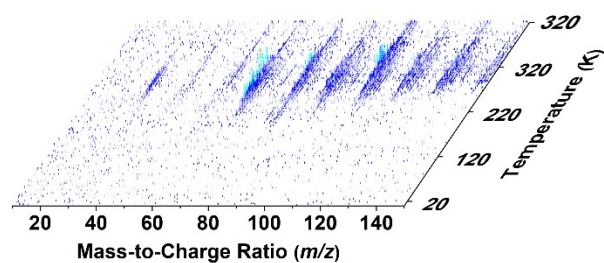
a HCN ice, 11.10 eV



b HCN ice, 10.49 eV



c HCN ice, 9.34 eV



d HCN ice, 7.60 eV

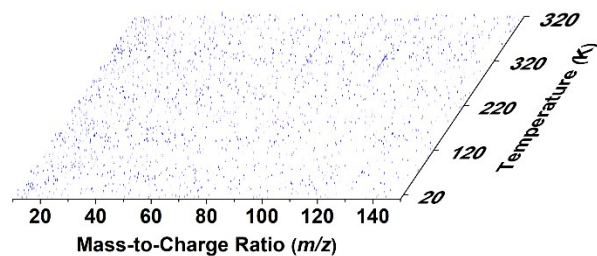


Figure S4. PI-ReToF-MS data of irradiated HCN ices during TPD, recorded at 11.10 (a), 10.49 (b), 9.34 (c), and 7.60 eV (d).

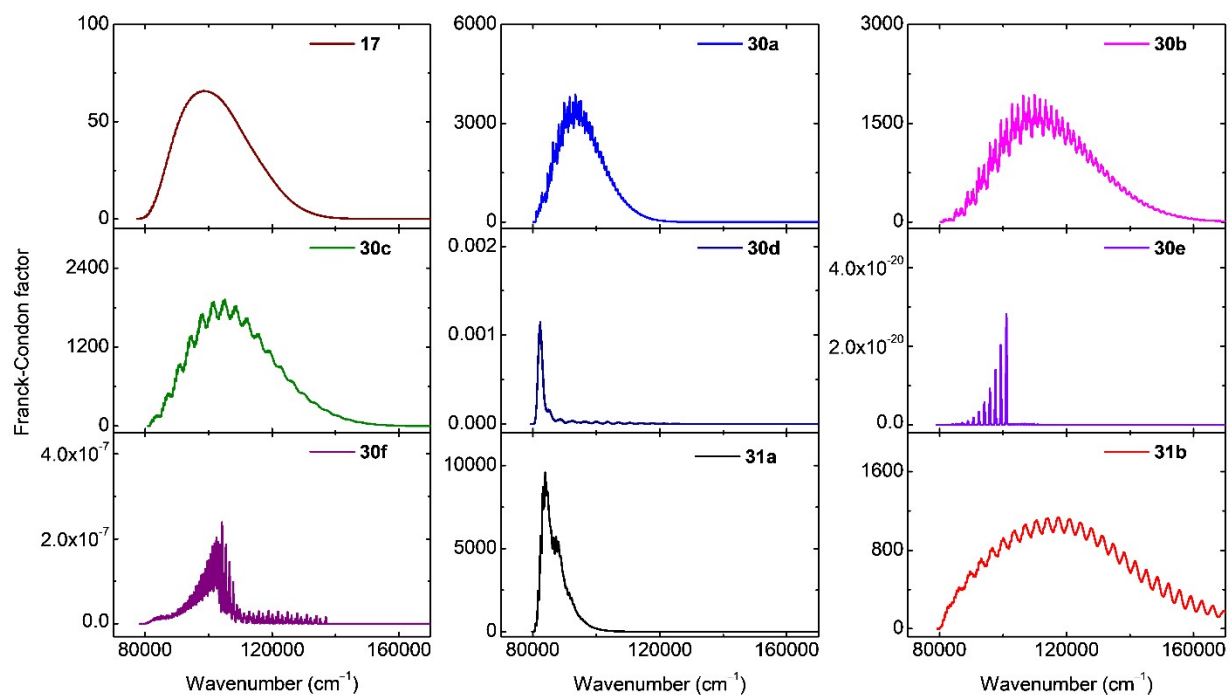


Figure S5. Calculated Franck–Condon factors for isomers **17**, **30**, and **31** as a function of the energy.

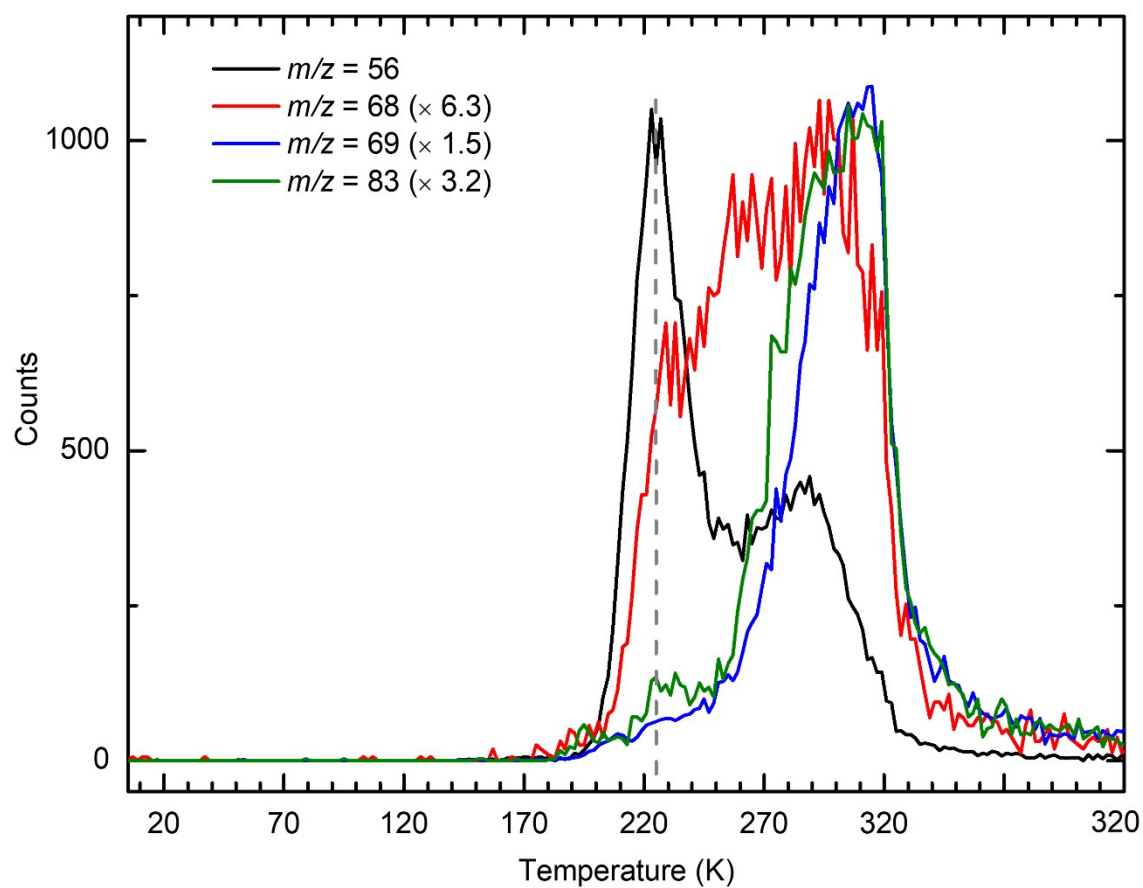


Figure S6. TPD profiles of $m/z = 56$, 68, 69, and 83 in irradiated HCN ice measured at 10.49 eV.

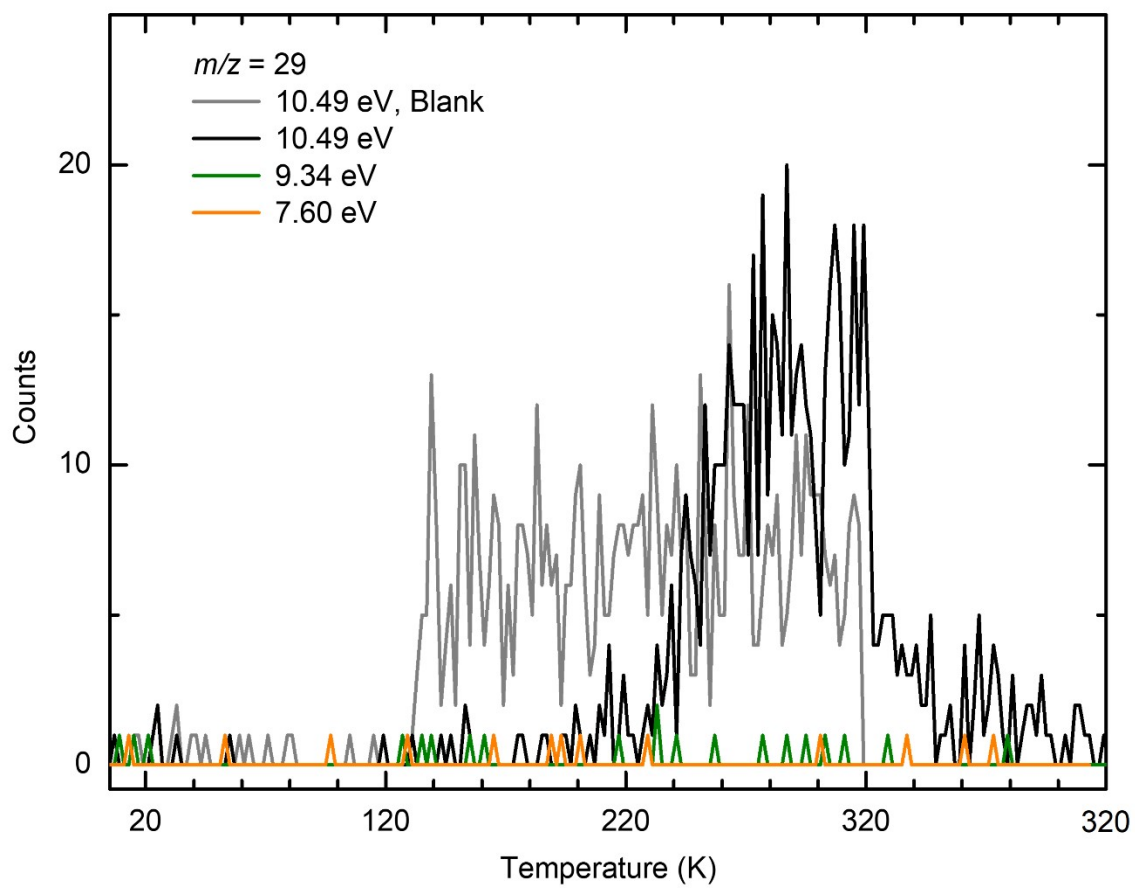


Figure S7. TPD profiles of irradiated HCN ices at $m/z = 29$ recorded at photon energies of 10.49, 9.34, and 7.60 eV.

