

Supporting Information

Non-Equilibrium Preparation of (*E*)-Phosphinimine (HPNH, X¹A') – A Precursor to Prebiotic Phosphorylating Agents

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Methods

Experimental. All experiments were conducted in an ultrahigh vacuum chamber with base pressures of a few 10^{-11} Torr, achieved using magnetically suspended turbomolecular pumps backed by an oil-free scroll pump.¹ A polished silver substrate was mounted to a cold head connected to a closed-cycle helium compressor (Sumitomo Heavy Industries, RDK-415E). The cold head can be moved vertically and rotated about the vertical axis.¹ Experimental procedures have been described in detail previously.² Phosphine (PH_3 , Sigma-Aldrich, 99.9995%), ammonia (NH_3 , Matheson, 99.9992%), and isotopically labeled ammonia- ^{15}N ($^{15}\text{NH}_3$, Sigma-Aldrich, 98% ^{15}N) were used. Once the silver substrate reached 5 K, phosphine and ammonia were co-deposited onto the substrate via a pair of glass capillary arrays with partial pressures of 1×10^{-8} Torr for each reactant. Utilizing laser interferometry with a helium-neon laser (632.8 nm),³ the thickness of the deposited PH_3 - NH_3 ice was calculated to be 1410 ± 50 nm; the ratio of phosphine to ammonia was estimated to be $(1.6 \pm 0.5):1$ based on the integrated infrared absorption and absorption coefficients of reactants.² The absorption coefficients of 5.1×10^{-19} cm molecule $^{-1}$ of PH_3 (ν_2)³ and 5.6×10^{-18} cm molecule $^{-1}$ for NH_3 (ν_4)^{4,5} were used. Infrared spectra were collected via a Fourier Transform Infrared (FTIR) spectrometer (Nicolet 6700) with a resolution of 4 cm $^{-1}$. After deposition, the PH_3 - NH_3 ice mixtures were exposed to energetic (5 keV) electrons at a current of 20 nA for 15 minutes. These electrons simulate secondary electrons produced by GCRs as they pass through the interstellar ices in a molecular cloud.⁶ The irradiation doses of 0.8 ± 0.2 eV per PH_3 molecule and 0.4 ± 0.1 eV per NH_3 molecule^{2,7} simulate the energy input by GCRs over timescales equivalent to lifetimes of up to 3×10^6 years for cold molecular clouds,⁸ corresponding to their early evolutionary stage. Utilizing the densities of PH_3 (0.90 g cm $^{-3}$)^{3,9} and NH_3 (0.74 g cm $^{-3}$),⁴ approximately 99% of the incident electron energy was deposited within the upper 700 ± 50 nm of the ice mixture using CASINO 2.42;⁷ this penetration depth is much less than the total ice thickness, ensuring that electrons do not interact with the substrate.

After irradiation, the ices were warmed from 5 to 320 K at a ramping rate of 1 K min $^{-1}$ during temperature-programmed desorption (TPD). As molecules sublime, they are photoionized by pulsed VUV photons generated via the four-wave mixing method in a krypton/xenon gas jet (30 Hz).¹⁰ The generation parameters for photon energies of 10.49, 9.47, and 8.80 eV are listed in Table S3. Specifically, 10.49 eV photons were produced by tripling the third harmonic (355 nm) of an Nd:YAG laser (Spectra-Physics, Quanta Ray PRO 250-30) in xenon gas. To generate 9.47

eV photons, the third harmonic of an Nd:YAG laser (Spectra-Physics, Quanta Ray PRO 270-30) pumped a dye laser (Sirah Lasertechnik, Cobra-Stretch) operating with stilbene 420 dye, yielding 212.556 nm (ω_1) after second harmonic generation with a beta-barium borate (BBO) crystal. Meanwhile, a separate Nd:YAG laser pumped a dye laser operating with the Rhodamine 590 dye to generate 564.583 nm (ω_2). The combination of $2\omega_1$ and ω_2 in krypton gas produced 9.47 eV photons via four-wave difference frequency mixing. The 9.39 eV or 8.80 eV photons were generated in xenon gas using $\omega_1 = 222.566$ nm and $\omega_2 = 707.956$ nm or 529.553 nm. The ω_1 beam was obtained by frequency doubling 445.132 nm light from Coumarin 450 dye pumped by the third harmonic (355 nm) of an Nd:YAG laser, while ω_2 was produced by pumping Coumarin 450 dye with the second harmonic (532 nm) of another Nd:YAG laser. The output wavelengths of the dye lasers were calibrated using a wavelength meter (Coherent, WaveMaster) with an accuracy of 0.1 cm^{-1} , resulting in an uncertainty of less than 0.001 eV in the photon energy. The VUV photons were separated from the dye laser beams using a biconvex lithium fluoride lens in an off-axis configuration and directed to pass 2.0 ± 0.5 mm above the substrate surface. VUV photons ionize molecules via single-photon ionization, which produces exclusively singly charged cations. The resulting ions were detected using a reflectron time-of-flight mass spectrometer (ReToF-MS, Jordan TOF Products, Inc.). Ion signals were amplified with a preamplifier (Ortec 9305) and collected using a multichannel scaler (FAST ComTec, MCS6A). Each mass spectrum was accumulated over 3600 sweeps (2 minutes) during the temperature-programmed desorption process.

