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 (NH_3, 99.999%, Matheson), and phosphine (PH_3, 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 NH_3−HCN and PH_3–HCN ice mixtures, NH_3 or PH_3 gas was introduced independently from HCN via an additional capillary array, at partial pressures of 6×10^{-9} Torr (NH_3) and 5×10^{-9} Torr (PH_3). 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, NH_3–HCN, and PH_3–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 NH_3–HCN (n = 1.36 ± 0.04) and PH_3–HCN (n = 1.43 ± 0.12) ice mixtures. Refractive indices of 1.38 ± 0.03 for NH_3 at 13 K[4] and 1.51 ± 0.04 for PH_3 at 5.5 K[2] 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 calculted 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 ± 0.5)× 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 CH_2N_2, CH_4N_2, $C_2H_2N_2$, and $C_2H_4N_2$ isomers were performed using Gaussian 16, Revision C.01.[8] The density functional theory (DFT) B3LYP functional[9-11] 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 cluster[13-16] 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, IE = 9.88 ± 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 $C_3H_4N_2$ isomers such as 1H-pyrazole (IE = 9.27 ± 0.05 eV)[20] and 1H-imidazole (IE = 8.81 ± 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 C_4H_7N and/or $C_2H_3N_3$ isomers, such as 1H-1,2,4-triazole (IE = 9.80 eV)[22] and 1-pyrroline (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 $C_3H_3N_3$ isomers such as aminomalononitrile (**6**) and 1,3,5-triazine (*c*-$C_3H_3N_3$, IE = 10.01 ± 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 $C_3H_5N_3$, $C_4H_3N_3$, $C_4H_4N_4$, $C_4H_3N_5$, $C_5H_5N_5$, and $C_5H_6N_6$ 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 $C_4H_4N_4$; and 2,6-diaminopurine ($C_5H_6N_6$, **12**) for $C_5H_6N_6$ isomers. Notably, the $C_5H_5N_5$ isomers may be linked to adenine (**3**, IE = 8.267 ± 0.005 eV)[27] and/or 2-aminopurine (**12**, 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 cm^{-1}, corresponding to the 0–0 band of the ππ* 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.

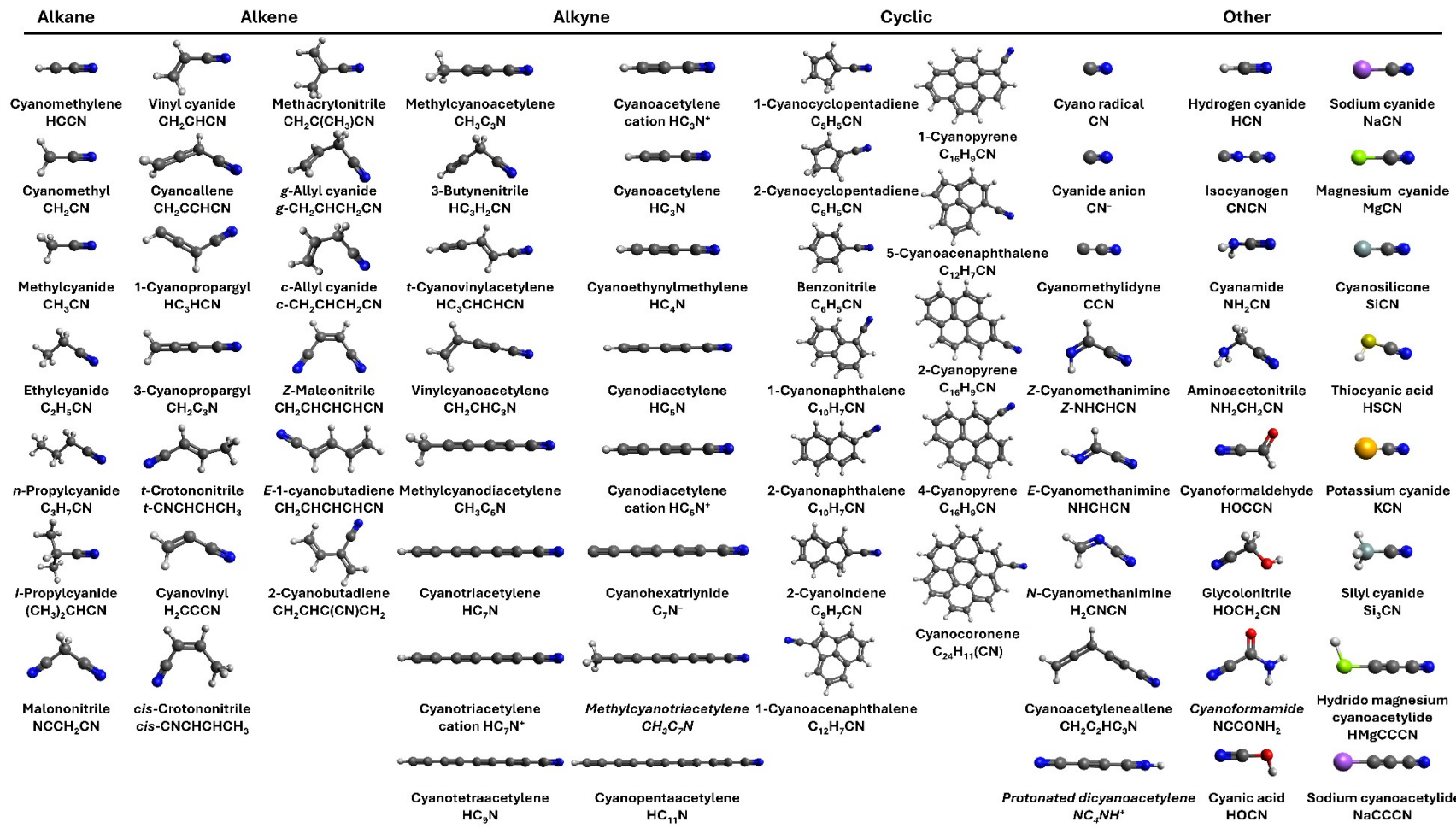


Figure S1. Known interstellar C≡N-containing molecules. Atoms are color-coded as follows: hydrogen (white), carbon (gray), nitrogen (blue), oxygen (red), sodium (purple), magnesium (green), potassium (orange), silicon (silver), and sulfur (yellow). Tentative identified molecules are shown in italics.

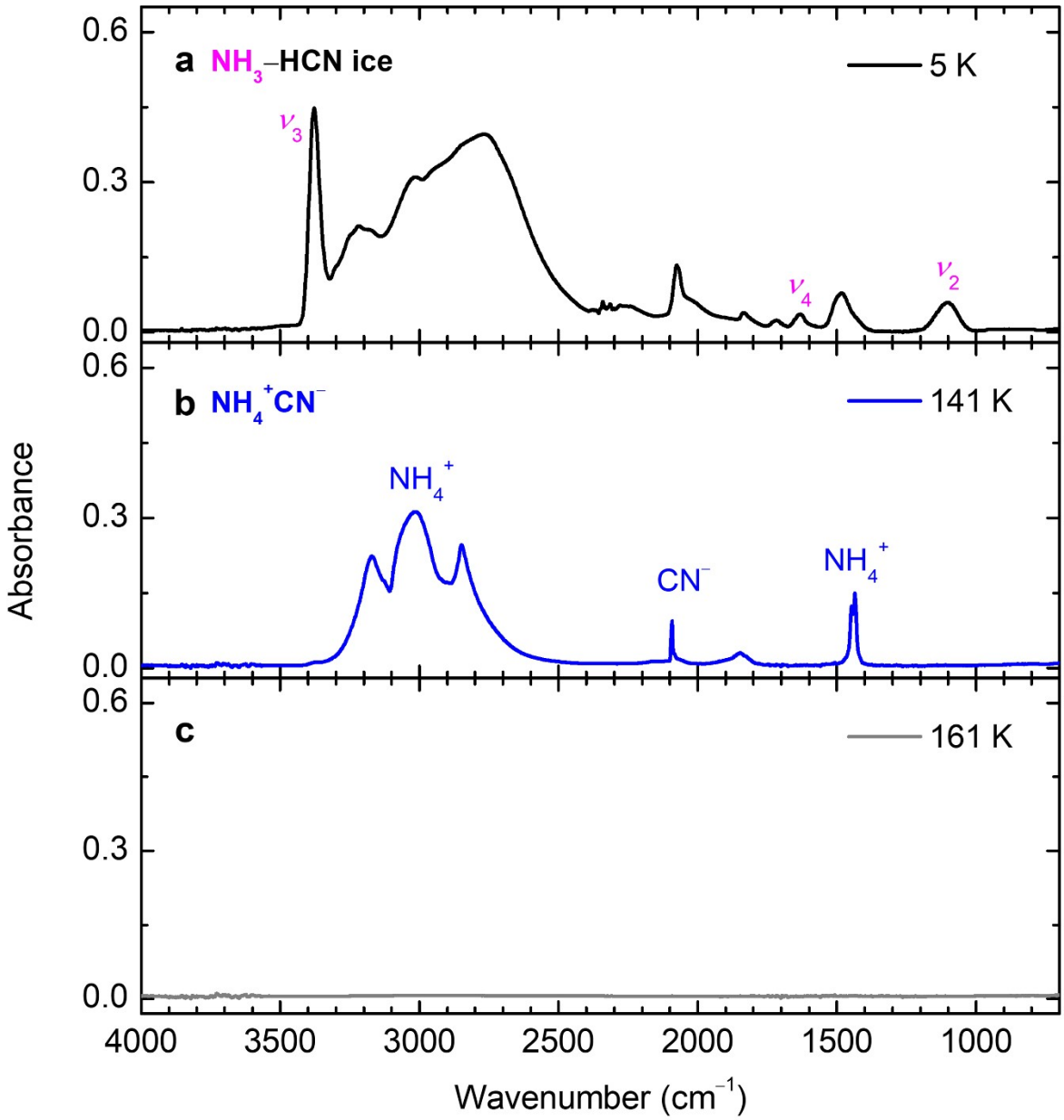


Figure S2. Infrared spectra of NH_3–HCN ice with a thickness of 820 ± 50 nm recorded at 5 K (a), 141 K (b), and 161 K (c). After deposition at 5 K, the ice was heated to 320 K at 1 K min^{-1}. At 141 K, NH_3 and HCN sublime, leaving only NH_4CN, which remains until 161 K. The NH_4CN spectrum matches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