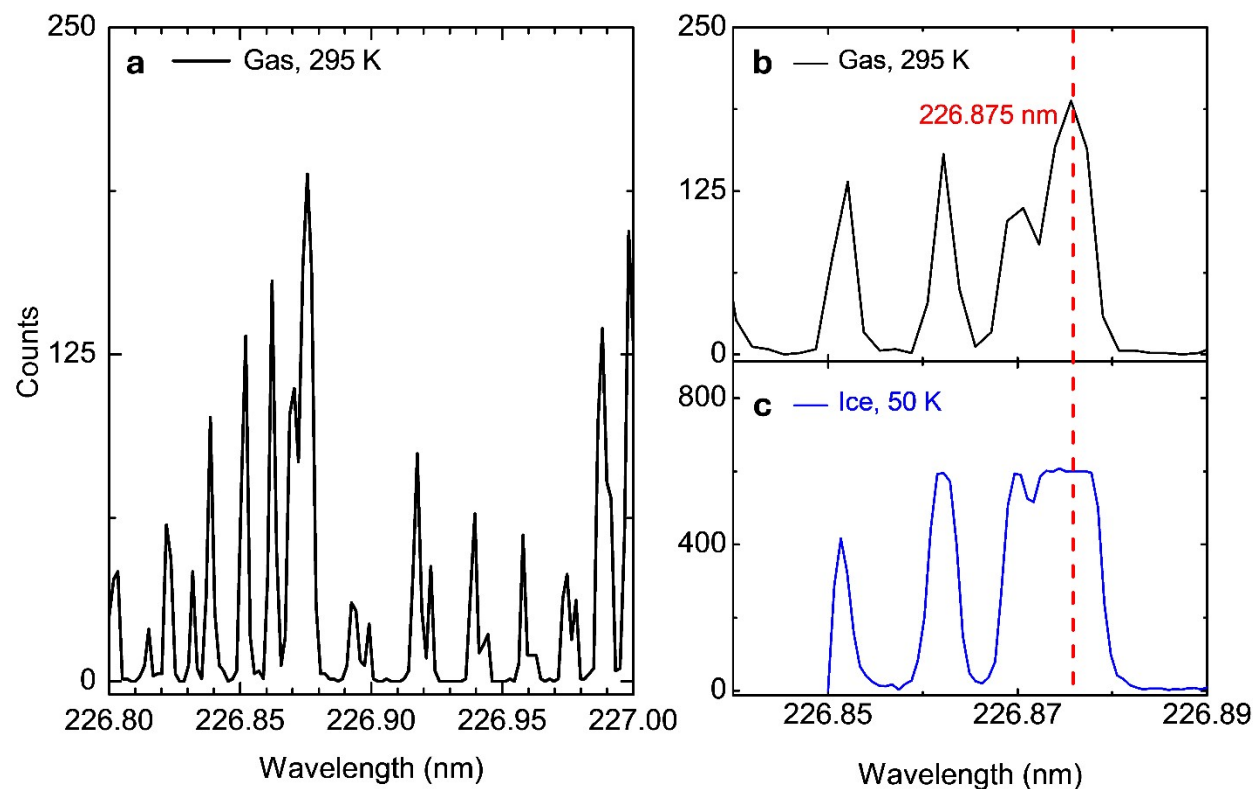


Figure S8. REMPI scan from 226.80–227.00 nm for nitrogen monoxide (NO) at 295 K in the gas phase (a and b) and NO ice at 50 K. The red dashed line indicates the wavelength at the maximum signal, which corresponds to transition from a higher ground state at 226.875 nm ($A^2\Sigma^+ \leftarrow X^2\Pi_{3/2}$). Due to the thermal occupation of the $X^2\Pi_{3/2}$ state at relative higher temperatures, this transition is around 121 cm^{-1} higher than the that from ground state ($A^2\Sigma^+ \leftarrow X^2\Pi_{1/2}$).³²

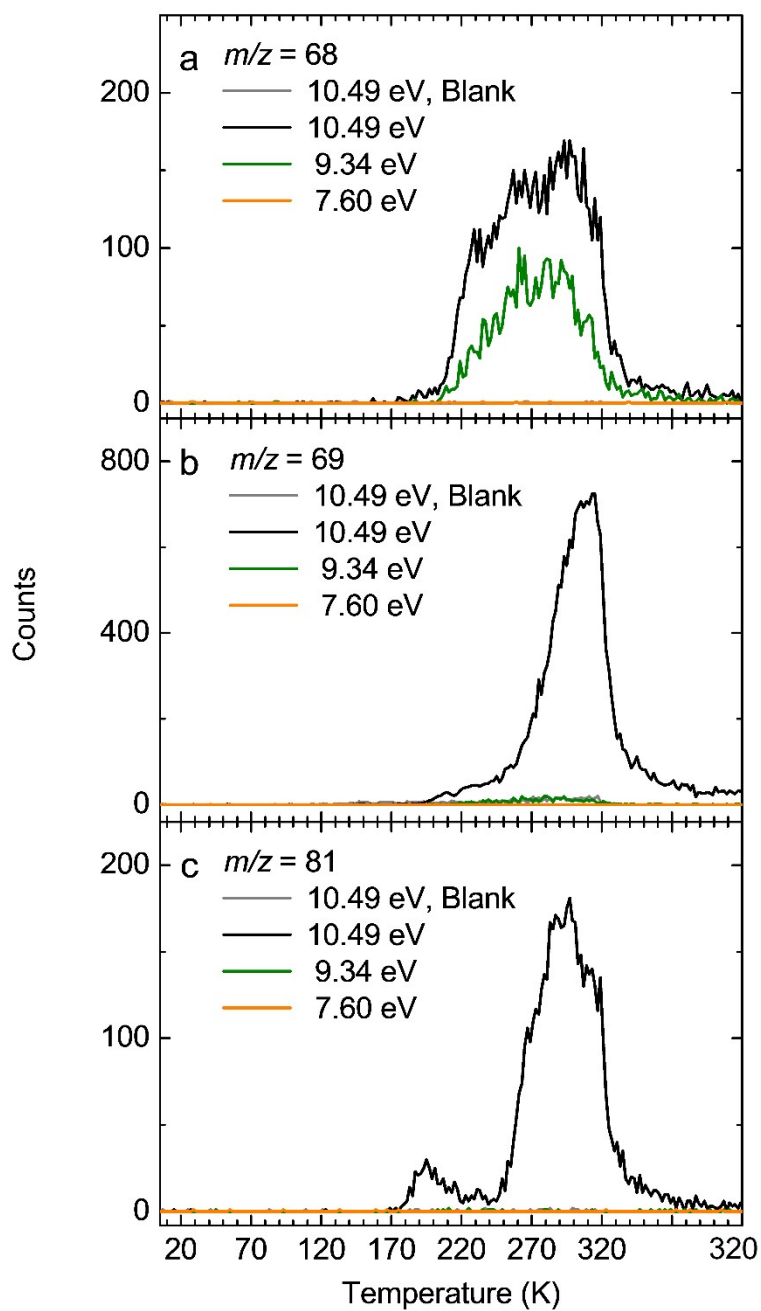


Figure S9. TPD profiles of irradiated HCN ices at $m/z = 68$ (a), 69 (b), and 81 (c) recorded at photon energies of 10.49, 9.34, and 7.60 eV.

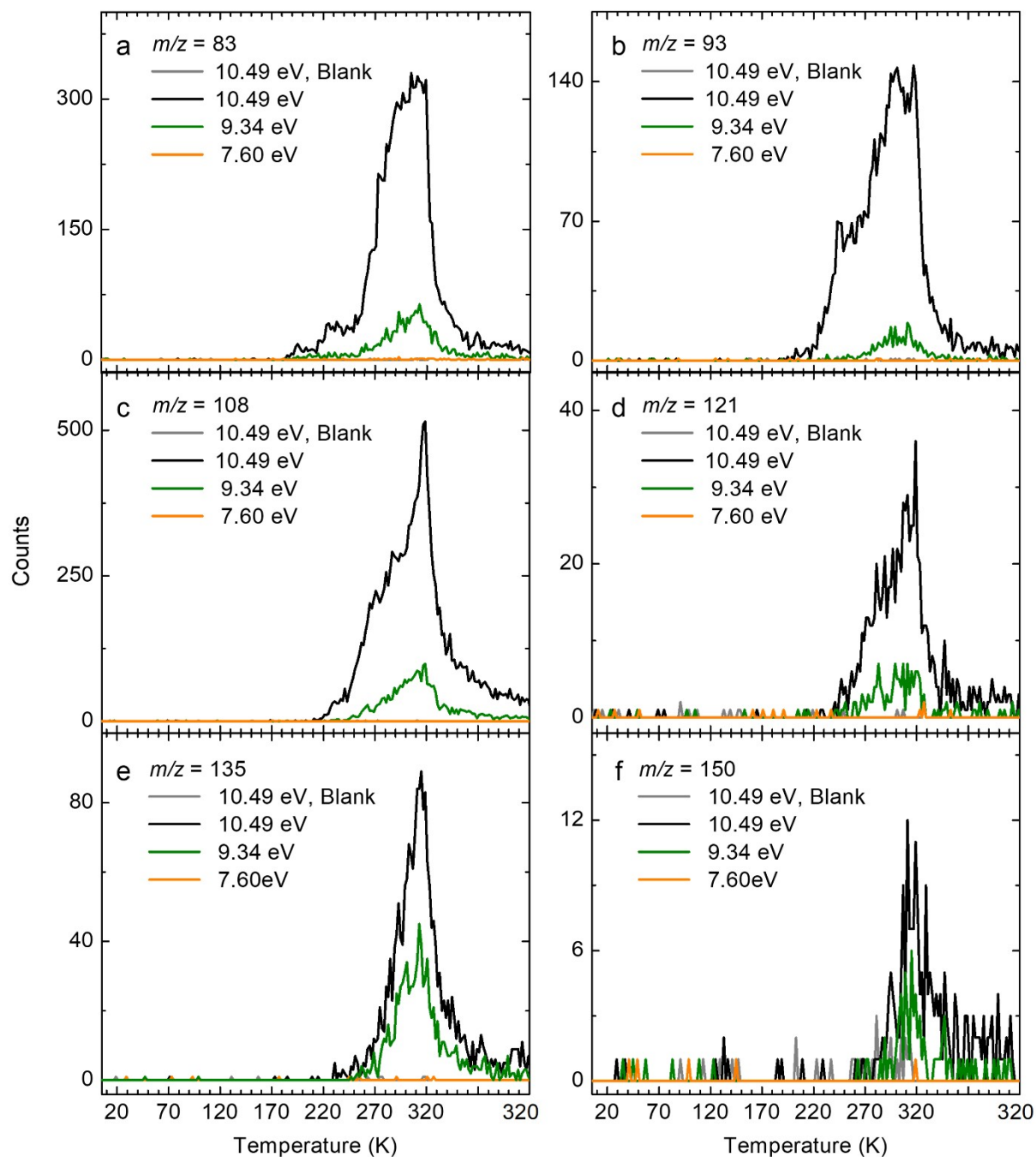


Figure S10. TPD profiles of irradiated HCN ices at $m/z = 83$ (a), 93 (b), 108 (c), 121 (d), 135 (e) and 150 (f) recorded at photon energies of 10.49, 9.34, and 7.60 eV.

Table S1. Observed absorption peaks of HCN ice before and after irradiation at 5 K. Vibration mode: stretching (ν), bending (δ).