Computational. The coupled cluster¹¹⁻¹⁴ CCSD/cc-pVTZ calculations are carried out to obtain optimized geometries, harmonic vibrational frequencies, and infrared intensities of neutral H₂PN isomers and cations. The energies are refined by computing coupled cluster CCSD(T)/cc-pVDZ, CCSD(T)/cc-pVTZ, and CCSD(T)/cc-pVQZ energies, which are extrapolated to completed basis set limits,¹⁵ CCSD(T)/CBS, with CCSD/cc-pVTZ zero-point energy corrections. The adiabatic ionization energies (IEs) are calculated by taking the difference in energies between the ionic and the neutral states of similar conformation. The Cartesian coordinates, harmonic vibrational frequencies, and infrared intensities of the computed structures are provided in Tables S4–S9. To assess whether the single-reference coupled cluster methods are appropriate for the present system, the T₁ diagnostic^{16,17} is examined for both close-shell and open-shell species in Figs. 1, 4, and 6. As seen in Table S10, for the close-shell species **4**, **ts (6-3+H₂)**, and the open-shell species (*E*)-**3**⁺,

(*Z*)-**3**⁺, and **4**⁺, the T_1 diagnostic values are exceeded 0.02, and 0.044, respectively, which may indicate appreciable multi-reference character. Thus, the multi-reference configuration interaction (MRCI) calculations are also performed based on the CCSD/cc-pVTZ optimized geometries of (*E*)-**3**, (*E*)-**3**⁺, (*Z*)-**3**, (*Z*)-**3**⁺, **4**, **4**⁺, **6**, and **ts** (**6-3**+H₂). The Hartree Fock (HF/cc-pVTZ) orbital energies at CCSD/cc-pVTZ optimized geometries for these species indicate there is a descent energy gap between the third highest occupied orbital (third HOMO) and the fourth HOMO, while among the first three HOMO's, two of them are often almost degenerate, in particular for cations. Thus, three HOMO's included in active space for all species would be reasonable to have a uniform level of calculations, which also constitutes 6 and 5 active electrons for neutrals and cations, respectively. Additional 1, 2, 4, and 6 more lowest unoccupied molecular orbitals (LUMO's), (active space (6,4), (6,5), (6,7), and (6,9)) are included in the active orbitals to push the limit for the number of electron configurations; eventually, only the results of the largest active space: 6 or 5 electrons in 9 active orbitals are presented. The reference space and molecular orbitals are provided by MCSCF (6,9)/(5,9), 6 (or 5) active electrons in 9 orbitals for neutrals and cations, respectively. Likewise, MRCI/cc-pVDZ, MRCI/cc-pVTZ, and MRCI/cc-pVQZ energies with Davidson corrections are extrapolated to yield the MRCI/CBS energies with CCSD/cc-pVTZ zero-point energy corrections as shown in Table S11. The Gaussian 16 program is employed in the *ab initio* electronic structure calculations,¹⁸ and MOLPRO¹⁹ is used for the computations of MCSCF, and MRCI. It is important to note that combined error bounds of $-0.03/+0.06$ eV are applied to the calculated IEs based on the benchmarking against experimental and calculated IEs of molecular systems.²⁰ The ionization energies are subject to small shifts due to Stark effects in the photoionization region with an extraction electric field of 200 V cm^{-1} and from the internal thermal energy of the desorbing molecules at 153 K; these contributions are estimated to result in a combined shift of approximately -0.03 eV, comprising for the thermal (-0.014 eV) and Stark effects (-0.011 eV).²¹ The ultraviolet-visible (UV-Vis) spectra of (*E*)-**3**, (*Z*)-**3**, and **4** were calculated at the TD-B3LYP/cc-pVTZ level of theory.

Evidence for the formation of hydrazine (N₂H₄) and diphosphine (P₂H₄)

At 10.49 eV, the TPD profile of the ion signal at $m/z = 32$ from irradiated PH₃-NH₃ ice reveals three sublimation events peaking at 79, 115, and 165 K (Fig. S5a). The blank experiment shows a sublimation event at 79 K, indicating that this peak is likely due to contamination in the samples. Given the molecular weights of the reactants, the ion signal of $m/z = 32$ could be attributed to PH⁺ and/or N₂H₄⁺. When the PH₃-NH₃ ice is replaced with PH₃-¹⁵NH₃ ice, the TPD profile of $m/z = 34$ exhibits a broad, saturated sublimation feature between 60 and 140 K due to the PH₃ reactant, along with a later peak at 165 K, suggesting that this higher-temperature event can be attributed to an N₂H₄ isomer. Previous studies of electron-irradiated ammonia-water (NH₃-H₂O) ices at 10 and 50 K suggested that hydrazine (N₂H₄) sublimates at a peak temperature of 170 K,²² supporting the assignment of the 165 K peak to hydrazine.

In addition, the TPD profile of $m/z = 66$ from irradiated PH₃-NH₃ ice at 10.49 eV reveals a strong sublimation event peaking at 122 K (Fig. S5b). No sublimation event is observed at $m/z = 66$ in the blank experiment, indicating that this event originates from electron-induced processing of the ice. Considering the molecular weights of the reactants, the ion signal at $m/z = 66$ can only be assigned to a species with the molecular formula P₂H₄. Substitution of PH₃-NH₃ ice with PH₃-¹⁵NH₃ ice results in no mass shift of the TPD profile, indicating the absence of nitrogen incorporation and further confirming the assignment to P₂H₄. Previous studies on electron-irradiated phosphine ices at 5 K reported that diphosphine (P₂H₄) sublimates with a strong event peaking at 121 K,³ which closely matches our result (122 K), supporting the assignment of this sublimation peak to diphosphine.