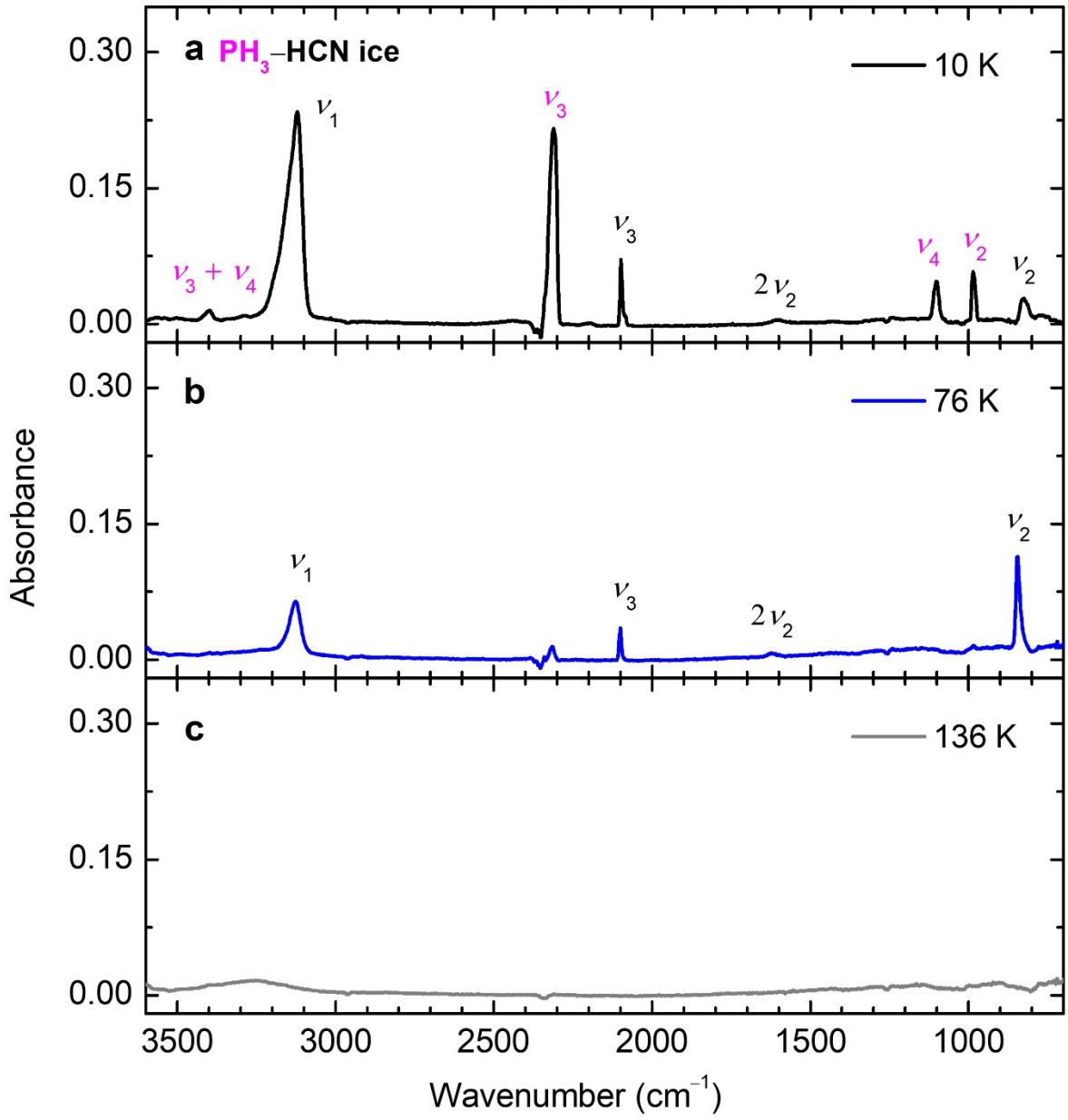


Figure S3. Infrared spectra of PH_3–HCN ice with a thickness of 670 ± 80 nm recorded at 10 K (a), 76 K (b), and 136 K (c). After deposition at 10 K, the PH_3–HCN ice was heated to 320 K at 1 K min^{-1}. At 76 K, PH_3 sublimes and only HCN remains; at 136 K both reactant sublime. Absorptions of PH_3 and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

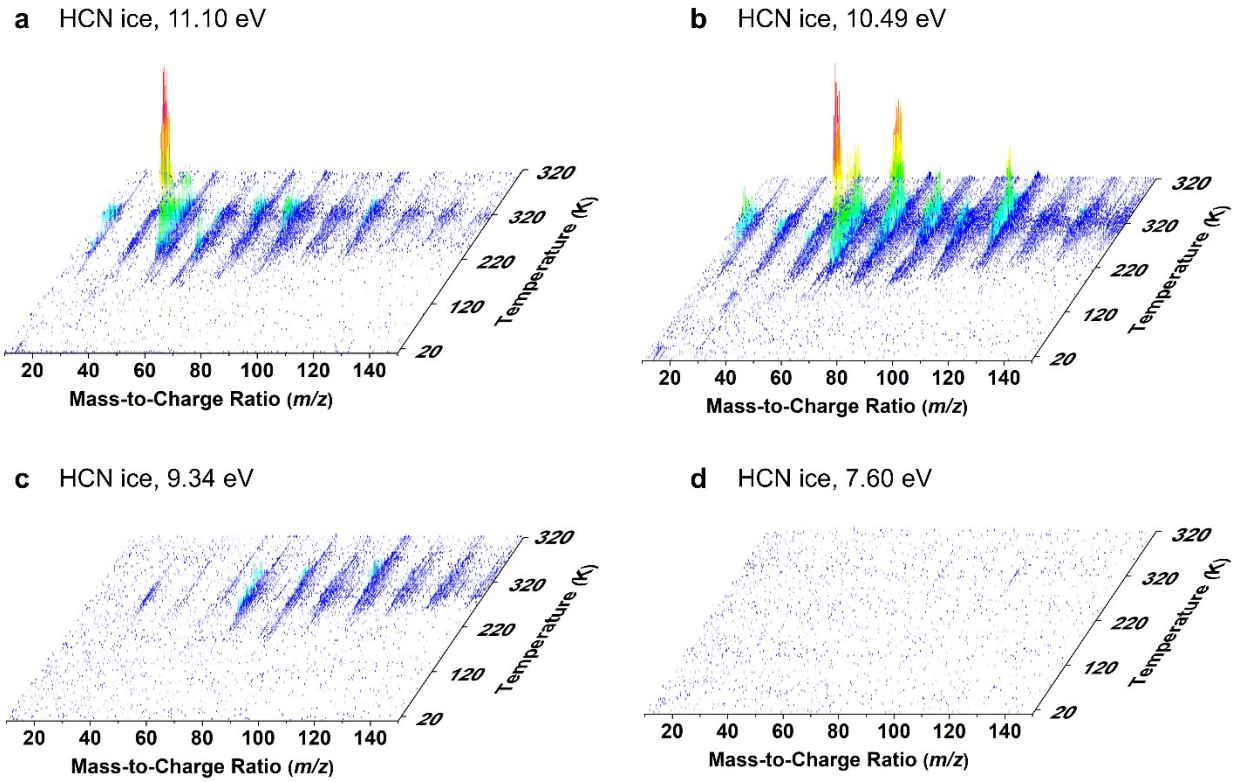


Figure S4. PI-ReToF-MS data of irradiated HCN ices during TPD, recorded at 11.10 (a), 10.49 (b), 9.34 (c), and 7.60 eV (d).

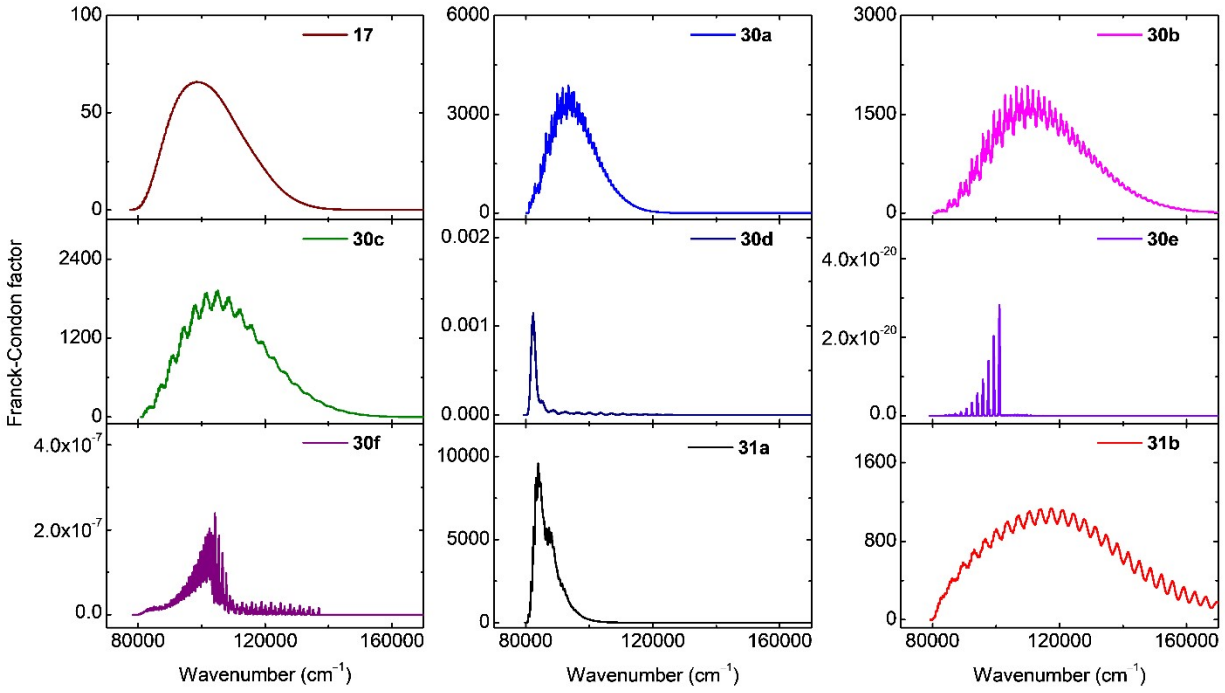


Figure S5. Calculated Franck–Condon factors for isomers **17**, **30**, and **31** as a function of the energy.