Pristine ice, absorptions before irradiation (cm^{-1})	
HCN	Assignment ³
3977	$\nu_1 + \nu_2$
3118	ν_1 (CH stretch)
2100	ν_3 (CN stretch)
1618	$2\nu_2$
841	ν_2 (HCN bend)
New absorptions after irradiation (cm^{-1})	
	Assignment
3312, 3161	$\nu(\text{NH})$ ³³
2978	$\nu(\text{CH})$ ³³
2303	ν_1 (CNCN) ³⁴
2259, 2213	$\nu(\text{C}\equiv\text{N})$ ³³
2142	$\nu(\text{NCCN})$ ³⁵
	$\nu(-\text{N}\equiv\text{C})$ ³³
2090, 2068	$\nu(\text{C}\equiv\text{N})$ (CN^-) ³⁶
1454	$\nu(\text{NH})$ (NH_4^+) ³⁷
Absorptions after TPD (cm^{-1})	
	Assignment
3331, 3187	$\nu(\text{NH})$ ³³
2978	$\nu(\text{CH})$ ³³
2230	$\nu(\text{C}\equiv\text{N})$ ³³
	$\nu(\text{C}\equiv\text{N})$
2193, 2165, 2142	$\nu(\text{C}=\text{C}=\text{N})$ ³³
1686, 1632, 1559	$\nu(\text{C}=\text{N})$ ³³
1359	$\delta(\text{CH})$ ³⁸

Table S2. Observed absorption peaks of PH₃–HCN ice before and after irradiation at 10 K.
Vibration mode: stretching (ν), bending (δ).

Pristine ice, absorptions before irradiation (cm ⁻¹)	
HCN	Assignment ³
3960	$\nu_1 + \nu_2$
3122	ν_1 (CH stretch)
2098	ν_3 (CN stretch)
1602	$2\nu_2$
826	ν_2 (HCN bend)
PH ₃	Assignment ²
4547	$2\nu_1$
3399	$\nu_3 + \nu_4$
2085	$\nu_2 + \nu_4$
2311	ν_3 (PH stretch)
1101	ν_4 (δ (HPH))
985	ν_2 (δ (HPH))

Table S3. Experimental conditions of hydrogen cyanide (HCN) ices including ice thickness, irradiation current, time and dose, and vacuum ultraviolet (VUV) photon energy.

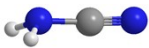
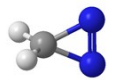
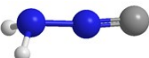
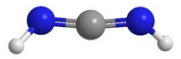
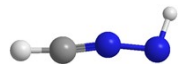
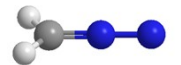
Ice Composition	Thickness (nm)	Current (nA)	Irradiation time (s)	Dose (eV/HCN)	VUV Photon energy (eV)
HCN	590 ± 50	—	—	—	10.49
HCN	540 ± 50	104 ± 3	3600 ± 10	8.2 ± 1.3	10.49
HCN ^a	540 ± 50	101 ± 3	3600 ± 10	8.0 ± 1.3	10.49
HCN	540 ± 50	107 ± 3	3600 ± 10	8.4 ± 1.3	9.34
HCN	540 ± 50	106 ± 1	3600 ± 10	8.3 ± 1.3	7.60
HCN	540 ± 50	105 ± 1	3600 ± 10	8.3 ± 1.3	9.61–9.79
HCN	540 ± 50	107 ± 3	3600 ± 10	8.4 ± 1.3	9.82–9.93
HCN	540 ± 50	106 ± 1	3600 ± 10	8.3 ± 1.3	11.10
HCN ^a	540 ± 50	106 ± 5	3600 ± 10	8.3 ± 1.4	11.10
HCN–NH ₃	820 ± 50	—	—	—	—
HCN–PH ₃	670 ± 80	—	—	—	—

^a repeat experiment

Table S4. Four-wave mixing parameters for the generation of VUV photons, with an energy uncertainty of less than 0.001 eV.

VUV photon energy (eV)	Nonlinear medium	Laser wavelength for ω_1 (nm)	Dye for ω_1	Laser wavelength for ω_2 (nm)	Dye for ω_2
11.10 ($2\omega_1 + \omega_2$)	Xenon	249.628	Coumarin 503	1064	–
10.49 ($3\omega_1$)	Xenon	355	–	–	–
9.61–9.79	Krypton	212.556	Stilbene 420	532	DCM
9.82–9.93	Krypton	212.556	Stilbene 420	532	LDS 698
9.34 ($2\omega_1 - \omega_2$)	Krypton	212.556	Stilbene 420	532	–
7.60 ($2\omega_1 - \omega_2$)	Xenon	249.628	Coumarin 503	532	–

Table S5. Error analysis of IEs and relative energies (ΔE) of CH_2N_2 isomers computed at the CCSD(T)/CBS//B3LYP/aug-cc-pVTZ level including zero-point vibrational energy (ZPVE) corrections. The IE ranges are corrected for combined computational uncertainties of $-0.05/+0.05$ eV and the thermal and Stark effects of -0.03 eV.

Isomer	Structure	ΔE (kJ mol ⁻¹)	T1 diagnostic	Computed IE (eV)	Corrected IE ranges (eV)
11		0	0.013	10.58	10.50–10.60
21		178	0.019	10.43	10.35–10.45
22		186	0.014	10.29	10.21–10.31
23		11	0.017	10.24	10.16–10.26
24		236	0.026*	9.08	9.00–9.10
25		32	0.012	9.00	8.92–9.02

* The T1 value is slightly larger than the threshold of 0.02 and the employed single-reference-based electron correlation method is probably not very reliable for isodiazomethane and the result might not be highly accurate.³⁹

Table S6. Error analysis of IEs and relative energies (ΔE) of CH_4N_2 isomers computed at the CCSD(T)/CBS//B3LYP/aug-cc-pVTZ level including ZPVE corrections. The IE ranges are corrected for combined computational uncertainties of $-0.05/+0.05$ eV and the thermal and Stark effects of -0.03 eV.

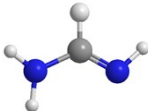
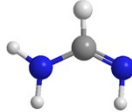
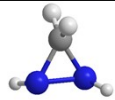
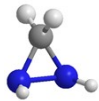
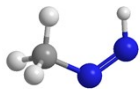
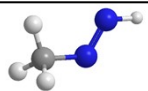
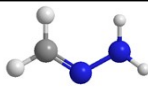
Isomer	Structure	ΔE (kJ mol ⁻¹)	T1 diagnostic	Computed IE (eV)	Corrected IE ranges (eV)
26a		0	0.013	9.21	9.13–9.23
26b		2	0.013	9.14	9.06–9.16
27a		45	0.009	9.30	9.22–9.32
27b		50	0.010	9.00	8.92–9.02
28a		35	0.012	9.01	8.93–9.03
28b		31	0.011	8.93	8.85–8.95
29		29	0.012	8.82	8.74–8.84

Table S7. Error analysis of IEs and relative energies (ΔE) of $C_2H_2N_2$ isomers computed at the CCSD(T)/CBS//B3LYP/aug-cc-pVTZ level including ZPVE corrections. The IE ranges are corrected for combined computational uncertainties of $-0.05/+0.05$ eV and the thermal and Stark effects of -0.03 eV.

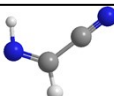
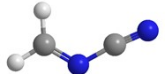
Isomer	Structure	ΔE (kJ mol ⁻¹)	T1 diagnostic	Computed IE (eV)	Corrected IE ranges (eV)
5a		0	0.013	10.98	10.90–11.00
5b		1	0.013	10.95	10.87–10.97
15		7	0.016	10.56	10.48–10.58

Table S8. Error analysis of IEs and relative energies (ΔE) of $C_2H_4N_2$ isomers computed at the CCSD(T)/CBS//B3LYP/aug-cc-pVTZ level including ZPVE corrections. The IE ranges are corrected for combined computational uncertainties of $-0.05/+0.05$ eV and the thermal and Stark effects of -0.03 eV.

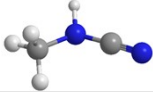
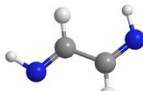
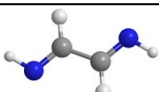
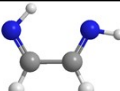
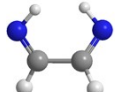
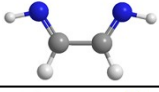
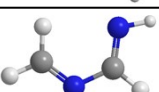
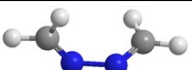
Isomer	Structure	ΔE (kJ mol ⁻¹)	T1 diagnostic	Computed IE (eV)	Corrected IE ranges (eV)
17		6	0.012	9.83	9.75–9.85
30a		15	0.012	10.01	9.93–10.03
30b		14	0.012	10.04	9.96–10.06
30c		13	0.012	10.10	10.02–10.12
30d		15	0.012	9.99	9.91–10.01
30e		17	0.013	9.92	9.84–9.94
30f		19	0.012	9.81	9.73–9.83
31a		0	0.011	9.97	9.89–9.99
31b		2	0.011	9.91	9.83–9.93
32a		18	0.014	9.34	9.26–9.36
32b		17	0.014	9.38	9.30–9.40
33		36	0.014	8.95	9.87–9.97

Table S9. Optimized Cartesian coordinates (Å), electronic energies (hartree), zero-point vibrational energies (ZPVE), harmonic frequencies (cm^{-1}), and infrared intensities (km mol^{-1}) of CH_2N_2 isomers (**11**, **21–25**) calculated at the B3LYP/aug-cc-pVTZ level of theory.