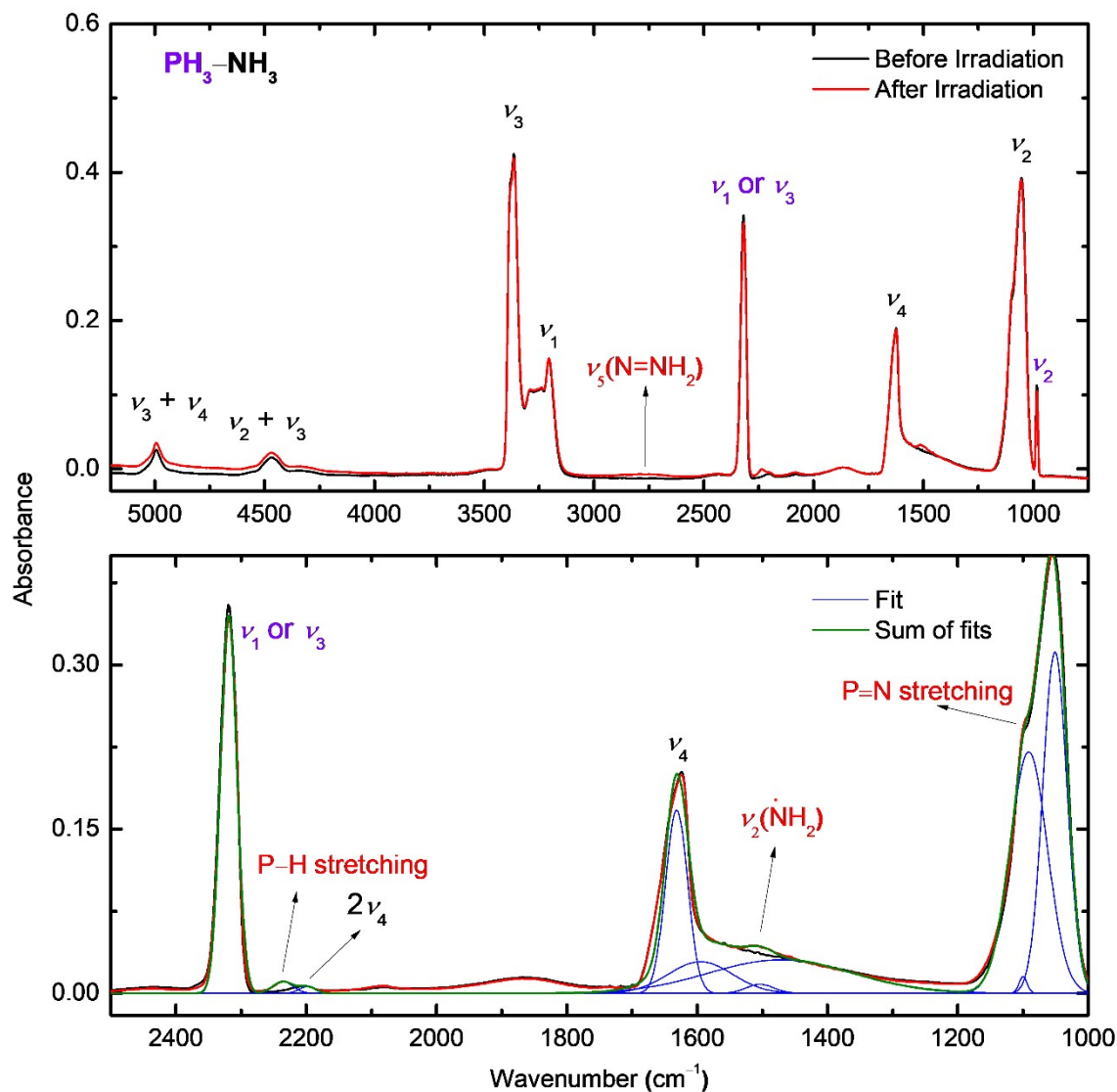


Figure S1. Infrared spectra of PH₃-NH₃ ice before and after electron irradiation at 5 K. The bottom panel shows a magnified, baseline-corrected view of the 2500–1000 cm⁻¹ region with Gaussian deconvolution. Assignments of absorptions of PH₃, NH₃, and new features are indicated in purple, black, and red, respectively. Detailed band assignments are provided in Table S1.