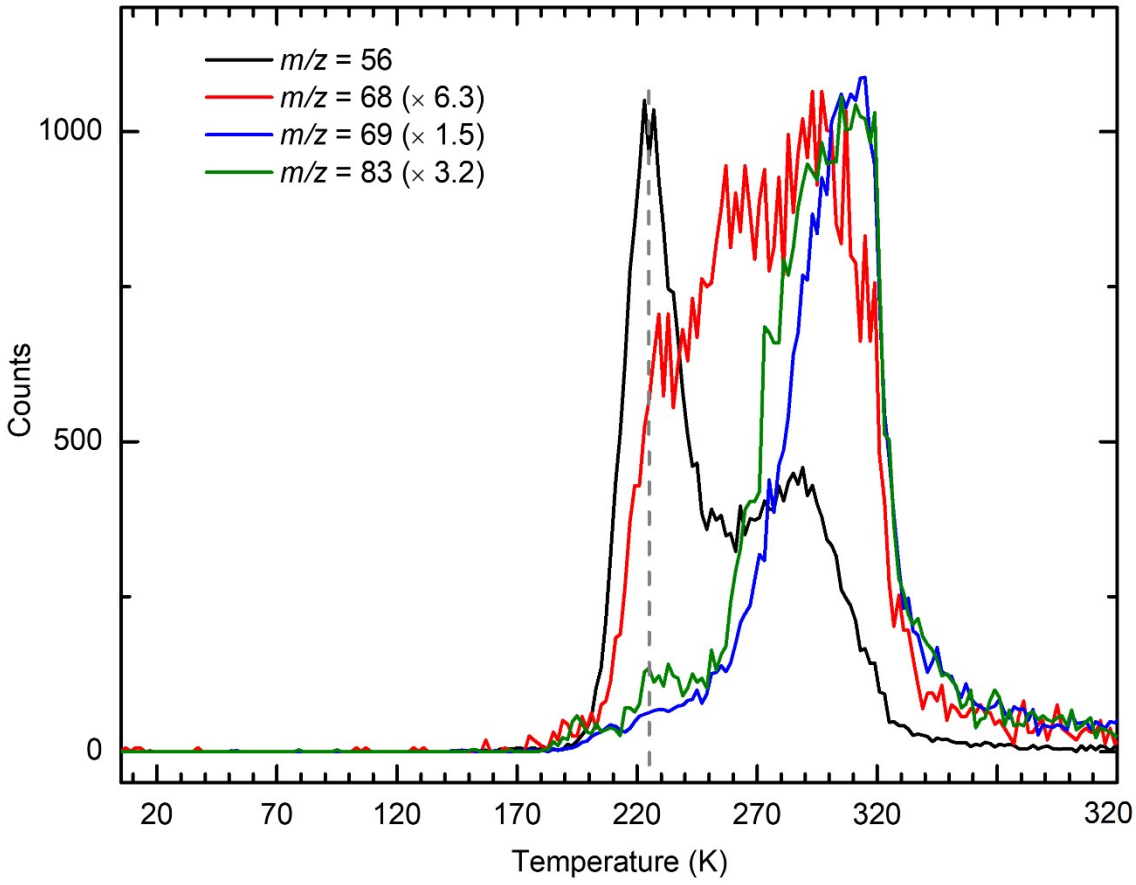


Figure S6. TPD profiles of *m/z* = 56, 68, 69, and 83 in irradiated HCN ice measured at 10.49 eV.

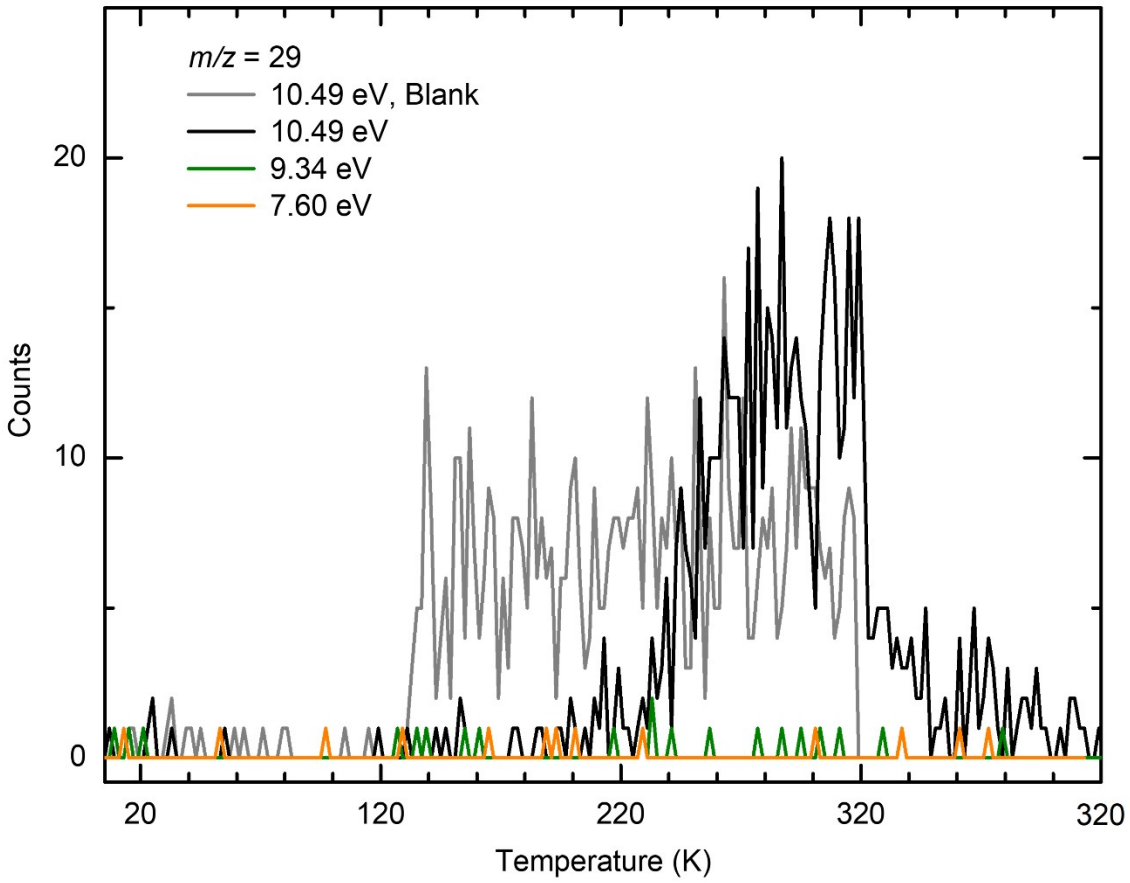


Figure S7. TPD profiles of irradiated HCN ices at *m/z* = 29 recorded at photon energies of 10.49, 9.34, and 7.60 eV.

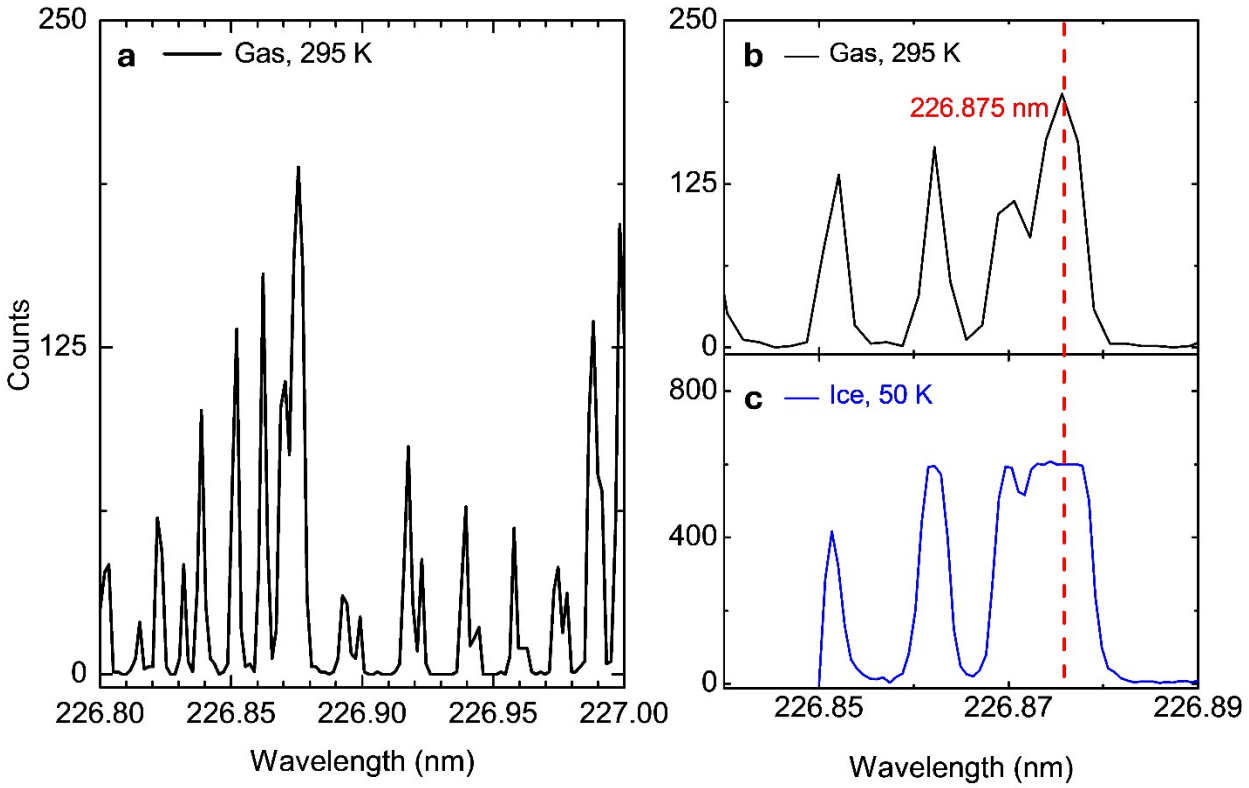


Figure S8. REMPI scan from 226.80–227.00 nm for nitrogen monoxide (NO) at 295 K in the gas phase (a and b) and NO ice at 50 K. The red dashed line indicates the wavelength at the maximum signal, which corresponds to transition from a higher ground state at 226.875 nm ($A^2\Sigma^+ \leftarrow X^2\Pi_{3/2}$). 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]