11				11 radical cation			
N	1.192742	−0.009308	−0.000000	N	1.134508	−0.202112	−0.000000
C	−0.147453	−0.001016	0.000000	C	−0.134290	−0.035812	0.000000
H	1.625330	−0.354866	−0.843507	H	1.655212	−0.270493	−0.879711
H	1.625330	−0.354866	0.843507	H	1.655212	−0.270493	0.879711
N	−1.300337	0.061259	0.000000	N	−1.313994	0.118733	0.000000
E = −148.8486067 E[CCSD(T)/CBS] = −148.6218664 ZPVE = 21.3255 kcal mol ^{−1}				E = −148.4666977 E[CCSD(T)/CBS] = −148.2320102 ZPVE = 20.5533 kcal mol ^{−1}			
Frequency	Intensity			Frequency	Intensity		
411.5221	0.2169			379.4516	0.8966		
489.7130	79.3987			409.9781	0.4718		
563.8031	141.7468			759.3035	186.8130		
1093.7343	10.0069			1126.7964	3.7895		
1194.3711	0.0390			1183.8209	0.7914		
1632.5373	39.2154			1601.7577	80.4213		
2350.3298	118.4330			2063.5870	69.8052		
3545.7901	40.0852			3378.5865	300.8298		
3635.6087	65.8218			3473.9556	273.7512		
21				21 radical cation			
N	0.000000	−0.607674	0.475872	N	−0.000000	0.534480	−0.521510
N	−0.000000	0.607674	0.475872	N	0.000000	−0.597988	−0.687787
C	0.000000	−0.000000	−0.872672	C	−0.000000	0.071502	0.933342
H	0.931848	0.000000	−1.416551	H	0.977205	−0.009838	1.388629
H	−0.931848	−0.000000	−1.416551	H	−0.977205	−0.009838	1.388629
E = −148.7759796 E[CCSD(T)/CBS] = −148.5532859 ZPVE = 20.8699 kcal mol ^{−1}				E = −148.3944089 E[CCSD(T)/CBS] = −148.1668715 ZPVE = 18.8910 kcal mol ^{−1}			
Frequency	Intensity			Frequency	Intensity		
827.6801	14.0601			224.1791	4.1822		
988.2258	0.0000			509.5657	0.0107		
1002.7159	32.6710			674.7281	12.5296		
1025.6857	4.2675			878.0015	31.1768		
1144.6669	3.7669			1067.3884	3.2289		
1499.3441	3.1667			1404.3983	12.1320		
1730.6800	23.1397			2012.4778	22.3882		
3132.6337	6.1645			3127.9804	42.8812		
3247.0452	9.4391			3315.7052	75.2802		
22				22 radical cation			
N	1.154127	0.010092	−0.000000	N	1.058215	−0.263142	−0.000000
N	−0.200442	−0.014110	0.000000	N	−0.186828	−0.048893	0.000000
H	1.496798	−0.463085	−0.828831	H	1.551752	−0.348026	−0.894629

H	1.496798	-0.463085	0.828831	H	1.551752	-0.348026	0.894629
C	-1.364295	0.082473	0.000000	C	-1.379951	0.155752	0.000000
E = -148.7779304 E[CCSD(T)/CBS] = -148.5505730 ZPVE = 21.1217 kcal mol ⁻¹				E = -148.4049327 E[CCSD(T)/CBS] = -148.1704840 ZPVE = 19.9534 kcal mol ⁻¹			
Frequency		Intensity		Frequency		Intensity	
265.2047		1.3549		175.4666		0.5911	
352.4071		5.3779		200.5967		13.5137	
844.4880		123.4833		680.8759		159.9760	
1053.5386		20.4404		1184.4584		5.7116	
1342.8954		4.3799		1235.4504		0.3794	
1659.9976		20.8101		1629.3049		49.6841	
2217.9883		33.3598		2020.0144		329.4370	
3475.3431		10.6086		3352.5758		217.4749	
3562.9747		30.3254		3478.8618		238.6257	
23				23 radical cation			
C	0.000198	-0.017909	-0.001709	C	-0.000000	0.000000	0.083712
N	-1.210768	0.085927	-0.094204	N	1.200028	-0.000000	-0.075291
N	1.210975	0.071883	0.106055	N	-1.200028	0.000000	-0.075291
H	1.815238	-0.464925	-0.499808	H	-2.006664	0.000000	0.547749
H	-1.814131	-0.533026	0.428497	H	2.006664	-0.000000	0.547749
E = -148.8497725 E[CCSD(T)/CBS] = -148.6162695 ZPVE = 20.4910 kcal mol ⁻¹				E = -148.4734161 E[CCSD(T)/CBS] = -148.2364167 ZPVE = 18.1807 kcal mol ⁻¹			
Frequency		Intensity		Frequency		Intensity	
545.1149		0.4443		222.7380		351.8951	
548.9176		72.7798		471.8782		13.1116	
715.7462		89.5040		517.2969		28.5769	
916.9507		441.9046		592.9679		0.0000	
918.5857		14.6197		760.4516		109.7934	
1288.0138		0.0000		1318.4123		0.1256	
2216.4862		703.4179		1805.2224		8.9475	
3590.3990		147.2469		3504.3791		705.5516	
3593.4584		23.8482		3524.2359		150.0997	
24				24 radical cation			
N	0.271502	-1.115568	0.073407	N	-1.176243	-0.090731	-0.000000
N	-0.025194	0.081571	-0.024001	N	0.081251	0.054106	-0.000000
C	-0.461331	1.161709	-0.248514	C	1.234581	-0.014317	0.000000
H	1.285438	-1.225761	0.024303	H	-1.647936	0.829678	-0.000000
H	-0.701095	1.993220	0.387868	H	2.311445	-0.049892	0.000000
E = -148.7640902 E[CCSD(T)/CBS] = -148.5295357 ZPVE = 19.8592 kcal mol ⁻¹				E = -148.4296348 E[CCSD(T)/CBS] = -148.1943337 ZPVE = 18.8538 kcal mol ⁻¹			
Frequency		Intensity		Frequency		Intensity	
475.0401		8.9772		421.8955		33.3892	
529.5602		116.8626		436.6575		26.3120	
646.9055		283.3073		624.0977		44.9530	
839.1999		40.2271		646.6780		22.7624	

1246.2942	118.4964			1045.8051	85.0470		
1319.3475	54.5182			1288.9587	74.9042		
2126.2701	421.2551			2084.0177	3.9990		
3290.3256	51.9843			3310.1024	420.3964		
3418.7885	14.0301			3330.1860	63.9670		
25				25 radical cation			
N	-0.000000	0.000000	1.287561	N	-0.000000	-0.000000	1.291807
N	-0.000000	-0.000000	0.155450	N	-0.000000	-0.000000	0.179451
C	0.000000	0.000000	-1.136620	C	0.000000	0.000000	-1.154312
H	0.000000	0.950107	-1.640680	H	0.000000	0.966573	-1.645958
H	-0.000000	-0.950107	-1.640680	H	-0.000000	-0.966573	-1.645958
E = -148.8015772				E = -148.4679643			
E[CCSD(T)/CBS] = -148.5682504				E[CCSD(T)/CBS] = -148.2368420			
ZPVE = 19.8652 kcal mol ⁻¹				ZPVE = 19.5092 kcal mol ⁻¹			
Frequency	Intensity			Frequency	Intensity		
429.6356	0.2021			386.6022	0.9245		
438.1438	127.1371			434.8546	0.4029		
581.1458	7.9300			747.7559	44.6997		
1116.9036	2.3631			1051.2604	0.2939		
1208.8382	4.9737			1111.6317	3.1503		
1439.8783	35.8292			1401.7917	31.1897		
2190.8264	446.9922			2150.5166	25.4517		
3184.9355	14.1755			3107.9938	97.4798		
3305.5990	2.7494			3254.4665	88.7894		

Table S10. Optimized Cartesian coordinates (Å), electronic energies (hartree), zero-point vibrational energies (ZPVE), harmonic frequencies (cm⁻¹), and infrared intensities (km mol⁻¹) of CH₄N₂ isomers (**26–29**) calculated at the B3LYP/aug-cc-pVTZ level of theory.

26a				26a radical cation			
C	0.124215	0.390795	0.004104	C	0.062044	0.395623	0.000188
N	-1.130788	-0.149640	-0.039827	N	-1.105475	-0.172708	0.017445
H	-1.917006	0.414319	0.225670	H	-1.949034	0.385708	0.016288
H	-1.209396	-1.142963	0.107689	H	-1.206010	-1.181046	0.054195
N	1.173886	-0.327652	0.007392	N	1.206968	-0.252159	-0.103154
H	2.010191	0.245278	-0.005731	H	1.966975	-0.092900	0.562890
H	0.117497	1.484319	0.001316	H	0.105358	1.488570	-0.034542
E = -150.0747509 E[CCSD(T)/CBS] = -149.8416057 ZPVE = 36.2767 kcal mol ⁻¹				E = -149.7457201 E[CCSD(T)/CBS] = -149.5015206 ZPVE = 35.3635 kcal mol ⁻¹			
Frequency	Intensity			Frequency	Intensity		
323.9944	189.2314			409.7630	68.2658		
529.7157	52.7422			479.2961	3.0502		
566.4464	56.3726			656.2661	146.4758		
799.8562	52.6571			727.4472	168.2941		
1045.7063	0.1550			824.0285	248.8064		
1085.9738	1.4998			1016.9103	19.7374		
1106.1327	135.0403			1098.0430	13.3955		
1327.6269	34.3001			1192.4395	27.7616		
1405.6192	27.3661			1372.6349	11.3494		
1623.5773	23.9199			1608.3038	8.1793		
1717.5330	333.8229			1702.3254	187.8618		
3037.7056	52.9597			3062.7115	24.1714		
3523.6432	8.1441			3458.0587	223.8259		
3575.8011	27.9227			3506.8820	167.6935		
3706.6268	38.8390			3622.0355	173.9917		
26b				26b radical cation			
C	-0.123033	0.419650	0.005029	C	-0.062024	0.395941	-0.000181
N	1.114821	-0.176808	-0.039900	N	1.105372	-0.172856	-0.017482
H	1.924851	0.370207	0.193426	H	1.949249	0.385138	-0.016605
H	1.188113	-1.166086	0.130512	H	1.205731	-1.181250	-0.053679
N	-1.272408	-0.121709	0.003629	N	-1.206989	-0.252036	0.103261
H	-1.222104	-1.140964	-0.001128	H	-1.966594	-0.094155	-0.563590
H	-0.064633	1.507563	0.005718	H	-0.104924	1.488867	0.034507
E = -150.0715111 E[CCSD(T)/CBS] = -149.8386295 ZPVE = 36.1586 kcal mol ⁻¹				E = -149.7457201 E[CCSD(T)/CBS] = -149.5015238 ZPVE = 35.3610 kcal mol ⁻¹			
Frequency	Intensity			Frequency	Intensity		
324.8763	222.9546			408.6556	68.4002		
479.6169	8.0422			479.5326	3.0434		
542.2013	12.1539			656.3551	146.4057		
834.1795	31.0380			727.6848	168.3981		

1047.2382	26.8859			823.9620	248.4861		
1076.1640	44.4313			1016.8942	19.7846		
1112.9817	18.0452			1097.9142	13.4087		
1313.2689	154.3167			1192.3128	27.6890		
1421.7872	1.3285			1372.4803	11.3832		
1637.2208	29.0139			1608.0689	8.3471		
1710.6281	322.8984			1702.1135	187.7688		
3097.6048	24.9002			3063.1413	24.1844		
3432.9580	10.6909			3457.9088	223.8729		
3572.2889	22.2152			3506.6759	167.6829		
3690.3003	26.0450			3621.6785	173.8637		
27a				27a radical cation			
C	0.000000	0.000000	0.796035	C	0.000000	0.000000	0.865470
N	0.001750	0.749348	-0.438722	N	-0.000227	0.655237	-0.434820
N	-0.001750	-0.749348	-0.438722	N	0.000227	-0.655237	-0.434820
H	-0.910937	0.080246	1.377899	H	-0.929419	0.096563	1.409837
H	0.910937	-0.080246	1.377899	H	0.929419	-0.096563	1.409837
H	-0.957543	-0.997388	-0.680134	H	-0.621249	-1.272217	-0.963919
H	0.957543	0.997388	-0.680134	H	0.621249	1.272217	-0.963919
E = -149.9980822 E[CCSD(T)/CBS] = -149.7703197 ZPVE = 36.9505 kcal mol ⁻¹				E = -149.6676134 E[CCSD(T)/CBS] = -149.4268374 ZPVE = 35.7669 kcal mol ⁻¹			
Frequency	Intensity			Frequency	Intensity		
759.8100	1.6634			509.8498	298.9290		
878.6514	47.0992			758.5124	46.5912		
974.1207	33.2830			778.0105	19.0386		
979.6626	3.7176			1050.2442	1.0426		
1150.5893	21.2648			1072.5562	0.2975		
1200.9833	39.1312			1085.0983	44.1764		
1212.3224	42.4932			1182.1598	45.4709		
1242.6917	7.0034			1184.7756	3.4939		
1324.3763	8.7343			1202.7666	43.7611		
1393.4893	0.2538			1416.2681	11.4134		
1530.8527	0.2801			1536.3842	0.0001		
3092.5163	29.9202			3133.9925	1.5030		
3174.3345	16.2290			3255.9712	8.8249		
3462.5017	2.0730			3419.5168	309.9401		
3470.3176	1.1106			3433.2319	126.2067		
27b				27b radical cation			
C	0.077309	0.791311	-0.000000	C	0.056732	0.861805	0.000000
N	0.076337	-0.443950	0.752719	N	0.056732	-0.439433	0.657763
N	0.076337	-0.443950	-0.752719	N	0.056732	-0.439433	-0.657763
H	1.011107	1.339064	-0.000000	H	1.004454	1.379601	0.000000
H	-0.816911	1.405544	-0.000000	H	-0.864601	1.430517	0.000000
H	-0.872749	-0.623936	-1.076546	H	-0.637246	-0.914439	-1.238573
H	-0.872749	-0.623936	1.076546	H	-0.637246	-0.914439	1.238573
E = -149.9901330 E[CCSD(T)/CBS] = -149.7625037 ZPVE = 36.6441 kcal mol ⁻¹				E = -149.6712951 E[CCSD(T)/CBS] = -149.4310582 ZPVE = 36.1034 kcal mol ⁻¹			
Frequency	Intensity			Frequency	Intensity		