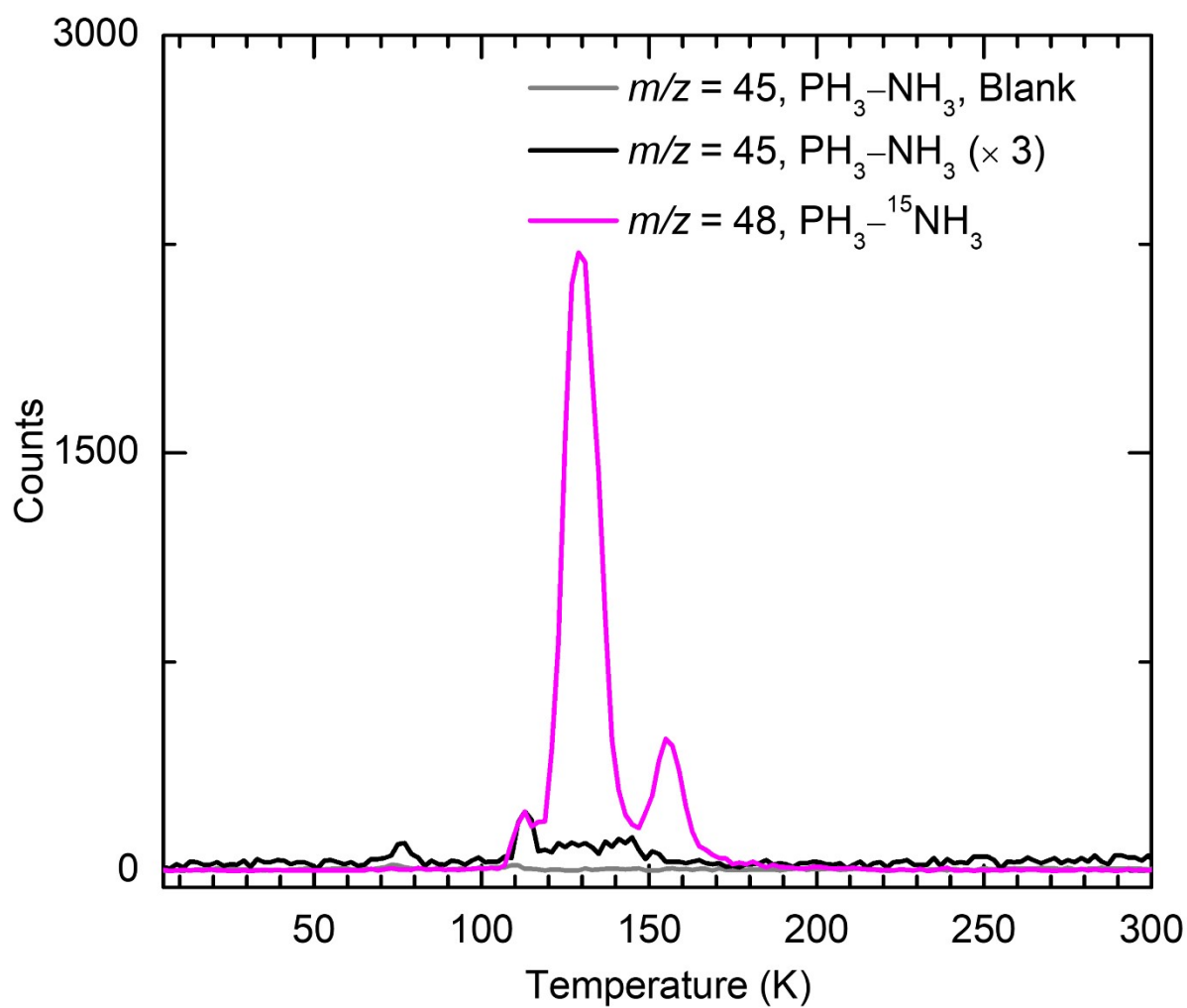


Figure S2. TPD profiles of $m/z = 45$ from blank and irradiated $\text{PH}_3\text{-NH}_3$ ices, and $m/z = 48$ from irradiated $\text{PH}_3\text{-}^{15}\text{NH}_3$ ices measured at 10.49 eV.

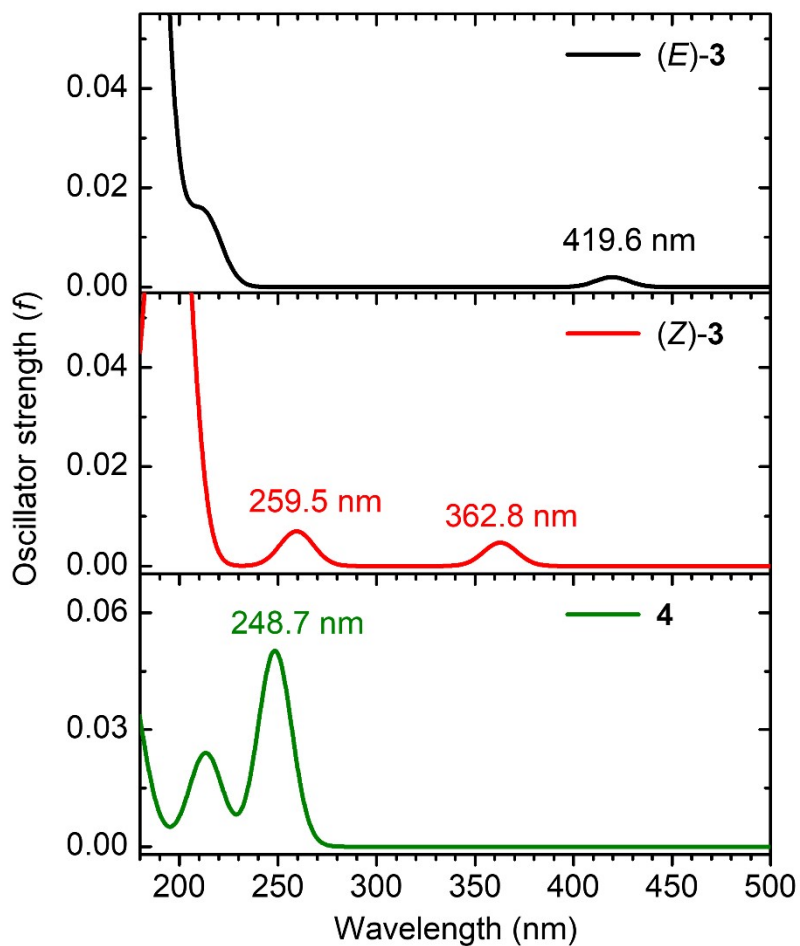


Figure S3. Simulated ultraviolet-visible spectra of (*E*)-**3**, (*Z*)-**3**, and **4** calculated at the TD-B3LYP/cc-pVTZ level of theory. The spectra were convoluted using a Gaussian function with a full width at half maximum of 20 nm.