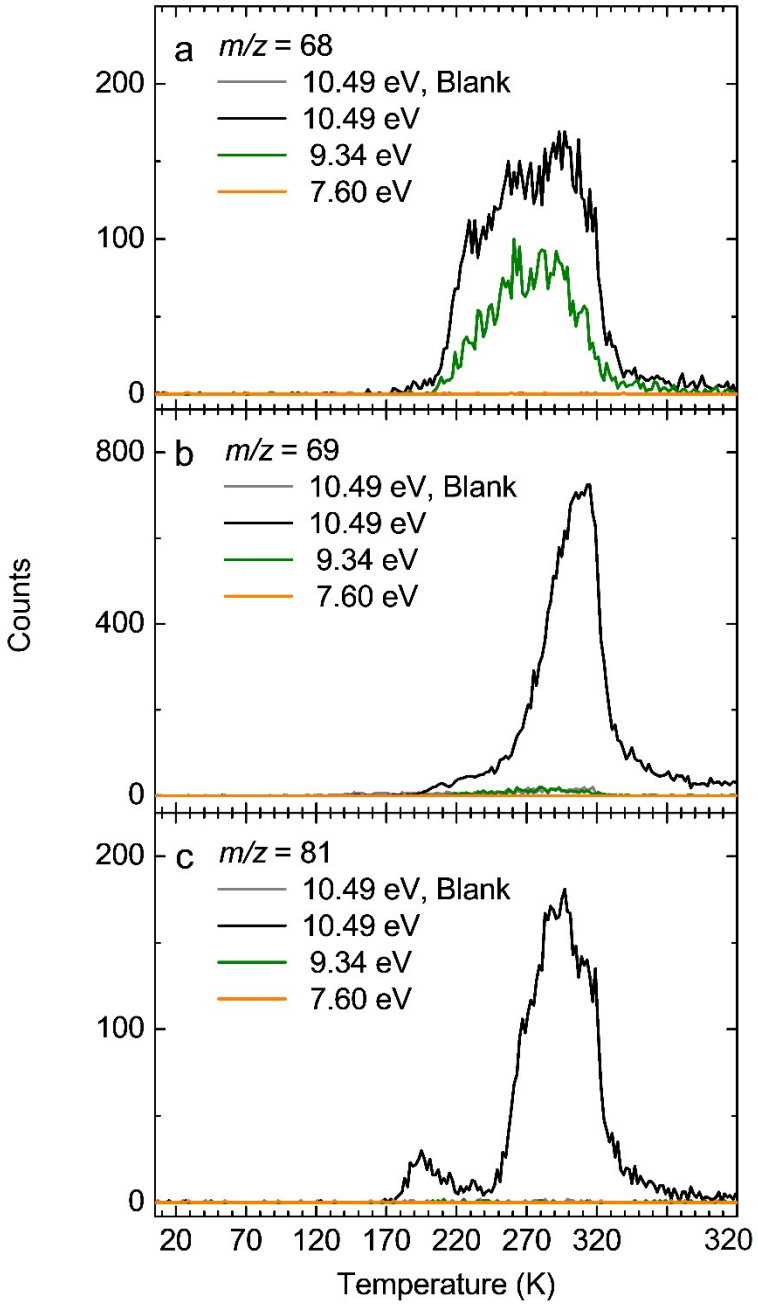


Figure S9. TPD profiles of irradiated HCN ices at *m/z* = 68 (a), 69 (b), and 81 (c) recorded at photon energies of 10.49, 9.34, and 7.60 eV.

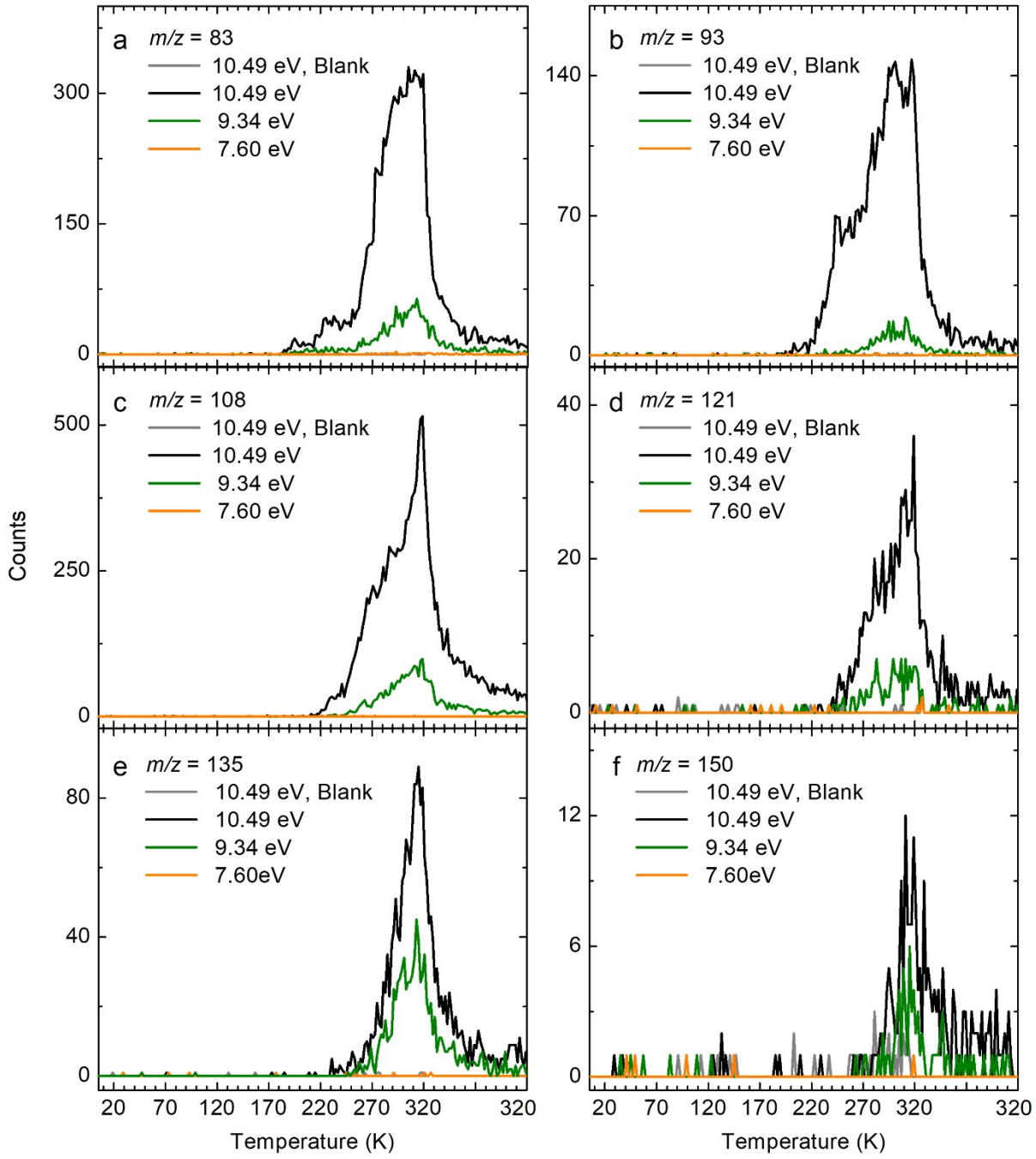


Figure S10. TPD profiles of irradiated HCN ices at *m/z* = 83 (a), 93 (b), 108 (c), 121 (d), 135 (e) and 150 (f) recorded at photon energies of 10.49, 9.34, and 7.60 eV.

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	ν(NH)[33]
2978	ν(CH)[33]
2303	ν_1 (CNCN)[34]
2259, 2213	ν(C≡N)[33]
2142	ν(NCCN)[35] ν(−N≡C)[33]
2090, 2068	ν(C≡N) (CN^-)[36]
1454	ν(NH) (NH_4^+)[37]
Absorptions after TPD (cm^{-1})	Assignment
3331, 3187	ν(NH)[33]
2978	ν(CH)[33]
2230	ν(C≡N)[33]
2193, 2165, 2142	ν(C≡N) ν(C=C=N)[33]
1686, 1632, 1559	ν(C=N)[33]
1359	δ(CH)[38]

Table S2. Observed absorption peaks of PH_3–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.

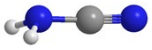
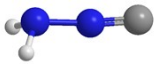
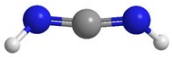
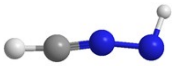
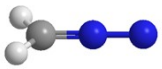
Ice Composition	Thickness (nm)	Current (nA)	Irradiation time (s)	Dose (eV/ HCN)	VUV Photon energy (eV)
HCN	590 ± 50	–	–	–	10.49
HCN	540 ± 50	104 ± 3	3600 ± 10	8.2 ± 1.3	10.49
HCN[a]	540 ± 50	101 ± 3	3600 ± 10	8.0 ± 1.3	10.49
HCN	540 ± 50	107 ± 3	3600 ± 10	8.4 ± 1.3	9.34
HCN	540 ± 50	106 ± 1	3600 ± 10	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.