736.7964	0.6498			664.7188	155.4441		
841.5707	48.5828			780.4221	9.9362		
948.6906	0.3041			800.6745	117.0918		
970.5709	26.8681			1000.8804	4.9833		
1166.4982	7.3409			1039.9269	10.5999		
1174.2894	0.0202			1090.4992	18.3888		
1188.1894	3.9306			1187.8346	7.1021		
1235.4651	17.9341			1234.4027	43.3762		
1332.3320	25.1505			1234.7182	109.0802		
1374.2869	27.3562			1406.8574	15.5759		
1528.2634	0.9069			1530.3822	0.0152		
3091.8606	28.2343			3135.5047	2.9036		
3179.6453	14.2658			3261.8176	12.5383		
3416.6876	0.0087			3432.5745	158.6206		
3447.7912	3.1705			3453.5017	197.9753		
28a				28a radical cation			
C	-0.989846	-0.503599	0.000000	C	-1.015113	-0.656918	0.000000
N	-0.000818	0.572451	0.000000	N	0.000000	0.395414	0.000000
N	1.193659	0.286802	0.000000	N	1.138136	0.563617	0.000000
H	1.344584	-0.749895	0.000000	H	1.895338	-0.155922	0.000000
H	-1.623066	-0.381721	0.879439	H	-1.625124	-0.493132	0.888701
H	-0.522189	-1.496666	0.000000	H	-0.521366	-1.629532	0.000000
H	-1.623066	-0.381721	-0.879439	H	-1.625124	-0.493132	-0.888701
E = -150.0150922 E[CCSD(T)/CBS] = -149.7842167 ZPVE = 35.0829 kcal mol ⁻¹				E = -149.6943748 E[CCSD(T)/CBS] = -149.4514699 ZPVE = 34.1198 kcal mol ⁻¹			
Frequency	Intensity			Frequency	Intensity		
208.2163	5.8096			147.0872	31.9718		
579.4525	0.8886			365.8564	5.0759		
870.8177	39.5767			658.3581	63.0480		
904.4311	6.4323			770.1225	6.5335		
1145.3661	4.3879			948.3961	272.8297		
1159.9319	7.2415			1104.9284	0.2011		
1406.4976	11.3572			1119.8540	4.6655		
1456.3965	6.9166			1395.3739	13.6974		
1466.2552	2.6795			1416.1121	20.8768		
1495.6093	84.9995			1454.5211	42.4526		
1672.6118	22.8868			2091.5867	23.9620		
2968.2290	33.6876			3026.7145	43.4215		
3023.1743	89.1685			3103.1839	111.4169		
3082.0125	10.0084			3128.2895	24.8058		
3101.8589	4.5678			3136.7586	8.9612		
28b				28b radical cation			
C	-1.007934	-0.522876	0.000000	C	-1.013338	-0.661197	0.000000
N	0.000598	0.533659	0.000000	N	0.000000	0.382507	0.000000
N	1.157998	0.106065	0.000000	N	1.163200	0.379551	0.000000
H	1.783659	0.924711	0.000000	H	1.713726	1.259709	0.000000
H	-1.638978	-0.378921	0.878174	H	-1.625227	-0.495532	0.887817
H	-0.561367	-1.518591	0.000000	H	-0.525645	-1.635864	0.000000
H	-1.638978	-0.378921	-0.878174	H	-1.625227	-0.495532	-0.887817
E = -150.0217257				E = -149.7033324			

E[CCSD(T)/CBS] = -149.7907622 ZPVE = 35.5096 kcal mol ⁻¹				E[CCSD(T)/CBS] = -149.4609245 ZPVE = 34.5380 kcal mol ⁻¹			
Frequency		Intensity		Frequency		Intensity	
195.2610		0.8065		153.6476		0.1875	
558.7014		17.3038		418.0294		50.6485	
864.0721		32.0747		666.0487		112.4381	
925.6871		13.4825		798.6984		22.1873	
1143.3842		10.1659		1032.9628		80.4799	
1172.2263		20.5642		1124.0429		1.8719	
1407.1693		6.2293		1208.5032		55.0146	
1469.5217		9.9938		1397.2858		17.4825	
1470.1713		16.3367		1416.6520		27.4828	
1491.5368		24.5535		1449.7526		31.4300	
1653.3528		5.5782		1970.2394		10.5554	
3017.0722		15.6479		3028.7899		48.7004	
3094.0883		7.1010		3119.7750		23.6184	
3104.3057		14.3348		3139.0737		17.4227	
3272.7724		12.0852		3236.1816		215.3598	
29				29 radical cation			
N	1.111029	0.143243	-0.089198	N	-1.088002	-0.355291	0.000000
N	-0.083105	-0.513409	0.008279	N	0.000000	0.376037	0.000000
H	1.116367	1.104498	0.241398	H	-1.618859	-0.366977	0.869379
H	1.858183	-0.407910	0.301480	H	-1.618859	-0.366977	-0.869379
C	-1.154647	0.167686	0.008549	C	1.225105	0.099730	0.000000
H	-2.095341	-0.364448	0.031042	H	1.930749	0.923561	0.000000
H	-1.169649	1.260297	-0.021156	H	1.572353	-0.933209	0.000000
E = -150.0281272 E[CCSD(T)/CBS] = -149.7941943 ZPVE = 35.7082 kcal mol ⁻¹				E = -149.7156101 E[CCSD(T)/CBS] = -149.4696973 ZPVE = 35.4198 kcal mol ⁻¹			
Frequency		Intensity		Frequency		Intensity	
426.9034		23.0557		150.2583		43.9329	
514.4623		16.5645		431.5269		61.2781	
651.0041		246.1064		705.1632		161.8448	
785.9061		7.4487		713.2885		0.3349	
942.1191		36.0009		1103.6062		22.2637	
1061.5669		31.8982		1106.2616		12.1810	
1179.1985		12.9848		1178.3696		22.5570	
1309.5395		18.6717		1233.7957		0.5772	
1477.3574		6.0908		1472.7290		13.6090	
1652.9529		38.9486		1632.4049		42.6283	
1691.7617		14.4815		1786.4776		6.6226	
3025.8062		38.7899		3076.1357		23.0821	
3196.6211		8.4956		3207.6316		23.4903	
3440.6914		3.0741		3432.3602		196.1799	
3622.3447		22.3621		3546.4998		164.0092	

Table S11. Optimized Cartesian coordinates (Å), electronic energies (hartree), zero-point vibrational energies (ZPVE), harmonic frequencies (cm⁻¹), and infrared intensities (km mol⁻¹) of C₂H₂N₂ isomers (**5** and **15**) calculated at the B3LYP/aug-cc-pVTZ level of theory.

5a				5a radical cation			
C	0.562377	-0.581042	0.000000	C	0.562531	-0.562751	0.000000
C	-0.000000	0.750694	-0.000000	C	0.000021	0.746552	-0.000000
N	-0.109111	-1.655239	0.000000	N	-0.147090	-1.586308	0.000000
H	-1.114208	-1.478136	0.000000	H	-1.054654	-2.057618	0.000000
H	1.648687	-0.629753	0.000000	H	1.655382	-0.682555	0.000000
N	-0.449280	1.810950	-0.000000	N	-0.420929	1.820244	-0.000000
E = -186.9418663 E[CCSD(T)/CBS] = -186.6483726 ZPVE = 24.7725 kcal mol ⁻¹				E = -186.5425134 E[CCSD(T)/CBS] = -186.2410030 ZPVE = 22.4557 kcal mol ⁻¹			
Frequency	Intensity			Frequency	Intensity		
235.2439	15.6877			199.5764	11.6697		
335.7732	20.6316			291.5168	4.3077		
622.6798	4.0725			457.7857	135.6810		
852.9507	10.4249			461.7004	58.1650		
918.3712	20.9551			693.3758	60.4278		
1132.7840	65.7737			926.1205	23.9116		
1244.0648	88.4049			961.2027	48.2813		
1417.5565	17.4516			1255.2744	4.6013		
1669.3117	33.7051			1654.0945	37.2319		
2331.6271	1.6749			2328.6888	136.1481		
3121.0929	3.9714			3005.3768	103.0340		
3447.1340	7.7269			3473.3147	486.3871		
5b				5b radical cation			
C	-0.000000	0.764331	0.000000	C	-0.000302	0.737118	0.000000
C	-0.475812	-0.598501	-0.000000	C	-0.492862	-0.592170	-0.000000
N	1.241822	1.012087	0.000000	N	1.205094	1.047654	0.000000
H	1.410802	2.017425	0.000000	H	1.926623	1.771230	0.000000
H	-0.791534	1.515768	0.000000	H	-0.732674	1.567748	0.000000
N	-0.922450	-1.658969	-0.000000	N	-0.952893	-1.649159	-0.000000
E = -186.9410027 E[CCSD(T)/CBS] = -186.6473818 ZPVE = 24.6756 kcal mol ⁻¹				E = -186.5429638 E[CCSD(T)/CBS] = -186.2412348 ZPVE = 22.3132 kcal mol ⁻¹			
Frequency	Intensity			Frequency	Intensity		
247.7738	6.5342			211.6317	0.2645		
331.8109	3.5107			283.6615	7.5793		
626.5735	4.7108			450.9963	131.0887		
829.9474	44.1062			485.0325	29.9703		
907.9491	53.2961			685.7635	68.4628		
1116.9376	5.4813			871.8806	7.6186		
1237.0619	42.1105			975.7689	47.5775		
1411.6394	26.9656			1237.2364	16.8101		
1680.3831	42.3694			1673.0845	35.5790		