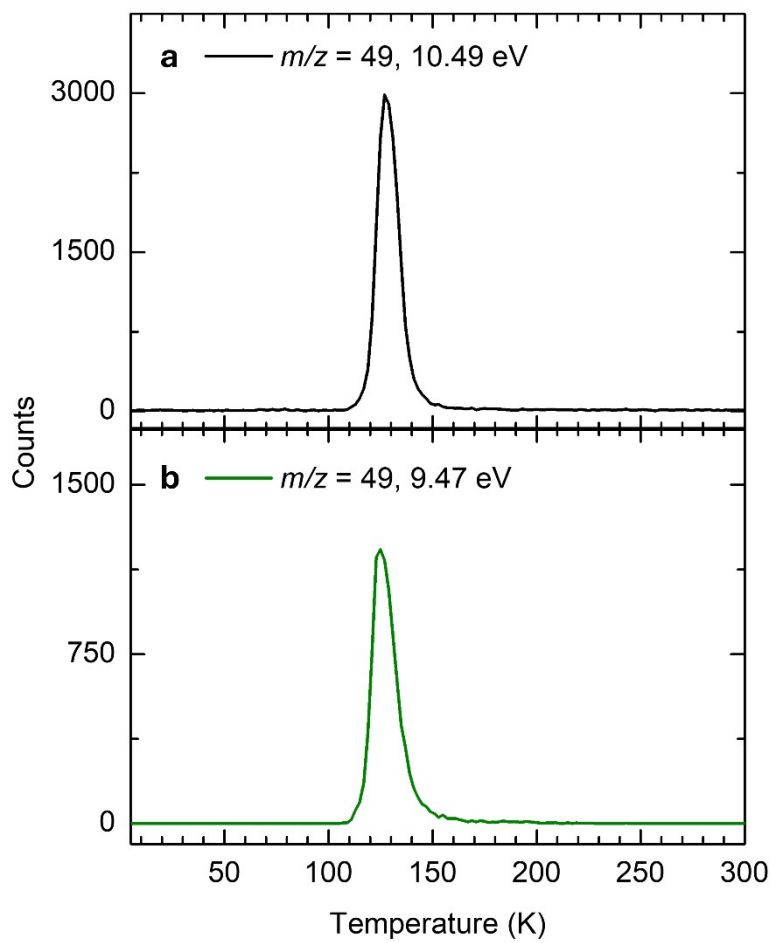


Figure S4. TPD profiles of ion signal at $m/z = 49$ from irradiated $\text{PH}_3\text{-NH}_3$ ices measured at 10.49 eV (a) and 9.47 eV (b).

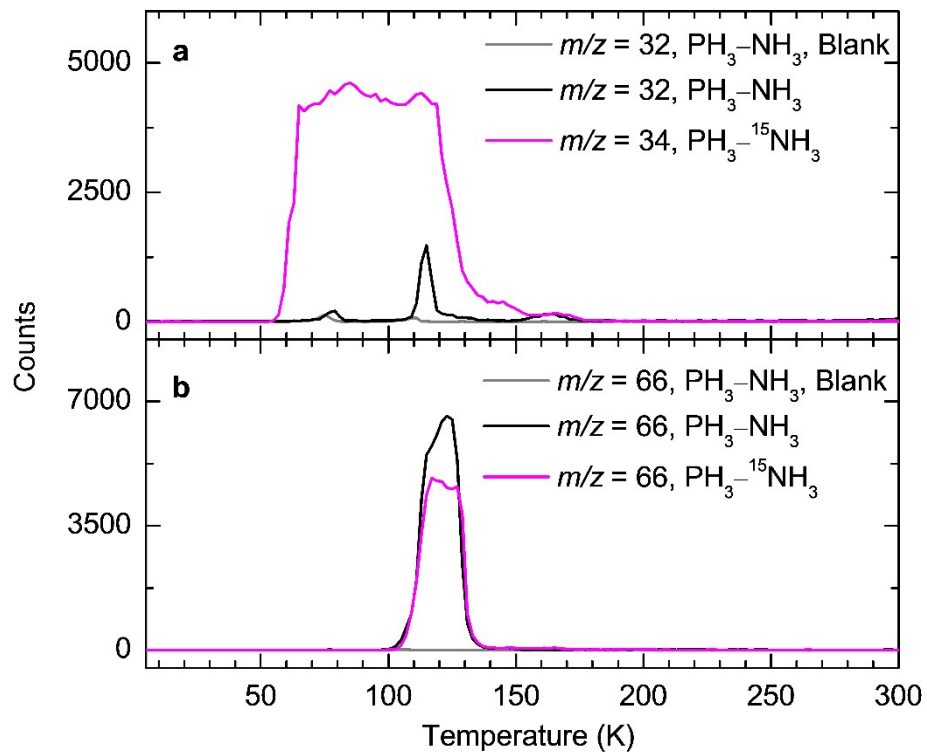
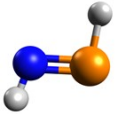
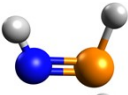
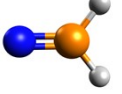
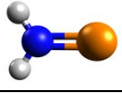


Figure S5. Ion signals of phosphine–ammonia ices recorded at 10.49 eV. TPD profiles of $m/z = 32$ and 34 from $\text{PH}_3\text{-NH}_3$ and $\text{PH}_3\text{-}^{15}\text{NH}_3$ ices, respectively (a), and $m/z = 66$ from both ices (b).

Table S1. Infrared absorption peaks of PH₃-NH₃ ice before and after electron irradiation at 5 K.

Absorptions before irradiation (cm ⁻¹)	
PH ₃	Assignment ³
2319	ν_1 or ν_3
2199	$2\nu_4$
1873	$2\nu_2$
1091	ν_4
983	ν_2
NH ₃	Assignment ²³
4994	$\nu_3 + \nu_4$
4470	$\nu_2 + \nu_3$
3369	ν_3
3295	$2\nu_4$
3207	ν_1
1632	ν_4
1051	ν_2
New absorptions after irradiation (cm ⁻¹)	
2768	$\nu_5(\text{N}=\text{NH}_2)^{24}$
2236	P-H stretching ²⁵
1504	NH ₂ bending (ν_2) ^{26,27}
1100	P=N stretching ^{2,25}

Table S2. Error analysis of adiabatic ionization energies (IEs) and relative energies (ΔE) of H₂PN isomers, computed at the MRCI/CBS//CCSD/cc-pVTZ level including CCSD/cc-pVTZ zero-point vibrational energy (ZPVE) corrections. IEs have been corrected for thermal and Stark effects by -0.03 eV, and an uncertainty of -0.03 – $+0.06$ eV is applied.^{20,21,28,29}

Isomers	Structure	ΔE (kJ mol ⁻¹)	Computed IE (eV)	Corrected IE ranges (eV)
(<i>E</i>)- 3		0	9.30	9.24–9.33
(<i>Z</i>)- 3		2	9.49	9.43–9.52
4		154	9.50	9.44–9.53
5		60	7.51 ^a	7.45–7.54

^a Computed at both the CCSD(T)/CBS//CCSD/cc-pVTZ and CCSD(T)/CBS//B3LYP/cc-pVTZ levels of theory including CCSD/cc-pVTZ zero-point vibrational energy corrections.