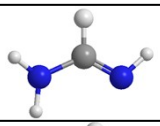
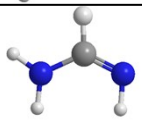
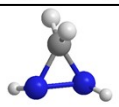
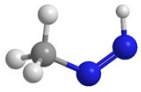
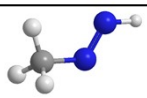
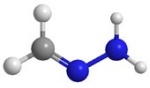
Isomer	Structure	ΔE (kJ mol^{-1})	T1 diagnostic	Computed IE (eV)	Corrected IE ranges (eV)
26a		0	0.013	9.21	9.13–9.23
26b		2	0.013	9.14	9.06–9.16
27a		45	0.009	9.30	9.22–9.32
27b		50	0.010	9.00	8.92–9.02
28a		35	0.012	9.01	8.93–9.03
28b		31	0.011	8.93	8.85–8.95
29		29	0.012	8.82	8.74–8.84

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.

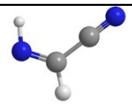
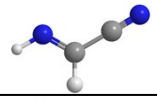
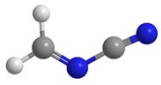
Isomer	Structure	ΔE (kJ mol^{-1})	T1 diagnostic	Computed IE (eV)	Corrected IE ranges (eV)
5a		0	0.013	10.98	10.90–11.00
5b		1	0.013	10.95	10.87–10.97
15		7	0.016	10.56	10.48–10.58

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.

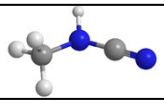
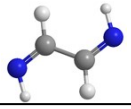
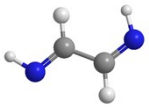
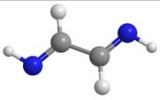
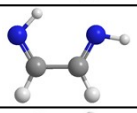
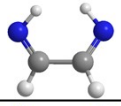
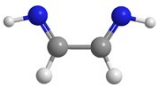
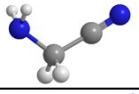
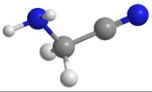
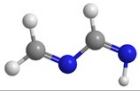
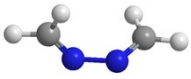
Isomer	Structure	ΔE (kJ mol^{-1})	T1 diagnostic	Computed IE (eV)	Corrected IE ranges (eV)
17		6	0.012	9.83	9.75–9.85
30a		15	0.012	10.01	9.93–10.03
30b		14	0.012	10.04	9.96–10.06
30c		13	0.012	10.10	10.02–10.12
30d		15	0.012	9.99	9.91–10.01
30e		17	0.013	9.92	9.84–9.94
30f		19	0.012	9.81	9.73–9.83
31a		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 = –148.4666977			
E[CCSD(T)/CBS] = –148.6218664				E[CCSD(T)/CBS] = –148.2320102			
ZPVE = 21.3255 kcal mol^{-1}				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 = –148.3944089			
E[CCSD(T)/CBS] = –148.5532859				E[CCSD(T)/CBS] = –148.1668715			
ZPVE = 20.8699 kcal mol^{-1}				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
C	–1.364295	0.082473	0.000000

E = –148.7779304
E[CCSD(T)/CBS] = –148.5505730
ZPVE = 21.1217 kcal mol^{-1}

Frequency	**Intensity**
265.2047	1.3549
352.4071	5.3779
844.4880	123.4833
1053.5386	20.4404
1342.8954	4.3799
1659.9976	20.8101
2217.9883	33.3598
3475.3431	10.6086
3562.9747	30.3254

H	1.551752	–0.348026	0.894629
C	–1.379951	0.155752	0.000000

E = –148.4049327
E[CCSD(T)/CBS] = –148.1704840
ZPVE = 19.9534 kcal mol^{-1}

Frequency	**Intensity**
175.4666	0.5911
200.5967	13.5137
680.8759	159.9760
1184.4584	5.7116
1235.4504	0.3794
1629.3049	49.6841
2020.0144	329.4370
3352.5758	217.4749
3478.8618	238.6257

23

C	0.000198	–0.017909	–0.001709
N	–1.210768	0.085927	–0.094204
N	1.210975	0.071883	0.106055
H	1.815238	–0.464925	–0.499808
H	–1.814131	–0.533026	0.428497

E = –148.8497725
E[CCSD(T)/CBS] = –148.6162695
ZPVE = 20.4910 kcal mol^{-1}

Frequency	**Intensity**
545.1149	0.4443
548.9176	72.7798
715.7462	89.5040
916.9507	441.9046
918.5857	14.6197
1288.0138	0.0000
2216.4862	703.4179
3590.3990	147.2469
3593.4584	23.8482

23 radical cation

C	–0.000000	0.000000	0.083712
N	1.200028	–0.000000	–0.075291
N	–1.200028	0.000000	–0.075291
H	–2.006664	0.000000	0.547749
H	2.006664	–0.000000	0.547749

E = –148.4734161
E[CCSD(T)/CBS] = –148.2364167
ZPVE = 18.1807 kcal mol^{-1}

Frequency	**Intensity**
222.7380	351.8951
471.8782	13.1116
517.2969	28.5769
592.9679	0.0000
760.4516	109.7934
1318.4123	0.1256
1805.2224	8.9475
3504.3791	705.5516
3524.2359	150.0997

24

N	0.271502	–1.115568	0.073407
N	–0.025194	0.081571	–0.024001
C	–0.461331	1.161709	–0.248514
H	1.285438	–1.225761	0.024303
H	–0.701095	1.993220	0.387868

E = –148.7640902
E[CCSD(T)/CBS] = –148.5295357
ZPVE = 19.8592 kcal mol^{-1}

Frequency	**Intensity**
475.0401	8.9772
529.5602	116.8626
646.9055	283.3073
839.1999	40.2271

24 radical cation

N	–1.176243	–0.090731	–0.000000
N	0.081251	0.054106	–0.000000
C	1.234581	–0.014317	0.000000
H	–1.647936	0.829678	–0.000000
H	2.311445	–0.049892	0.000000

E = –148.4296348
E[CCSD(T)/CBS] = –148.1943337
ZPVE = 18.8538 kcal mol^{-1}

Frequency	Intensity
421.8955	33.3892
436.6575	26.3120
624.0977	44.9530
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 CH_4N_2 isomers (**26**–**29**) calculated at the B3LYP/aug-cc-pVTZ level of theory.

26a

C	0.124215	0.390795	0.004104
N	–1.130788	–0.149640	–0.039827
H	–1.917006	0.414319	0.225670
H	–1.209396	–1.142963	0.107689
N	1.173886	–0.327652	0.007392
H	2.010191	0.245278	–0.005731
H	0.117497	1.484319	0.001316

E = –150.0747509
E[CCSD(T)/CBS] = –149.8416057
ZPVE = 36.2767 kcal mol^{-1}

Frequency	Intensity
323.9944	189.2314
529.7157	52.7422
566.4464	56.3726
799.8562	52.6571
1045.7063	0.1550
1085.9738	1.4998
1106.1327	135.0403
1327.6269	34.3001
1405.6192	27.3661
1623.5773	23.9199
1717.5330	333.8229
3037.7056	52.9597
3523.6432	8.1441
3575.8011	27.9227
3706.6268	38.8390

26a radical cation

C	0.062044	0.395623	0.000188
N	–1.105475	–0.172708	0.017445
H	–1.949034	0.385708	0.016288
H	–1.206010	–1.181046	0.054195
N	1.206968	–0.252159	–0.103154
H	1.966975	–0.092900	0.562890
H	0.105358	1.488570	–0.034542

E = –149.7457201
E[CCSD(T)/CBS] = –149.5015206
ZPVE = 35.3635 kcal mol^{-1}

Frequency	Intensity
409.7630	68.2658
479.2961	3.0502
656.2661	146.4758
727.4472	168.2941
824.0285	248.8064
1016.9103	19.7374
1098.0430	13.3955
1192.4395	27.7616
1372.6349	11.3494
1608.3038	8.1793
1702.3254	187.8618
3062.7115	24.1714
3458.0587	223.8259
3506.8820	167.6935
3622.0355	173.9917

26b

C	–0.123033	0.419650	0.005029
N	1.114821	–0.176808	–0.039900
H	1.924851	0.370207	0.193426
H	1.188113	–1.166086	0.130512
N	–1.272408	–0.121709	0.003629
H	–1.222104	–1.140964	–0.001128
H	–0.064633	1.507563	0.005718

E = –150.0715111
E[CCSD(T)/CBS] = –149.8386295
ZPVE = 36.1586 kcal mol^{-1}

Frequency	Intensity
324.8763	222.9546
479.6169	8.0422
542.2013	12.1539
834.1795	31.0380

26b radical cation

C	–0.062024	0.395941	–0.000181
N	1.105372	–0.172856	–0.017482
H	1.949249	0.385138	–0.016605
H	1.205731	–1.181250	–0.053679
N	–1.206989	–0.252036	0.103261
H	–1.966594	–0.094155	–0.563590
H	–0.104924	1.488867	0.034507

E = –149.7457201
E[CCSD(T)/CBS] = –149.5015238
ZPVE = 35.3610 kcal mol^{-1}

Frequency	Intensity
408.6556	68.4002
479.5326	3.0434
656.3551	146.4057
727.6848	168.3981

1047.2382	26.8859
1076.1640	44.4313
1112.9817	18.0452
1313.2689	154.3167
1421.7872	1.3285
1637.2208	29.0139
1710.6281	322.8984
3097.6048	24.9002
3432.9580	10.6909
3572.2889	22.2152
3690.3003	26.0450