2344.9053	4.0564			2337.9771	152.8917		
3063.8927	13.2611			2911.9787	117.5385		
3461.9853	9.8370			3483.3236	594.3120		
15				15 radical cation			
N	-6.530330	0.827607	-0.126978	N	-1.954828	-0.000155	0.000008
N	-4.141700	0.133658	-0.005872	N	0.479370	0.000059	-0.000010
C	-5.404906	0.565788	-0.077983	C	-0.763652	-0.000039	-0.000001
C	-3.166996	0.946666	-0.092014	C	1.728077	0.000122	-0.000019
H	-2.162105	0.544241	-0.027398	H	2.272333	-0.948675	-0.000021
H	-3.288383	2.021001	-0.226674	H	2.272257	0.948960	-0.000022
E = -186.9337164				E = -186.5578011			
E[CCSD(T)/CBS] = -186.6366964				E[CCSD(T)/CBS] = -186.2456710			
ZPVE = 24.4001 kcal mol ⁻¹				ZPVE = 22.5022 kcal mol ⁻¹			
Frequency	Intensity			Frequency	Intensity		
255.4134	5.9942			109.1348	5.4140		
374.3086	8.4366			218.2672	1.4348		
633.8846	5.3526			380.4205	14.1916		
778.4085	1.6746			517.5388	11.5554		
955.8108	6.3260			971.4264	5.4893		
1098.6045	18.6336			1071.4644	25.6945		
1225.9328	11.4211			1074.0673	0.7812		
1503.0029	15.1289			1437.3148	37.6114		
1697.7046	28.9901			1816.6541	49.8632		
2298.3428	37.4431			2003.7250	125.4657		
3064.4753	17.3371			3016.3382	118.1704		
3182.2189	4.1503			3124.1512	60.9592		

Table S12. Optimized Cartesian coordinates (Å), electronic energies (hartree), zero-point vibrational energies (ZPVE), harmonic frequencies (cm^{-1}), and infrared intensities (km mol^{-1}) of $\text{C}_2\text{H}_4\text{N}_2$ isomers (**17**, **30–33**) calculated at the B3LYP/aug-cc-pVTZ level of theory.

17				17 radical cation			
N	−1.803328	−0.268356	−0.148823	N	−1.841685	−0.224087	−0.020333
C	−0.718499	0.119051	−0.041764	C	−0.714793	0.124270	0.005415
N	0.532991	0.546553	0.135335	N	0.523685	0.493594	0.032932
C	1.639168	−0.405831	−0.010473	C	1.667743	−0.422326	−0.020917
H	0.708080	1.476422	−0.213809	H	0.707133	1.499045	0.097087
H	2.550508	0.069699	0.345157	H	1.315273	−1.445782	−0.086738
H	1.781611	−0.733867	−1.042821	H	2.266846	−0.261068	0.880105
H	1.439838	−1.275523	0.611214	H	2.272974	−0.149312	−0.890360
E = −188.1650100 E[CCSD(T)/CBS] = −187.8692561 ZPVE = 39.3395 kcal mol ^{−1}				E = −187.8131055 E[CCSD(T)/CBS] = −187.5061839 ZPVE = 38.3036 kcal mol ^{−1}			
Frequency	Intensity			Frequency	Intensity		
148.3619	0.4630			123.0694	0.0488		
221.3267	6.5320			225.2462	3.2261		
411.2689	79.5341			394.0122	0.1382		
540.7744	23.2254			576.9780	2.2040		
634.8435	22.7482			666.5952	78.0328		
927.7727	2.7808			861.3535	11.6984		
1143.5033	9.5391			1083.3013	0.0272		
1159.5970	34.0294			1137.7312	2.9011		
1203.8779	9.7250			1195.8407	48.3616		
1463.1153	8.5606			1392.0492	26.6092		
1468.7771	11.7078			1434.9136	24.3781		
1495.2351	9.3225			1459.8144	9.6100		
1520.9333	16.0972			1508.0784	38.2255		
2337.7800	139.0153			2044.0907	243.6161		
3022.8902	48.3394			3010.5172	82.7118		
3100.0210	17.8949			3071.2666	18.2086		
3133.5923	10.1013			3180.5932	14.4297		
3584.7191	37.0883			3428.3195	191.3093		
30a				30a radical cation			
N	−1.804768	−0.060206	0.000017	N	−1.570738	−0.331427	0.190008
C	−0.623811	0.399347	0.000027	C	−0.756154	0.256233	−0.490818
C	0.623810	−0.399346	−0.000000	C	0.755638	−0.264279	−0.487324
N	1.804767	0.060208	0.000026	N	1.570916	0.334576	0.182842
H	−1.798556	−1.083749	0.000003	H	−2.566970	−0.191211	0.340742
H	−0.490618	1.484297	−0.000018	H	−0.894947	1.126290	−1.143766
H	0.490617	−1.484295	−0.000037	H	0.893742	−1.144975	−1.125993
H	1.798555	1.083751	0.000046	H	2.567318	0.196771	0.334697
E = −188.1501192 E[CCSD(T)/CBS] = −187.8553274 ZPVE = 39.3975 kcal mol ^{−1}				E = −187.7970338 E[CCSD(T)/CBS] = −187.4821270 ZPVE = 35.9487 kcal mol ^{−1}			

Frequency	Intensity	Frequency	Intensity
141.6611	3.6914	66.5313	8.3053
334.2961	34.1567	346.8916	28.4859
566.0635	0.0000	384.3400	24.4474
665.8400	50.0719	497.0294	1483.5325
946.6689	0.0000	594.1431	35.2628
1020.6312	0.0000	686.3272	73.7259
1117.7792	0.0000	702.0685	184.9760
1155.9573	111.9335	874.6726	55.4078
1197.3631	149.3270	927.8408	8.8379
1297.1341	0.0000	981.3173	65.6589
1405.1930	68.6478	1163.7096	22.6937
1412.9578	0.0000	1171.6610	162.5219
1680.0470	61.1823	1787.1678	6.9345
1702.7951	0.0000	1893.3440	35.5643
3055.6112	0.0000	3014.6340	66.0851
3059.9840	51.1767	3019.1277	18.4698
3397.7499	4.1478	3513.5473	869.8649
3401.2089	0.0000	3522.1596	20.6651
30b			
N	-1.748834	-0.151578	-0.000013
C	-0.608499	0.401993	-0.000076
C	0.619184	-0.421315	0.000033
N	1.806496	0.025419	0.000005
H	-2.499783	0.538006	-0.000038
H	-0.446562	1.487553	-0.000127
H	0.454521	-1.498278	0.000088
H	1.810359	1.049463	-0.000073
E = -188.1512237 E[CCSD(T)/CBS] = -187.8565984 ZPVE = 39.4052 kcal mol ⁻¹			
Frequency	Intensity	Frequency	Intensity
160.7250	8.5297	66.5313	8.3053
342.3648	17.4625	346.8916	28.4859
578.0939	8.9068	384.3400	24.4474
656.9856	7.4810	497.0294	1483.5325
936.0374	49.5588	594.1431	35.2628
1004.0120	74.6532	686.3272	73.7259
1114.6941	33.8228	702.0685	184.9760
1152.2060	29.9925	874.6726	55.4078
1191.1101	4.3541	927.8408	8.8379
1287.0109	73.0778	981.3173	65.6589
1393.2867	6.1250	1163.7096	22.6937
1416.5915	43.2345	1171.6610	162.5219
1681.2171	61.5248	1787.1678	6.9345
1707.7658	0.8121	1893.3440	35.5643
2995.1947	47.9751	3014.6340	66.0851
3103.5563	13.4722	3019.1277	18.4698
3389.3299	4.2308	3513.5473	869.8649
3454.1706	1.6077	3522.1596	20.6651
30c			
N	-1.752099	-0.108811	-0.000011
30b radical cation			
N	-1.570738	-0.331427	0.190008
C	-0.756154	0.256233	-0.490818
C	0.755638	-0.264279	-0.487324
N	1.570916	0.334576	0.182842
H	-2.566970	-0.191211	0.340742
H	-0.894947	1.126290	-1.143766
H	0.893742	-1.144975	-1.125993
H	2.567318	0.196771	0.334697
E = -187.7970338 E[CCSD(T)/CBS] = -187.4821270 ZPVE = 35.9487 kcal mol ⁻¹			
Frequency	Intensity	Frequency	Intensity
66.5313	8.3053	66.5313	8.3053
346.8916	28.4859	346.8916	28.4859
384.3400	24.4474	384.3400	24.4474
497.0294	1483.5325	497.0294	1483.5325
594.1431	35.2628	594.1431	35.2628
686.3272	73.7259	686.3272	73.7259
702.0685	184.9760	702.0685	184.9760
874.6726	55.4078	874.6726	55.4078
927.8408	8.8379	927.8408	8.8379
981.3173	65.6589	981.3173	65.6589
1163.7096	22.6937	1163.7096	22.6937
1171.6610	162.5219	1171.6610	162.5219
1787.1678	6.9345	1787.1678	6.9345
1893.3440	35.5643	1893.3440	35.5643
3014.6340	66.0851	3014.6340	66.0851
3019.1277	18.4698	3019.1277	18.4698
3513.5473	869.8649	3513.5473	869.8649
3522.1596	20.6651	3522.1596	20.6651
30c radical cation			
N	-1.570738	-0.331427	0.190008

C	-0.601337	0.426331	-0.000046	C	-0.756154	0.256233	-0.490818
C	0.601312	-0.426340	-0.000005	C	0.755638	-0.264279	-0.487324
N	1.752074	0.108801	-0.000014	N	1.570916	0.334576	0.182842
H	-2.487365	0.597510	-0.000013	H	-2.566970	-0.191211	0.340742
H	-0.403349	1.501829	-0.000056	H	-0.894947	1.126290	-1.143766
H	0.403321	-1.501837	0.000037	H	0.893742	-1.144975	-1.125993
H	2.487340	-0.597521	0.000013	H	2.567318	0.196771	0.334697
E = -188.1536124 E[CCSD(T)/CBS] = -187.8589809 ZPVE = 39.4918 kcal mol ⁻¹				E = -187.7970338 E[CCSD(T)/CBS] = -187.4821270 ZPVE = 35.9487 kcal mol ⁻¹			
Frequency	Intensity			Frequency	Intensity		
178.1103	11.0934			66.5313	8.3053		
345.6936	44.0429			346.8916	28.4859		
589.7267	0.0000			384.3400	24.4474		
657.2077	137.9290			497.0294	1483.5325		
929.3581	0.0000			594.1431	35.2628		
997.5003	0.0000			686.3272	73.7259		
1120.1165	0.0000			702.0685	184.9760		
1144.9148	11.5205			874.6726	55.4078		
1180.0323	103.8193			927.8408	8.8379		
1279.6685	0.0000			981.3173	65.6589		
1380.4900	60.4224			1163.7096	22.6937		
1427.3793	0.0000			1171.6610	162.5219		
1681.8465	62.6497			1787.1678	6.9345		
1713.4931	0.0000			1893.3440	35.5643		
3045.2338	0.0000			3014.6340	66.0851		
3047.8677	59.1332			3019.1277	18.4698		
3452.8059	2.6670			3513.5473	869.8649		
3453.4931	0.0000			3522.1596	20.6651		
30d				30d radical cation			
N	-1.449977	0.606365	-0.001770	N	-1.570738	-0.331427	0.190008
C	-0.796852	-0.477106	0.002202	C	-0.756154	0.256233	-0.490818
C	0.694459	-0.584702	0.001495	C	0.755638	-0.264279	-0.487324
N	1.410025	0.459985	-0.002359	N	1.570916	0.334576	0.182842
H	-0.793347	1.394161	-0.005375	H	-2.566970	-0.191211	0.340742
H	-1.344730	-1.419985	0.006331	H	-0.894947	1.126290	-1.143766
H	1.100143	-1.601392	0.004965	H	0.893742	-1.144975	-1.125993
H	2.403979	0.239930	-0.002050	H	2.567318	0.196771	0.334697
E = -188.1491970 E[CCSD(T)/CBS] = -187.8550330 ZPVE = 39.4869 kcal mol ⁻¹				E = -187.7970338 E[CCSD(T)/CBS] = -187.4821270 ZPVE = 35.9487 kcal mol ⁻¹			
Frequency	Intensity			Frequency	Intensity		
153.0806	25.3937			66.5313	8.3053		
305.5086	6.9812			346.8916	28.4859		
635.1107	8.1423			384.3400	24.4474		
740.0107	48.7500			497.0294	1483.5325		
895.5058	7.4090			594.1431	35.2628		
928.8865	46.1548			686.3272	73.7259		
1121.4898	14.8019			702.0685	184.9760		
1165.8074	47.8124			874.6726	55.4078		
1183.1874	42.6588			927.8408	8.8379		