Table S3. Generation parameters of vacuum ultraviolet (VUV) photons via four-wave mixing. The uncertainty in the VUV photon energy is less than 0.001 eV.

VUV photon energy (eV)	Nonlinear medium	ω_1 wavelength (nm)	ω_1 dye	ω_2 wavelength (nm)	ω_2 dye
10.49 ($3\omega_1$)	Xenon	355	–	–	–
9.47 ($2\omega_1 - \omega_2$)	Krypton	212.556	Stilbene 420	564.583	Rhodamine 590
9.39 ($2\omega_1 - \omega_2$)	Xenon	222.566	Coumarin450	707.956	LDS 722
8.80 ($2\omega_1 - \omega_2$)	Xenon	222.566	Coumarin450	529.553	Coumarin 540A

Table S4. Optimized Cartesian coordinates (Å) on the adiabatic singlet ground state potential energy surfaces of H₂PN isomers and their doublet cations calculated at the CCSD/cc-pVTZ level of theory. The point group symmetries and electronic ground states are provided.

Atom	X	Y	Z	Atom	X	Y	Z
<i>(E)</i> - 3 , C _s , ¹ A'				<i>(E)</i> - 3 ⁺ , C _s , ² A'			
N	0.018773	1.052725	0.000000	N	0.037199	0.996229	0.000000
H	0.982774	1.383485	0.000000	H	0.564618	1.863941	0.000000
P	0.018773	-0.533713	0.000000	P	0.037199	-0.538075	0.000000
H	-1.395772	-0.746863	0.000000	H	-1.382987	-0.766419	0.000000
<i>(Z)</i> - 3 , C _s , ¹ A'				<i>(Z)</i> - 3 ⁺ , C _s , ² A			
N	0.096378	1.049634	0.000000	N	-1.000012	0.031246	0.000089
H	-0.819576	1.487244	0.000000	H	-1.989307	0.232937	0.000335
P	0.096378	-0.528933	0.000000	P	0.509031	-0.102073	-0.000054
H	-1.300747	-0.900695	0.000000	H	1.353923	1.079444	-0.000147
4 , C _{2v} , ¹ A ₁				4 ⁺ , C _{2v} , ² B ₂			
N	0.000000	0.000000	-1.147109	N	0.000000	0.000000	-1.179917
P	0.000000	0.000000	0.370466	P	0.000000	0.000000	0.401754
H	0.000000	1.115858	1.236384	H	0.000000	1.207376	1.116555
H	0.000000	-1.115858	1.236384	H	0.000000	-1.207376	1.116555
5 , C _{2v} , ¹ A ₁				5 ⁺ , C _{2v} , ² B ₂			
N	0.000000	0.000000	-0.977843	N	0.000000	0.000000	-0.952230
P	0.000000	0.000000	0.660692	P	0.000000	0.000000	0.645626
H	0.000000	0.842600	-1.532740	H	0.000000	0.852667	-1.509393
H	0.000000	-0.842600	-1.532740	H	0.000000	-0.852667	-1.509393

Table S5. Vibrational frequencies (cm^{-1}) and infrared intensities (km mol^{-1}) on the adiabatic singlet and doublet ground state potential energy surfaces of H_2PN isomers and their cations, calculated at the CCSD/cc-pVTZ level of theory.

Normal modes	Frequency	IR Intensity	Frequency	IR Intensity
(E)-3			(E)-3⁺	
1	926.8322	33.811	530.1662	157.7359
2	998.2809	28.8542	688.7967	170.262
3	1064.5824	53.0309	788.2739	36.7129
4	1139.5247	29.0192	1163.0617	3.5618
5	2330.9726	136.0119	2240.5992	15.189
6	3504.0297	10.6255	3589.3726	356.8944
(Z)-3			(Z)-3⁺	
1	847.677	74.611	255.5807	167.4222
2	939.544	74.5941	445.193	102.1566
3	1070.9877	37.6657	521.522	134.0936
4	1115.8919	4.867	1172.1334	11.0599
5	2235.0898	203.6221	2080.9832	17.4441
6	3547.295	10.1056	3657.1472	437.3042
4			4⁺	
1	488.8626	6.7262	467.6598	22.5644
2	721.7778	4.7703	581.5668	21.1837
3	1193.7408	29.1273	995.023	7.6401
4	1276.4759	5.9864	1083.5237	6.0212
5	2415.913	26.2943	2478.0211	51.7574
6	2426.2114	96.6474	2544.7231	73.5081
5			5⁺	
1	726.2532	193.8062	818.4276	218.1815
2	972.8484	18.3953	863.7864	9.7536
3	985.3374	34.5608	1067.9055	20.0477
4	1642.6269	7.9384	1608.6829	65.7932
5	3538.6051	7.089	3464.7819	198.4898
6	3627.6642	40.4515	3559.685	173.9561

Table S6. Optimized Cartesian coordinates (Å) on the adiabatic singlet ground state potential energy surfaces of structures for reactions of H_2PNH_2^+ and HNPH_3^+ loss H_2 calculated at the CCSD/cc-pVTZ level of theory.