823.9620	248.4861		
1016.8942	19.7846		
1097.9142	13.4087		
1192.3128	27.6890		
1372.4803	11.3832		
1608.0689	8.3471		
1702.1135	187.7688		
3063.1413	24.1844		
3457.9088	223.8729		
3506.6759	167.6829		
3621.6785	173.8637		

27a

C	0.000000	0.000000	0.796035
N	0.001750	0.749348	–0.438722
N	–0.001750	–0.749348	–0.438722
H	–0.910937	0.080246	1.377899
H	0.910937	–0.080246	1.377899
H	–0.957543	–0.997388	–0.680134
H	0.957543	0.997388	–0.680134

E = –149.9980822
E[CCSD(T)/CBS] = –149.7703197
ZPVE = 36.9505 kcal mol^{-1}

Frequency	Intensity
759.8100	1.6634
878.6514	47.0992
974.1207	33.2830
979.6626	3.7176
1150.5893	21.2648
1200.9833	39.1312
1212.3224	42.4932
1242.6917	7.0034
1324.3763	8.7343
1393.4893	0.2538
1530.8527	0.2801
3092.5163	29.9202
3174.3345	16.2290
3462.5017	2.0730
3470.3176	1.1106

27a radical cation

C	0.000000	0.000000	0.865470
N	–0.000227	0.655237	–0.434820
N	0.000227	–0.655237	–0.434820
H	–0.929419	0.096563	1.409837
H	0.929419	–0.096563	1.409837
H	–0.621249	–1.272217	–0.963919
H	0.621249	1.272217	–0.963919

E = –149.6676134
E[CCSD(T)/CBS] = –149.4268374
ZPVE = 35.7669 kcal mol^{-1}

Frequency	Intensity
509.8498	298.9290
758.5124	46.5912
778.0105	19.0386
1050.2442	1.0426
1072.5562	0.2975
1085.0983	44.1764
1182.1598	45.4709
1184.7756	3.4939
1202.7666	43.7611
1416.2681	11.4134
1536.3842	0.0001
3133.9925	1.5030
3255.9712	8.8249
3419.5168	309.9401
3433.2319	126.2067

27b

C	0.077309	0.791311	–0.000000
N	0.076337	–0.443950	0.752719
N	0.076337	–0.443950	–0.752719
H	1.011107	1.339064	–0.000000
H	–0.816911	1.405544	–0.000000
H	–0.872749	–0.623936	–1.076546
H	–0.872749	–0.623936	1.076546

E = –149.9901330
E[CCSD(T)/CBS] = –149.7625037
ZPVE = 36.6441 kcal mol^{-1}

Frequency	Intensity

27b radical cation

C	0.056732	0.861805	0.000000
N	0.056732	–0.439433	0.657763
N	0.056732	–0.439433	–0.657763
H	1.004454	1.379601	0.000000
H	–0.864601	1.430517	0.000000
H	–0.637246	–0.914439	–1.238573
H	–0.637246	–0.914439	1.238573

E = –149.6712951
E[CCSD(T)/CBS] = –149.4310582
ZPVE = 36.1034 kcal mol^{-1}

Frequency	Intensity

736.7964	0.6498
841.5707	48.5828
948.6906	0.3041
970.5709	26.8681
1166.4982	7.3409
1174.2894	0.0202
1188.1894	3.9306
1235.4651	17.9341
1332.3320	25.1505
1374.2869	27.3562
1528.2634	0.9069
3091.8606	28.2343
3179.6453	14.2658
3416.6876	0.0087
3447.7912	3.1705

664.7188	155.4441		
780.4221	9.9362		
800.6745	117.0918		
1000.8804	4.9833		
1039.9269	10.5999		
1090.4992	18.3888		
1187.8346	7.1021		
1234.4027	43.3762		
1234.7182	109.0802		
1406.8574	15.5759		
1530.3822	0.0152		
3135.5047	2.9036		
3261.8176	12.5383		
3432.5745	158.6206		
3453.5017	197.9753		

28a

C	–0.989846	–0.503599	0.000000
N	–0.000818	0.572451	0.000000
N	1.193659	0.286802	0.000000
H	1.344584	–0.749895	0.000000
H	–1.623066	–0.381721	0.879439
H	–0.522189	–1.496666	0.000000
H	–1.623066	–0.381721	–0.879439

E = –150.0150922
E[CCSD(T)/CBS] = –149.7842167
ZPVE = 35.0829 kcal mol^{-1}

Frequency	Intensity
208.2163	5.8096
579.4525	0.8886
870.8177	39.5767
904.4311	6.4323
1145.3661	4.3879
1159.9319	7.2415
1406.4976	11.3572
1456.3965	6.9166
1466.2552	2.6795
1495.6093	84.9995
1672.6118	22.8868
2968.2290	33.6876
3023.1743	89.1685
3082.0125	10.0084
3101.8589	4.5678

28a radical cation

C	–1.015113	–0.656918	0.000000
N	0.000000	0.395414	0.000000
N	1.138136	0.563617	0.000000
H	1.895338	–0.155922	0.000000
H	–1.625124	–0.493132	0.888701
H	–0.521366	–1.629532	0.000000
H	–1.625124	–0.493132	–0.888701

E = –149.6943748
E[CCSD(T)/CBS] = –149.4514699
ZPVE = 34.1198 kcal mol^{-1}

Frequency	Intensity
147.0872	31.9718
365.8564	5.0759
658.3581	63.0480
770.1225	6.5335
948.3961	272.8297
1104.9284	0.2011
1119.8540	4.6655
1395.3739	13.6974
1416.1121	20.8768
1454.5211	42.4526
2091.5867	23.9620
3026.7145	43.4215
3103.1839	111.4169
3128.2895	24.8058
3136.7586	8.9612

28b

C	–1.007934	–0.522876	0.000000
N	0.000598	0.533659	0.000000
N	1.157998	0.106065	0.000000
H	1.783659	0.924711	0.000000
H	–1.638978	–0.378921	0.878174
H	–0.561367	–1.518591	0.000000
H	–1.638978	–0.378921	–0.878174

E = –150.0217257

28b radical cation

C	–1.013338	–0.661197	0.000000
N	0.000000	0.382507	0.000000
N	1.163200	0.379551	0.000000
H	1.713726	1.259709	0.000000
H	–1.625227	–0.495532	0.887817
H	–0.525645	–1.635864	0.000000
H	–1.625227	–0.495532	–0.887817

E = –149.7033324

E[CCSD(T)/CBS] = –149.7907622
ZPVE = 35.5096 kcal mol^{-1}

Frequency	Intensity
195.2610	0.8065
558.7014	17.3038
864.0721	32.0747
925.6871	13.4825
1143.3842	10.1659
1172.2263	20.5642
1407.1693	6.2293
1469.5217	9.9938
1470.1713	16.3367
1491.5368	24.5535
1653.3528	5.5782
3017.0722	15.6479
3094.0883	7.1010
3104.3057	14.3348
3272.7724	12.0852

E[CCSD(T)/CBS] = –149.4609245
ZPVE = 34.5380 kcal mol^{-1}

Frequency	Intensity
153.6476	0.1875
418.0294	50.6485
666.0487	112.4381
798.6984	22.1873
1032.9628	80.4799
1124.0429	1.8719
1208.5032	55.0146
1397.2858	17.4825
1416.6520	27.4828
1449.7526	31.4300
1970.2394	10.5554
3028.7899	48.7004
3119.7750	23.6184
3139.0737	17.4227
3236.1816	215.3598

29

N	1.111029	0.143243	–0.089198
N	–0.083105	–0.513409	0.008279
H	1.116367	1.104498	0.241398
H	1.858183	–0.407910	0.301480
C	–1.154647	0.167686	0.008549
H	–2.095341	–0.364448	0.031042
H	–1.169649	1.260297	–0.021156

E = –150.0281272
E[CCSD(T)/CBS] = –149.7941943
ZPVE = 35.7082 kcal mol^{-1}

Frequency	Intensity
426.9034	23.0557
514.4623	16.5645
651.0041	246.1064
785.9061	7.4487
942.1191	36.0009
1061.5669	31.8982
1179.1985	12.9848
1309.5395	18.6717
1477.3574	6.0908
1652.9529	38.9486
1691.7617	14.4815
3025.8062	38.7899
3196.6211	8.4956
3440.6914	3.0741
3622.3447	22.3621

29 radical cation

N	–1.088002	–0.355291	0.000000
N	0.000000	0.376037	0.000000
H	–1.618859	–0.366977	0.869379
H	–1.618859	–0.366977	–0.869379
C	1.225105	0.099730	0.000000
H	1.930749	0.923561	0.000000
H	1.572353	–0.933209	0.000000

E = –149.7156101
E[CCSD(T)/CBS] = –149.4696973
ZPVE = 35.4198 kcal mol^{-1}

Frequency	Intensity
150.2583	43.9329
431.5269	61.2781
705.1632	161.8448
713.2885	0.3349
1103.6062	22.2637
1106.2616	12.1810
1178.3696	22.5570
1233.7957	0.5772
1472.7290	13.6090
1632.4049	42.6283
1786.4776	6.6226
3076.1357	23.0821
3207.6316	23.4903
3432.3602	196.1799
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 $C_2H_2N_2$ isomers (**5** and **15**) calculated at the B3LYP/aug-cc-pVTZ level of theory.