1276.6704	102.2132			981.3173	65.6589		
1404.8819	41.4960			1163.7096	22.6937		
1444.7942	18.2860			1171.6610	162.5219		
1669.6348	15.6974			1787.1678	6.9345		
1730.2371	9.9196			1893.3440	35.5643		
3023.5629	50.6272			3014.6340	66.0851		
3084.8109	50.3710			3019.1277	18.4698		
3384.3164	1.3676			3513.5473	869.8649		
3474.0231	2.6856			3522.1596	20.6651		
30e				30e radical cation			
N	-1.520463	0.084425	0.474657	N	-1.570738	-0.331427	0.190008
C	-0.739529	0.117814	-0.521274	C	-0.756154	0.256233	-0.490818
C	0.739548	-0.117670	-0.521273	C	0.755638	-0.264279	-0.487324
N	1.520436	-0.084572	0.474704	N	1.570916	0.334576	0.182842
H	-1.017732	-0.143420	1.338190	H	-2.566970	-0.191211	0.340742
H	-1.176419	0.327488	-1.498712	H	-0.894947	1.126290	-1.143766
H	1.176497	-0.326966	-1.498766	H	0.893742	-1.144975	-1.125993
H	1.017660	0.143000	1.338283	H	2.567318	0.196771	0.334697
E = -188.1460166 E[CCSD(T)/CBS] = -187.8518820 ZPVE = 39.2704 kcal mol ⁻¹				E = -187.7970338 E[CCSD(T)/CBS] = -187.4821270 ZPVE = 35.9487 kcal mol ⁻¹			
Frequency	Intensity			Frequency	Intensity		
94.8282	0.3016			66.5313	8.3053		
324.5336	21.0622			346.8916	28.4859		
598.4258	38.4956			384.3400	24.4474		
737.6949	3.2796			497.0294	1483.5325		
881.7964	22.5649			594.1431	35.2628		
940.0155	2.2619			686.3272	73.7259		
1131.6255	2.6948			702.0685	184.9760		
1149.6834	108.9884			874.6726	55.4078		
1223.3553	81.2484			927.8408	8.8379		
1244.8506	130.2409			981.3173	65.6589		
1398.7957	10.4458			1163.7096	22.6937		
1441.4039	10.0213			1171.6610	162.5219		
1667.0358	21.2108			1787.1678	6.9345		
1724.6675	9.6787			1893.3440	35.5643		
3069.2324	11.1999			3014.6340	66.0851		
3088.7263	53.9442			3019.1277	18.4698		
3368.3990	7.5944			3513.5473	869.8649		
3384.9931	2.1737			3522.1596	20.6651		
30f				30f radical cation			
N	-1.438934	-0.559391	-0.068553	N	-1.570738	-0.331427	0.190008
C	-0.739983	0.485058	0.082803	C	-0.756154	0.256233	-0.490818
C	0.739983	0.485059	-0.082808	C	0.755638	-0.264279	-0.487324
N	1.438934	-0.559390	0.068550	N	1.570916	0.334576	0.182842
H	-2.426604	-0.360122	0.086761	H	-2.566970	-0.191211	0.340742
H	-1.163405	1.466932	0.323954	H	-0.894947	1.126290	-1.143766
H	1.163404	1.466931	-0.323967	H	0.893742	-1.144975	-1.125993
H	2.426603	-0.360122	-0.086768	H	2.567318	0.196771	0.334697
E = -188.1420806 E[CCSD(T)/CBS] = -187.8478381				E = -187.7970338 E[CCSD(T)/CBS] = -187.4821270			

ZPVE = 39.1572 kcal mol ⁻¹				ZPVE = 35.9487 kcal mol ⁻¹			
Frequency		Intensity		Frequency		Intensity	
91.3393		0.6251		66.5313		8.3053	
301.7412		2.7910		346.8916		28.4859	
564.8804		108.5640		384.3400		24.4474	
752.9079		67.8008		497.0294		1483.5325	
880.6683		6.8912		594.1431		35.2628	
918.0759		0.6859		686.3272		73.7259	
1121.2615		1.1882		702.0685		184.9760	
1136.7726		15.2552		874.6726		55.4078	
1200.7429		105.9826		927.8408		8.8379	
1249.2578		14.1290		981.3173		65.6589	
1401.1805		7.9023		1163.7096		22.6937	
1444.5350		40.3623		1171.6610		162.5219	
1688.5466		11.5325		1787.1678		6.9345	
1725.8629		20.8101		1893.3440		35.5643	
2991.9445		19.0690		3014.6340		66.0851	
3016.9299		110.1974		3019.1277		18.4698	
3451.5305		0.2513		3513.5473		869.8649	
3452.6481		0.1663		3522.1596		20.6651	
31a				31a radical cation			
N	-1.857965	-0.249580	0.000051	N	-1.848569	-0.311822	0.075313
C	-0.782124	0.159379	-0.000282	C	-0.778519	0.108582	0.040458
C	0.617608	0.623599	-0.000095	C	0.565099	0.641306	-0.004774
N	1.623391	-0.432674	0.000048	N	1.587798	-0.314605	0.222423
H	0.765463	1.259239	0.873973	H	0.696499	1.469452	0.722381
H	0.765623	1.259153	-0.874198	H	0.768295	1.143372	-0.973555
H	1.517490	-1.025731	-0.813987	H	1.380720	-1.298136	0.402652
H	1.517690	-1.025321	0.814401	H	2.567874	-0.031955	0.208789
E = -188.1712752 E[CCSD(T)/CBS] = -187.8797469 ZPVE = 39.8044 kcal mol ⁻¹				E = -187.8105343 E[CCSD(T)/CBS] = -187.5098329 ZPVE = 37.6978 kcal mol ⁻¹			
Frequency		Intensity		Frequency		Intensity	
217.0947		11.3256		203.1660		1.9421	
263.9836		48.4889		239.6376		8.5154	
392.3788		8.1530		318.0006		8.6304	
572.2917		8.7736		560.2146		2.6182	
834.9406		80.6571		648.6034		138.2538	
895.2402		0.0071		843.1803		11.6124	
920.1035		105.2844		851.5227		31.0078	
1098.3360		15.5268		1067.3237		29.0660	
1198.3888		0.0272		1092.5599		48.5262	
1365.9090		8.3000		1165.4292		4.7587	
1386.0396		0.0024		1317.8576		79.3659	
1470.8645		6.6008		1371.3915		1.6454	
1669.8475		22.6328		1612.2951		53.2138	
2342.5142		3.3294		2356.5692		142.0687	
3052.1575		10.8433		2869.2421		53.9387	
3084.9846		3.2925		2884.8530		122.6800	
3500.4286		2.6862		3423.3986		251.9815	
3578.0560		5.8865		3544.7266		186.3473	
31b				31b radical cation			

N	-1.856347	-0.276669	-0.049139	N	-1.848569	-0.311822	0.075313
C	-0.775348	0.114326	-0.040311	C	-0.778519	0.108582	0.040458
C	0.597057	0.625731	0.007326	C	0.565099	0.641306	-0.004774
N	1.563788	-0.471289	-0.008044	N	1.587798	-0.314605	0.222423
H	0.663717	1.296415	0.874291	H	0.696499	1.469452	0.722381
H	0.752490	1.240069	-0.881599	H	0.768295	1.143372	-0.973555
H	1.490067	-1.024635	0.836795	H	1.380720	-1.298136	0.402652
H	2.503773	-0.097755	-0.045632	H	2.567874	-0.031955	0.208789
E = -188.1678585 E[CCSD(T)/CBS] = -187.8770081 ZPVE = 39.6343 kcal mol ⁻¹				E = -187.8105343 E[CCSD(T)/CBS] = -187.5098329 ZPVE = 37.6978 kcal mol ⁻¹			
Frequency		Intensity		Frequency		Intensity	
201.2852		16.2372		203.1660		1.9421	
244.1847		22.3730		239.6376		8.5154	
376.5876		4.9211		318.0006		8.6304	
571.3265		5.8427		560.2146		2.6182	
820.9689		133.3829		648.6034		138.2538	
872.5464		9.4118		843.1803		11.6124	
1002.5787		19.2057		851.5227		31.0078	
1079.0460		12.0004		1067.3237		29.0660	
1193.9981		0.3073		1092.5599		48.5262	
1309.8890		6.8169		1165.4292		4.7587	
1420.8377		13.9038		1317.8576		79.3659	
1493.8847		3.1436		1371.3915		1.6454	
1660.1835		23.3277		1612.2951		53.2138	
2362.9770		2.5075		2356.5692		142.0687	
2968.4700		38.8787		2869.2421		53.9387	
3061.0183		5.4988		2884.8530		122.6800	
3501.1010		1.6018		3423.3986		251.9815	
3583.7071		4.7751		3544.7266		186.3473	
32a				32a radical cation			
N	1.509804	0.437350	-0.073144	N	1.667411	0.393777	0.175503
C	0.633542	-0.471427	-0.169993	C	0.713381	-0.434239	-0.215251
N	-0.663165	-0.472961	0.362563	N	-0.513734	0.007777	-0.198372
C	-1.549245	0.309919	-0.079112	C	-1.674404	0.428738	-0.188318
H	1.139468	1.250185	0.422849	H	2.584924	-0.057526	0.119551
H	0.897913	-1.418671	-0.639718	H	0.837732	-1.462480	-0.554947
H	-2.533870	0.314041	0.381590	H	-2.294028	0.312876	0.704945
H	-1.380179	0.994717	-0.915409	H	-2.088531	0.922363	-1.071653
E = -188.1464816 E[CCSD(T)/CBS] = -187.8499827 ZPVE = 38.9927 kcal mol ⁻¹				E = -187.8129866 E[CCSD(T)/CBS] = -187.5037426 ZPVE = 37.1191 kcal mol ⁻¹			
Frequency		Intensity		Frequency		Intensity	
131.5478		6.2286		146.2711		72.9913	
356.0414		6.4656		201.7486		19.5071	
488.9414		22.8266		498.9933		71.8530	
784.7910		21.2737		519.5742		0.5290	
898.0878		25.1899		624.2358		7.1366	
972.5266		30.7170		954.2008		15.1372	
1087.0189		9.5943		962.8500		4.2621	