Atom	X	Y	Z	Atom	X	Y	Z
H_2PNH_2^+				HNPH_3^+			
H	0.234825	1.575425	-0.850829	H	-0.898262	1.640139	0.000000
H	0.234825	1.575425	0.850829	H	0.744692	-0.874673	1.131539
H	-0.663915	-0.977577	1.145140	H	-1.202609	-1.143801	0.000000
H	-0.663915	-0.977577	-1.145140	N	0.027795	1.202636	0.000000
N	0.039008	1.063206	0.000000	P	0.027795	-0.477696	0.000000
P	0.039008	-0.575876	0.000000	H	0.744692	-0.874673	-1.131539
TS ($2^+ - 1^+$)				TS ($1^+ - 3^+ + \text{H}_2$)			
H	0.466988	-0.237807	1.169303	H	0.250301	1.203699	0.402138
H	1.630838	0.777726	-0.014830	H	1.660162	-0.728476	0.350081
H	-1.132228	-1.136270	-0.455117	H	-0.966741	-0.505995	1.184034
H	-1.223263	1.180337	-0.291845	H	-0.675913	1.405215	0.133811
N	1.137059	-0.112502	-0.138780	N	1.136208	0.052199	-0.049306
P	-0.513450	0.013568	0.037597	P	-0.548084	-0.115989	-0.114995
TS ($1^+ - 5^+ + \text{H}_2$)				TS ($2^+ - 3^+ + \text{H}_2$)			
H	-1.650273	-0.747031	0.180570	H	1.736040	-0.655513	0.192363
H	-1.541899	0.902964	-0.210327	H	-1.129310	1.166140	-0.227060
H	0.889744	1.335132	-0.338864	H	-1.140765	-0.920652	0.812993
H	0.899405	1.287358	0.558684	N	1.162007	0.175827	0.027060
N	-1.048979	0.049572	0.010196	P	-0.451306	-0.124338	-0.120746
P	0.583059	-0.208362	-0.017429	H	-0.830420	1.044310	0.843483
TS ($2^+ - 4^+ + \text{H}_2$)							
H	0.182743	1.324838	-0.001247				
H	-1.100717	-0.417536	1.167097				
H	-0.846581	1.459784	-0.001185				
N	1.236288	-0.059963	-0.000016				
P	-0.385816	-0.101744	0.000038				
H	-1.102220	-0.421188	-1.165126				

Table S7. Vibrational frequencies (cm^{-1}) and infrared intensities (km mol^{-1}) on the adiabatic singlet and doublet ground state potential energy surfaces of structures for reactions of H_2PNH_2^+ and HNPH_3^+ loss H_2 calculated at the CCSD/cc-pVTZ level of theory.

H_2PNH_2^+			HNPH_3^+	
Normal modes	Frequency(cm^{-1})	IR Inten	Frequency(cm^{-1})	IR Inten
1	410.43	9.0105	30.8	103.2913
2	575.85	206.5934	692.11	55.4508
3	755.29	1.5924	747.73	22.5744
4	755.45	38.8571	823.04	24.4976
5	969.54	10.9804	1035.25	30.9839
6	1041.32	31.4035	1066.4	35.3625
7	1061.08	14.7707	1107.65	14.607
8	1613.04	56.4178	1109.09	3.1584
9	2489.99	7.1706	2529.97	4.142
10	2542.74	6.5918	2568.09	12.4313
11	3545.22	241.9696	2569.52	20.4168
12	3651.22	164.3094	3476.75	99.4869
TS ($2^+ - 1^+$)			TS ($1^+ - 3^+ + \text{H}_2$)	
1	-1992.92	255.6836	-1701.29	104.6484
2	561.83	36.6491	498.28	127.9033
3	711.8	29.7022	582.76	2.2262
4	746.52	31.0977	719.65	46.8421
5	847.5	35.9993	838.77	21.4759
6	976.81	16.5059	958.69	30.5851
7	1042.22	30.4535	1012.08	15.4397
8	1080.09	17.9729	1249.2	25.0329
9	2075.39	92.2435	1877.39	57.0814
10	2492.04	9.7567	2090.46	4.7943
11	2574.85	20.9413	2405.64	0.1756
12	3465.94	118.2906	3500.7	125.1449
TS ($1^+ - 5^+ + \text{H}_2$)			TS ($2^+ - 3^+ + \text{H}_2$)	
1	-464.92	31.4303	-1299.15	298.3147
2	477.71	206.4676	452.04	89.4079
3	596.49	0.8764	636.6	43.5299
4	673.09	30.862	651.63	21.1891

5	853.65	3.6477	831.92	13.1039
6	925.59	17.6001	872.32	49.7817
7	944.28	28.5095	1016.95	29.2595
8	1586.15	11.6534	1113.14	17.0656
9	1612.09	58.3859	1831	13.8934
10	2455.79	24.5941	2281.42	77.9977
11	3551.42	243.0053	2482.19	23.668
12	3660.51	151.6562	3487.34	127.236
TS (2⁺- 4⁺+H₂)				
1	-2112.77	813.1127		
2	401.2	0.2232		
3	700.19	8.3132		
4	872.37	22.6323		
5	931.73	2.0936		
6	981.05	10.913		
7	1015.24	11.0967		
8	1181.02	41.8472		
9	1815.97	286.5772		
10	2068.27	81.0045		
11	2479.09	11.9515		
12	2521.8	24.1013		

Table S8. Optimized Cartesian coordinates (Å) on the adiabatic singlet ground state potential energy surfaces of H₄PN structures in Fig. 6 calculated at the CCSD/cc-pVTZ level of theory.