5a

C	0.562377	–0.581042	0.000000
C	–0.000000	0.750694	–0.000000
N	–0.109111	–1.655239	0.000000
H	–1.114208	–1.478136	0.000000
H	1.648687	–0.629753	0.000000
N	–0.449280	1.810950	–0.000000

E = –186.9418663
E[CCSD(T)/CBS] = –186.6483726
ZPVE = 24.7725 kcal mol^{-1}

Frequency	Intensity
235.2439	15.6877
335.7732	20.6316
622.6798	4.0725
852.9507	10.4249
918.3712	20.9551
1132.7840	65.7737
1244.0648	88.4049
1417.5565	17.4516
1669.3117	33.7051
2331.6271	1.6749
3121.0929	3.9714
3447.1340	7.7269

5a radical cation

C	0.562531	–0.562751	0.000000
C	0.000021	0.746552	–0.000000
N	–0.147090	–1.586308	0.000000
H	–1.054654	–2.057618	0.000000
H	1.655382	–0.682555	0.000000
N	–0.420929	1.820244	–0.000000

E = –186.5425134
E[CCSD(T)/CBS] = –186.2410030
ZPVE = 22.4557 kcal mol^{-1}

Frequency	Intensity
199.5764	11.6697
291.5168	4.3077
457.7857	135.6810
461.7004	58.1650
693.3758	60.4278
926.1205	23.9116
961.2027	48.2813
1255.2744	4.6013
1654.0945	37.2319
2328.6888	136.1481
3005.3768	103.0340
3473.3147	486.3871

5b

C	–0.000000	0.764331	0.000000
C	–0.475812	–0.598501	–0.000000
N	1.241822	1.012087	0.000000
H	1.410802	2.017425	0.000000
H	–0.791534	1.515768	0.000000
N	–0.922450	–1.658969	–0.000000

E = –186.9410027
E[CCSD(T)/CBS] = –186.6473818
ZPVE = 24.6756 kcal mol^{-1}

Frequency	Intensity
247.7738	6.5342
331.8109	3.5107
626.5735	4.7108
829.9474	44.1062
907.9491	53.2961
1116.9376	5.4813
1237.0619	42.1105
1411.6394	26.9656
1680.3831	42.3694

5b radical cation

C	–0.000302	0.737118	0.000000
C	–0.492862	–0.592170	–0.000000
N	1.205094	1.047654	0.000000
H	1.926623	1.771230	0.000000
H	–0.732674	1.567748	0.000000
N	–0.952893	–1.649159	–0.000000

E = –186.5429638
E[CCSD(T)/CBS] = –186.2412348
ZPVE = 22.3132 kcal mol^{-1}

Frequency	Intensity
211.6317	0.2645
283.6615	7.5793
450.9963	131.0887
485.0325	29.9703
685.7635	68.4628
871.8806	7.6186
975.7689	47.5775
1237.2364	16.8101
1673.0845	35.5790

2344.9053	4.0564
3063.8927	13.2611
3461.9853	9.8370

15			
N	–6.530330	0.827607	–0.126978
N	–4.141700	0.133658	–0.005872
C	–5.404906	0.565788	–0.077983
C	–3.166996	0.946666	–0.092014
H	–2.162105	0.544241	–0.027398
H	–3.288383	2.021001	–0.226674

E = –186.9337164
E[CCSD(T)/CBS] = –186.6366964
ZPVE = 24.4001 kcal mol^{-1}

Frequency	Intensity
255.4134	5.9942
374.3086	8.4366
633.8846	5.3526
778.4085	1.6746
955.8108	6.3260
1098.6045	18.6336
1225.9328	11.4211
1503.0029	15.1289
1697.7046	28.9901
2298.3428	37.4431
3064.4753	17.3371
3182.2189	4.1503

2337.9771	152.8917
2911.9787	117.5385
3483.3236	594.3120

15 radical cation			
N	–1.954828	–0.000155	0.000008
N	0.479370	0.000059	–0.000010
C	–0.763652	–0.000039	–0.000001
C	1.728077	0.000122	–0.000019
H	2.272333	–0.948675	–0.000021
H	2.272257	0.948960	–0.000022

E = –186.5578011
E[CCSD(T)/CBS] = –186.2456710
ZPVE = 22.5022 kcal mol^{-1}

Frequency	Intensity
109.1348	5.4140
218.2672	1.4348
380.4205	14.1916
517.5388	11.5554
971.4264	5.4893
1071.4644	25.6945
1074.0673	0.7812
1437.3148	37.6114
1816.6541	49.8632
2003.7250	125.4657
3016.3382	118.1704
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 $C_2H_4N_2$ isomers (**17**, **30**–**33**) calculated at the B3LYP/aug-cc-pVTZ level of theory.

17

N	–1.803328	–0.268356	–0.148823
C	–0.718499	0.119051	–0.041764
N	0.532991	0.546553	0.135335
C	1.639168	–0.405831	–0.010473
H	0.708080	1.476422	–0.213809
H	2.550508	0.069699	0.345157
H	1.781611	–0.733867	–1.042821
H	1.439838	–1.275523	0.611214

E = –188.1650100
E[CCSD(T)/CBS] = –187.8692561
ZPVE = 39.3395 kcal mol^{-1}

Frequency	Intensity
148.3619	0.4630
221.3267	6.5320
411.2689	79.5341
540.7744	23.2254
634.8435	22.7482
927.7727	2.7808
1143.5033	9.5391
1159.5970	34.0294
1203.8779	9.7250
1463.1153	8.5606
1468.7771	11.7078
1495.2351	9.3225
1520.9333	16.0972
2337.7800	139.0153
3022.8902	48.3394
3100.0210	17.8949
3133.5923	10.1013
3584.7191	37.0883

17 radical cation

N	–1.841685	–0.224087	–0.020333
C	–0.714793	0.124270	0.005415
N	0.523685	0.493594	0.032932
C	1.667743	–0.422326	–0.020917
H	0.707133	1.499045	0.097087
H	1.315273	–1.445782	–0.086738
H	2.266846	–0.261068	0.880105
H	2.272974	–0.149312	–0.890360

E = –187.8131055
E[CCSD(T)/CBS] = –187.5061839
ZPVE = 38.3036 kcal mol^{-1}

Frequency	Intensity
123.0694	0.0488
225.2462	3.2261
394.0122	0.1382
576.9780	2.2040
666.5952	78.0328
861.3535	11.6984
1083.3013	0.0272
1137.7312	2.9011
1195.8407	48.3616
1392.0492	26.6092
1434.9136	24.3781
1459.8144	9.6100
1508.0784	38.2255
2044.0907	243.6161
3010.5172	82.7118
3071.2666	18.2086
3180.5932	14.4297
3428.3195	191.3093

30a

N	–1.804768	–0.060206	0.000017
C	–0.623811	0.399347	0.000027
C	0.623810	–0.399346	–0.000000
N	1.804767	0.060208	0.000026
H	–1.798556	–1.083749	0.000003
H	–0.490618	1.484297	–0.000018
H	0.490617	–1.484295	–0.000037
H	1.798555	1.083751	0.000046

E = –188.1501192
E[CCSD(T)/CBS] = –187.8553274
ZPVE = 39.3975 kcal mol^{-1}

30a 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
141.6611	3.6914
334.2961	34.1567
566.0635	0.0000
665.8400	50.0719
946.6689	0.0000
1020.6312	0.0000
1117.7792	0.0000
1155.9573	111.9335
1197.3631	149.3270
1297.1341	0.0000
1405.1930	68.6478
1412.9578	0.0000
1680.0470	61.1823
1702.7951	0.0000
3055.6112	0.0000
3059.9840	51.1767
3397.7499	4.1478
3401.2089	0.0000

Frequency	Intensity
66.5313	8.3053
346.8916	28.4859
384.3400	24.4474
497.0294	1483.5325
594.1431	35.2628
686.3272	73.7259
702.0685	184.9760
874.6726	55.4078
927.8408	8.8379
981.3173	65.6589
1163.7096	22.6937
1171.6610	162.5219
1787.1678	6.9345
1893.3440	35.5643
3014.6340	66.0851
3019.1277	18.4698
3513.5473	869.8649
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
160.7250	8.5297
342.3648	17.4625
578.0939	8.9068
656.9856	7.4810
936.0374	49.5588
1004.0120	74.6532
1114.6941	33.8228
1152.2060	29.9925
1191.1101	4.3541
1287.0109	73.0778
1393.2867	6.1250
1416.5915	43.2345
1681.2171	61.5248
1707.7658	0.8121
2995.1947	47.9751
3103.5563	13.4722
3389.3299	4.2308
3454.1706	1.6077

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
66.5313	8.3053
346.8916	28.4859
384.3400	24.4474
497.0294	1483.5325
594.1431	35.2628
686.3272	73.7259
702.0685	184.9760
874.6726	55.4078
927.8408	8.8379
981.3173	65.6589
1163.7096	22.6937
1171.6610	162.5219
1787.1678	6.9345
1893.3440	35.5643
3014.6340	66.0851
3019.1277	18.4698
3513.5473	869.8649
3522.1596	20.6651

30c

N	–1.752099	–0.108811	–0.000011

30c radical cation

N	–1.570738	–0.331427	0.190008

C	–0.601337	0.426331	–0.000046
C	0.601312	–0.426340	–0.000005
N	1.752074	0.108801	–0.000014
H	–2.487365	0.597510	–0.000013
H	–0.403349	1.501829	–0.000056
H	0.403321	–1.501837	0.000037
H	2.487340	–0.597521	0.000013

E = –188.1536124
E[CCSD(T)/CBS] = –187.8589809
ZPVE = 39.4918 kcal mol^{-1}

Frequency	Intensity
178.1103	11.0934
345.6936	44.0429
589.7267	0.0000
657.2077	137.9290
929.3581	0.0000
997.5003	0.0000
1120.1165	0.0000
1144.9148	11.5205
1180.0323	103.8193
1279.6685	0.0000
1380.4900	60.4224
1427.3793	0.0000
1681.8465	62.6497
1713.4931	0.0000
3045.2338	0.0000
3047.8677	59.1332
3452.8059	2.6670
3453.4931	0.0000

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
66.5313	8.3053
346.8916	28.4859
384.3400	24.4474
497.0294	1483.5325
594.1431	35.2628
686.3272	73.7259
702.0685	184.9760
874.6726	55.4078
927.8408	8.8379
981.3173	65.6589
1163.7096	22.6937
1171.6610	162.5219
1787.1678	6.9345
1893.3440	35.5643
3014.6340	66.0851
3019.1277	18.4698
3513.5473	869.8649
3522.1596	20.6651