1096.0348	63.4294			1077.4466	25.5216		
1216.2903	47.3614			1078.4061	1.4133		
1244.3374	75.5316			1179.1502	41.9496		
1405.0068	25.4842			1252.3788	69.2401		
1504.2033	13.2974			1416.1556	37.0733		
1679.7313	135.8452			1451.0231	9.9398		
1731.0672	49.1981			1905.3280	3.7755		
3017.6547	39.5128			3022.1362	81.7791		
3097.0523	16.8549			3109.5781	5.9199		
3136.4059	21.3949			3120.8604	36.4340		
3429.0404	2.5891			3444.8679	77.8217		
32b				32b radical cation			
N	1.348550	0.491772	-0.031683	N	1.667411	0.393777	0.175503
C	0.606614	-0.531908	-0.113612	C	0.713381	-0.434239	-0.215251
N	-0.724179	-0.530037	0.320667	N	-0.513734	0.007777	-0.198372
C	-1.503622	0.376803	-0.088135	C	-1.674404	0.428738	-0.188318
H	2.293598	0.274082	-0.341144	H	2.584924	-0.057526	0.119551
H	0.931789	-1.517558	-0.454609	H	0.837732	-1.462480	-0.554947
H	-2.521952	0.410579	0.289935	H	-2.294028	0.312876	0.704945
H	-1.198047	1.137553	-0.809963	H	-2.088531	0.922363	-1.071653
E = -188.1476494 E[CCSD(T)/CBS] = -187.8515632 ZPVE = 39.1137 kcal mol ⁻¹				E = -187.8129866 E[CCSD(T)/CBS] = -187.5037426 ZPVE = 37.1191 kcal mol ⁻¹			
Frequency	Intensity			Frequency	Intensity		
175.0512	33.4383			146.2711	72.9913		
374.0774	32.5905			201.7486	19.5071		
523.5614	10.4428			498.9933	71.8530		
787.0167	8.6593			519.5742	0.5290		
881.0313	36.8408			624.2358	7.1366		
967.1744	97.1290			954.2008	15.1372		
1081.9783	6.8574			962.8500	4.2621		
1091.4083	13.5925			1077.4466	25.5216		
1221.1623	14.3682			1078.4061	1.4133		
1243.7137	39.9895			1179.1502	41.9496		
1408.0784	28.2169			1252.3788	69.2401		
1498.2804	19.4364			1416.1556	37.0733		
1672.4574	132.9289			1451.0231	9.9398		
1724.7459	42.6368			1905.3280	3.7755		
3035.5792	40.0882			3022.1362	81.7791		
3055.0074	33.5905			3109.5781	5.9199		
3145.7408	21.5563			3120.8604	36.4340		
3474.3770	1.1711			3444.8679	77.8217		
33				33 radical cation			
N	0.579134	0.430306	-0.353845	N	-0.528544	0.147501	-0.280981
N	-0.579129	0.430382	0.353781	N	0.587463	0.276432	0.371368
C	-1.546028	-0.279947	-0.054901	C	1.776606	0.211420	-0.051757
C	1.546014	-0.279982	0.054957	C	-1.717784	0.213747	0.141890
H	-2.479373	-0.226308	0.491143	H	2.571387	0.350330	0.672240
H	-1.479500	-0.928267	-0.928336	H	2.000500	0.024136	-1.100112
H	1.479458	-0.928182	0.928479	H	-1.941933	0.402024	1.190023
H	2.479370	-0.226436	-0.491078	H	-2.512526	0.075590	-0.582299

E = -188.1190334 E[CCSD(T)/CBS] = -187.8196334 ZPVE = 38.2201 kcal mol ⁻¹		E = -187.8025521 E[CCSD(T)/CBS] = -187.4907368 ZPVE = 38.1541 kcal mol ⁻¹	
Frequency	Intensity	Frequency	Intensity
99.3768	7.7500	175.4002	30.7183
379.6311	1.6901	271.9035	36.5294
468.7342	8.1363	576.1779	0.0000
808.3847	0.0854	643.5299	0.0158
841.1906	1.9835	680.5272	0.0000
893.9912	34.3193	971.8093	0.0000
1006.2452	22.4595	1077.6632	0.0301
1009.6015	27.2347	1078.4043	50.4622
1195.3877	9.9529	1104.9700	36.5644
1205.8219	14.5904	1191.3637	0.0000
1457.0066	6.7004	1436.3643	56.9847
1490.1173	1.7560	1470.9823	0.0000
1686.2351	3.3081	1686.1864	28.4630
1690.2271	0.3261	1705.6263	0.0019
3060.7358	37.6300	3090.2015	18.1115
3061.1499	12.5977	3090.2570	53.0022
3190.7435	20.8490	3218.6517	48.7280
3190.7907	2.6794	3219.1816	0.1864

References

- 1 M. J. Abplanalp, M. Forstel and R. I. Kaiser, *Chem. Phys. Lett.*, 2016, **644**, 79-98.
- 2 A. M. Turner, M. J. Abplanalp, S. Y. Chen, Y. T. Chen, A. H. H. Chang and R. I. Kaiser, *Phys. Chem. Chem. Phys.*, 2015, **17**, 27281-27291.
- 3 P. A. Gerakines, Y. Y. Yarnall and R. L. Hudson, *Mon. Not. R. Astron. Soc.*, 2021, **509**, 3515-3522.
- 4 M. Satorre, J. Leliwa-Kopystynski, C. Santonja and R. Luna, *Icarus*, 2013, **225**, 703-708.
- 5 J. Wang, C. Zhang, J. H. Marks, M. M. Evseev, O. V. Kuznetsov, I. O. Antonov and R. I. Kaiser, *Nat. Commun.*, 2024, **15**, 10189.
- 6 D. Drouin, A. R. Couture, D. Joly, X. Tastet, V. Aimez and R. Gauvin, *Scanning*, 2007, **29**, 92-101.
- 7 A. G. Yeghikyan, *Astrophysics*, 2011, **54**, 87-99.
- 8 M. Frisch, G. Trucks, H. Schlegel, G. Scuseria, M. Robb, J. Cheeseman, G. Scalmani, V. Barone, B. Mennucci and G. Petersson, et al., Gaussian 16, Revision C.1, Gaussian Inc., Wallingford CT, 2019.
- 9 A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648-5652.
- 10 A. D. Becke, *Phys. Rev. A*, 1988, **38**, 3098-3100.
- 11 C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785-789.
- 12 T. H. Dunning, *J. Chem. Phys.*, 1989, **90**, 1007-1023.
- 13 J. Čížek, *J. Chem. Phys.*, 1966, **45**, 4256-4266.
- 14 R. J. Bartlett, J. D. Watts, S. A. Kucharski and J. Noga, *Chem. Phys. Lett.*, 1990, **165**, 513-522.
- 15 K. Raghavachari, *Annu. Rev. Phys. Chem.*, 1991, **42**, 615-642.
- 16 J. F. Stanton, *Chem. Phys. Lett.*, 1997, **281**, 130-134.
- 17 F. Neese, *WIREs Comput. Mol. Sci.*, 2018, **8**, e1327.
- 18 K. A. Peterson, D. E. Woon and T. H. D. Jr., *J. Chem. Phys.*, 1994, **100**, 7410-7415.
- 19 N. A. Tarasenko, A. A. Tishenkov, V. G. Zaikin, V. V. Volkova and L. E. Gusel'nikov, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1986, **35**, 2196-2196.
- 20 A. D. Baker, D. Betteridge, N. R. Kemp and R. E. Kirby, *Anal. Chem.*, 1970, **42**, 1064-1073.
- 21 S. G. Lias, Ionization Energy Evaluation, in NIST Chemistry WebBook, NIST Standard Reference Database Number 69, ed. P. J. Linstrom and W. G. Mallard, National Institute of Standards and Technology, Gaithersburg MD, 20899, DOI: 10.18434/T4D303, accessed October 1, 2025.
- 22 M. H. Palmer, I. Simpson and J. R. Wheeler, *Z. Naturforsch. A*, 1981, **36**, 1246-1252.
- 23 H. Bock and R. Dammel, *Chem. Ber.*, 1987, **120**, 1971-1985.
- 24 C. Fridh, L. Åsbrink, B. Ö. Jonsson and E. Lindholm, *Int. J. Mass. Spectrom. Ion Phys.*, 1972, **8**, 85-99.
- 25 J. Kua and K. L. Thrush, *J. Phys. Chem. B*, 2016, **120**, 8175-8185.
- 26 M. Heaven, T. Sears, V. E. Bondybey and T. A. Miller, *J. Chem. Phys.*, 1981, **75**, 5271-5279.
- 27 D. Touboul, F. Gaie-Levrel, G. A. Garcia, L. Nahon, L. Poisson, M. Schwell and M. Hochlaf, *J. Chem. Phys.*, 2013, **138**.
- 28 A. Khan, *Comput. Theor. Chem.*, 2013, **1013**, 136-139.
- 29 N. J. Kim, G. Jeong, Y. S. Kim, J. Sung, S. Keun Kim and Y. D. Park, *J. Chem. Phys.*, 2000, **113**, 10051-10055.

- 30 E. Nir, K. Kleinermanns, L. Grace and M. S. de Vries, *J. Phys. Chem. A*, 2001, **105**, 5106-5110.
- 31 P. A. Gerakines, Y. Y. Yarnall and R. L. Hudson, *Icarus*, 2024, **413**, 116007.
- 32 T. Streibel, K. Hafner, F. Mühlberger, T. Adam and R. Zimmermann, *Appl. Spectrosc.*, 2006, **60**, 72-79.
- 33 G. Socrates, *Infrared and raman characteristic group frequencies: Tables and charts*, John Wiley & Sons, Ltd., New York, 3rd edn., 2004.
- 34 F. Stroh and M. Winnewisser, *Chem. Phys. Lett.*, 1989, **155**, 21-26.
- 35 R. J. Blanch and A. McCluskey, *Chem. Phys. Lett.*, 1995, **241**, 116-120.
- 36 P. A. Gerakines, M. H. Moore and R. L. Hudson, *Icarus*, 2004, **170**, 202-213.
- 37 J. R. Brucato, G. A. Baratta and G. Strazzulla, *Astron. Astrophys.*, 2006, **455**, 395-399.
- 38 G. Danger, F. Borget, M. Chomat, F. Duvernay, P. Theulé, J.-C. Guillemin, L. Le Sergeant d'Hendecourt and T. Chiavassa, *Astron. Astrophys.*, 2011, **535**, A47.
- 39 T. J. Lee and P. R. Taylor, *Int. J. Quantum Chem.*, 1989, **36**, 199-207.