30d

N	–1.449977	0.606365	–0.001770
C	–0.796852	–0.477106	0.002202
C	0.694459	–0.584702	0.001495
N	1.410025	0.459985	–0.002359
H	–0.793347	1.394161	–0.005375
H	–1.344730	–1.419985	0.006331
H	1.100143	–1.601392	0.004965
H	2.403979	0.239930	–0.002050

E = –188.1491970
E[CCSD(T)/CBS] = –187.8550330
ZPVE = 39.4869 kcal mol^{-1}

Frequency	Intensity
153.0806	25.3937
305.5086	6.9812
635.1107	8.1423
740.0107	48.7500
895.5058	7.4090
928.8865	46.1548
1121.4898	14.8019
1165.8074	47.8124
1183.1874	42.6588

30d 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
66.5313	8.3053
346.8916	28.4859
384.3400	24.4474
497.0294	1483.5325
594.1431	35.2628
686.3272	73.7259
702.0685	184.9760
874.6726	55.4078
927.8408	8.8379

1276.6704	102.2132
1404.8819	41.4960
1444.7942	18.2860
1669.6348	15.6974
1730.2371	9.9196
3023.5629	50.6272
3084.8109	50.3710
3384.3164	1.3676
3474.0231	2.6856

N	–1.520463	0.084425	0.474657
C	–0.739529	0.117814	–0.521274
C	0.739548	–0.117670	–0.521273
N	1.520436	–0.084572	0.474704
H	–1.017732	–0.143420	1.338190
H	–1.176419	0.327488	–1.498712
H	1.176497	–0.326966	–1.498766
H	1.017660	0.143000	1.338283

E = –188.1460166
E[CCSD(T)/CBS] = –187.8518820
ZPVE = 39.2704 kcal mol^{-1}

Frequency	Intensity
94.8282	0.3016
324.5336	21.0622
598.4258	38.4956
737.6949	3.2796
881.7964	22.5649
940.0155	2.2619
1131.6255	2.6948
1149.6834	108.9884
1223.3553	81.2484
1244.8506	130.2409
1398.7957	10.4458
1441.4039	10.0213
1667.0358	21.2108
1724.6675	9.6787
3069.2324	11.1999
3088.7263	53.9442
3368.3990	7.5944
3384.9931	2.1737

N	–1.438934	–0.559391	–0.068553
C	–0.739983	0.485058	0.082803
C	0.739983	0.485059	–0.082808
N	1.438934	–0.559390	0.068550
H	–2.426604	–0.360122	0.086761
H	–1.163405	1.466932	0.323954
H	1.163404	1.466931	–0.323967
H	2.426603	–0.360122	–0.086768

E = –188.1420806
E[CCSD(T)/CBS] = –187.8478381

981.3173	65.6589
1163.7096	22.6937
1171.6610	162.5219
1787.1678	6.9345
1893.3440	35.5643
3014.6340	66.0851
3019.1277	18.4698
3513.5473	869.8649
3522.1596	20.6651

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
66.5313	8.3053
346.8916	28.4859
384.3400	24.4474
497.0294	1483.5325
594.1431	35.2628
686.3272	73.7259
702.0685	184.9760
874.6726	55.4078
927.8408	8.8379
981.3173	65.6589
1163.7096	22.6937
1171.6610	162.5219
1787.1678	6.9345
1893.3440	35.5643
3014.6340	66.0851
3019.1277	18.4698
3513.5473	869.8649
3522.1596	20.6651

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

N	–1.856347	–0.276669	–0.049139
C	–0.775348	0.114326	–0.040311
C	0.597057	0.625731	0.007326
N	1.563788	–0.471289	–0.008044
H	0.663717	1.296415	0.874291
H	0.752490	1.240069	–0.881599
H	1.490067	–1.024635	0.836795
H	2.503773	–0.097755	–0.045632

E = –188.1678585
E[CCSD(T)/CBS] = –187.8770081
ZPVE = 39.6343 kcal mol^{-1}

Frequency	Intensity
201.2852	16.2372
244.1847	22.3730
376.5876	4.9211
571.3265	5.8427
820.9689	133.3829
872.5464	9.4118
1002.5787	19.2057
1079.0460	12.0004
1193.9981	0.3073
1309.8890	6.8169
1420.8377	13.9038
1493.8847	3.1436
1660.1835	23.3277
2362.9770	2.5075
2968.4700	38.8787
3061.0183	5.4988
3501.1010	1.6018
3583.7071	4.7751

N	–1.848569	–0.311822	0.075313
C	–0.778519	0.108582	0.040458
C	0.565099	0.641306	–0.004774
N	1.587798	–0.314605	0.222423
H	0.696499	1.469452	0.722381
H	0.768295	1.143372	–0.973555
H	1.380720	–1.298136	0.402652
H	2.567874	–0.031955	0.208789

E = –187.8105343
E[CCSD(T)/CBS] = –187.5098329
ZPVE = 37.6978 kcal mol^{-1}

Frequency	Intensity
203.1660	1.9421
239.6376	8.5154
318.0006	8.6304
560.2146	2.6182
648.6034	138.2538
843.1803	11.6124
851.5227	31.0078
1067.3237	29.0660
1092.5599	48.5262
1165.4292	4.7587
1317.8576	79.3659
1371.3915	1.6454
1612.2951	53.2138
2356.5692	142.0687
2869.2421	53.9387
2884.8530	122.6800
3423.3986	251.9815
3544.7266	186.3473

32a

N	1.509804	0.437350	–0.073144
C	0.633542	–0.471427	–0.169993
N	–0.663165	–0.472961	0.362563
C	–1.549245	0.309919	–0.079112
H	1.139468	1.250185	0.422849
H	0.897913	–1.418671	–0.639718
H	–2.533870	0.314041	0.381590
H	–1.380179	0.994717	–0.915409

E = –188.1464816
E[CCSD(T)/CBS] = –187.8499827
ZPVE = 38.9927 kcal mol^{-1}

Frequency	Intensity
131.5478	6.2286
356.0414	6.4656
488.9414	22.8266
784.7910	21.2737
898.0878	25.1899
972.5266	30.7170
1087.0189	9.5943

32a radical cation

N	1.667411	0.393777	0.175503
C	0.713381	–0.434239	–0.215251
N	–0.513734	0.007777	–0.198372
C	–1.674404	0.428738	–0.188318
H	2.584924	–0.057526	0.119551
H	0.837732	–1.462480	–0.554947
H	–2.294028	0.312876	0.704945
H	–2.088531	0.922363	–1.071653

E = –187.8129866
E[CCSD(T)/CBS] = –187.5037426
ZPVE = 37.1191 kcal mol^{-1}

Frequency	Intensity
146.2711	72.9913
201.7486	19.5071
498.9933	71.8530
519.5742	0.5290
624.2358	7.1366
954.2008	15.1372
962.8500	4.2621

1096.0348	63.4294
1216.2903	47.3614
1244.3374	75.5316
1405.0068	25.4842
1504.2033	13.2974
1679.7313	135.8452
1731.0672	49.1981
3017.6547	39.5128
3097.0523	16.8549
3136.4059	21.3949
3429.0404	2.5891

N	1.348550	0.491772	–0.031683
C	0.606614	–0.531908	–0.113612
N	–0.724179	–0.530037	0.320667
C	–1.503622	0.376803	–0.088135
H	2.293598	0.274082	–0.341144
H	0.931789	–1.517558	–0.454609
H	–2.521952	0.410579	0.289935
H	–1.198047	1.137553	–0.809963

E = –188.1476494
E[CCSD(T)/CBS] = –187.8515632
ZPVE = 39.1137 kcal mol^{-1}

Frequency	Intensity
175.0512	33.4383
374.0774	32.5905
523.5614	10.4428
787.0167	8.6593
881.0313	36.8408
967.1744	97.1290
1081.9783	6.8574
1091.4083	13.5925
1221.1623	14.3682
1243.7137	39.9895
1408.0784	28.2169
1498.2804	19.4364
1672.4574	132.9289
1724.7459	42.6368
3035.5792	40.0882
3055.0074	33.5905
3145.7408	21.5563
3474.3770	1.1711

N	–0.579129	0.430382	0.353781
C	–1.546028	–0.279947	–0.054901
C	1.546014	–0.279982	0.054957
H	–2.479373	–0.226308	0.491143
H	–1.479500	–0.928267	–0.928336
H	1.479458	–0.928182	0.928479
H	2.479370	–0.226436	–0.491078

1077.4466	25.5216
1078.4061	1.4133
1179.1502	41.9496
1252.3788	69.2401
1416.1556	37.0733
1451.0231	9.9398
1905.3280	3.7755
3022.1362	81.7791
3109.5781	5.9199
3120.8604	36.4340
3444.8679	77.8217

N	1.667411	0.393777	0.175503
C	0.713381	–0.434239	–0.215251
N	–0.513734	0.007777	–0.198372
C	–1.674404	0.428738	–0.188318
H	2.584924	–0.057526	0.119551
H	0.837732	–1.462480	–0.554947
H	–2.294028	0.312876	0.704945
H	–2.088531	0.922363	–1.071653

E = –187.8129866
E[CCSD(T)/CBS] = –187.5037426
ZPVE = 37.1191 kcal mol^{-1}

Frequency	Intensity
146.2711	72.9913
201.7486	19.5071
498.9933	71.8530
519.5742	0.5290
624.2358	7.1366
954.2008	15.1372
962.8500	4.2621
1077.4466	25.5216
1078.4061	1.4133
1179.1502	41.9496
1252.3788	69.2401
1416.1556	37.0733
1451.0231	9.9398
1905.3280	3.7755
3022.1362	81.7791
3109.5781	5.9199
3120.8604	36.4340
3444.8679	77.8217

N	–0.528544	0.147501	–0.280981
N	0.587463	0.276432	0.371368
C	1.776606	0.211420	–0.051757
C	–1.717784	0.213747	0.141890
H	2.571387	0.350330	0.672240
H	2.000500	0.024136	–1.100112
H	–1.941933	0.402024	1.190023
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

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