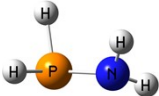

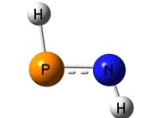
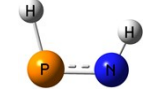
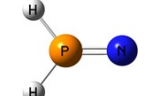
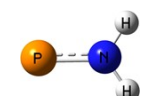
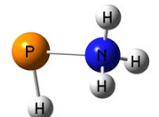
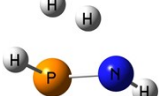
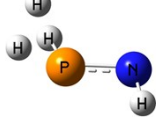
Atom	X	Y	Z	Atom	X	Y	Z
1, C₁, ¹A				2, C_s, ¹A'			
H	-1.590567	-0.805598	0.157990	H	-0.526942	-1.172624	1.069693
H	-1.521870	0.824804	0.400477	H	-0.891678	1.563156	0.000000
H	0.949698	0.448048	1.227779	H	1.346327	-0.884140	0.000000
H	0.946991	1.049112	-0.743897	H	-0.526942	-1.172624	-1.069693
N	-1.110699	0.044797	-0.085541	N	0.027238	1.142376	0.000000
P	0.599376	-0.121996	-0.029571	P	0.027238	-0.422026	0.000000
6, C_s, ¹A'				H₂PNH, C₁, ²A			
H	0.393258	1.538511	0.823901	H	-1.585953	0.764574	-0.028439
H	1.370162	-0.760186	0.000000	H	0.997381	-1.086226	0.605471
H	-1.017150	1.460502	0.000000	H	0.968984	1.059053	0.728161
H	0.393258	1.538511	-0.823901	N	-1.132849	-0.143271	0.060914
P	-0.051797	-0.790228	0.000000	P	0.503302	0.017700	-0.115440
N	-0.051797	1.153725	0.000000	H	-1.585953	0.764574	-0.028439
HPNH₂, C₁, ²A				TS (1 – 3+H₂)			
H	-0.866304	1.301956	-0.046330	H	0.197167	1.256935	-0.101280
H	1.577117	-0.812570	0.143328	H	1.577112	-0.273591	-0.674707
H	1.525181	0.854119	0.237641	H	-1.026044	0.049811	1.211454
P	-0.642441	-0.099122	0.010780	H	-0.741003	1.531752	-0.244643
N	1.057232	0.020474	-0.070905	N	1.103424	0.004219	0.180679
				P	-0.515413	-0.172963	-0.097038
TS (2 – 3+H₂)				TS (6 – 3+H₂)			
H	1.640051	0.507556	0.503469	H	-0.886623	1.242753	-0.483733
H	-1.090084	-1.125891	-0.416267	H	1.402504	-0.975158	0.041420
H	-1.407605	0.992526	0.051807	H	1.584649	0.654584	-0.264419
N	1.145255	-0.020780	-0.206834	P	-0.725890	-0.048819	0.085146
P	-0.390122	-0.057792	0.157192	N	0.913857	-0.131028	-0.215015
H	-1.307312	0.638142	-1.049060	H	2.390821	0.727307	0.934649

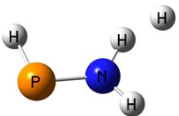
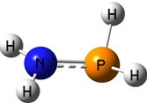
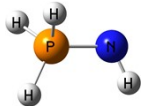
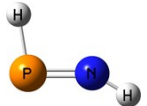
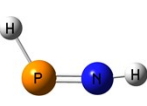
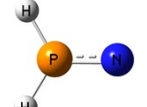
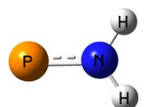
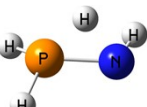
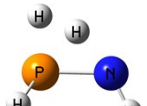
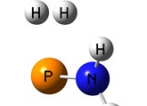
Table S9. Vibrational frequencies (cm^{-1}) and infrared intensities (km mol^{-1}) on the adiabatic singlet ground state potential energy surfaces of H_4PN structures.

1			2	
Normal modes	Frequency(cm^{-1})	IR Inten	Frequency(cm^{-1})	IR Inten
1	352.0043	20.6906	391.0997	103.327
2	555.6901	182.0434	784.5421	93.9638
3	833.9631	28.5677	791.5615	12.4935
4	862.4771	6.0879	923.661	78.6539
5	938.5796	33.6942	1119.1774	21.6473
6	1103.9535	34.2501	1135.564	8.9938
7	1179.6733	27.7275	1165.3115	37.0327
8	1635.2708	19.16	1238.9183	152.5785
9	2362.3737	130.2845	2367.1094	147.7712
10	2426.8186	84.5375	2400.5544	149.037
11	3591.8528	9.2124	2546.2275	35.1502
12	3689.459	22.7512	3615.5018	16.4082
6				
1	192.455	2.638		
2	511.1066	18.9833		
3	675.4189	3.1938		
4	744.2512	15.2505		
5	1004.996	42.0391		
6	1321.8389	76.7591		
7	1678.1218	28.1582		
8	1687.2321	30.7176		
9	2376.166	137.2136		
10	3498.4107	13.4492		
11	3603.9601	71.8222		
12	3614.1265	52.3658		
H₂PNH			HPNH₂	
1	374.1405	108.8495	374.1405	108.8495
2	449.1162	110.1364	449.1162	110.1364
3	817.7606	6.1604	817.7606	6.1604
4	868.7151	49.4187	868.7151	49.4187
5	1092.3873	32.6204	1092.3873	32.6204
6	1617.2749	26.1365	1617.2749	26.1365
7	2398.5841	94.8079	2398.5841	94.8079
8	3611.9792	28.0282	3611.9792	28.0282

9	3721.5063	32.9869	3721.5063	32.9869
TS (1 – 3+H₂)			TS (2 – 3+H₂)	
1	-2270.9958	540.662	-1532.8036	227.326
2	605.8949	26.8432	370.3654	47.2684
3	746.838	166.8139	689.7256	7.6128
4	916.694	24.4485	764.712	18.4564
5	948.7276	109.5384	916.1223	78.2181
6	1034.8644	12.6836	988.3745	84.5608
7	1145.4046	26.2071	1128.4774	10.9043
8	1152.3932	36.9452	1233.5152	50.0244
9	1746.1302	574.3579	1467.6316	384.8665
10	2030.6465	25.6896	2236.7761	12.9739
11	2377.2635	98.7605	2527.1451	14.0383
12	3523.1808	9.2119	3570.084	20.3612
TS (6 – 3+H₂)				
1	-755.6768	393.229		
2	443.6232	18.3514		
3	474.3493	32.5702		
4	655.5297	88.1966		
5	761.7058	22.5909		
6	829.886	11.1684		
7	917.1228	14.1732		
8	1083.0024	42.6138		
9	1555.9797	63.6455		
10	2399.1647	86.4143		
11	3150.247	392.1973		
12	3645.585	47.303		

Table S10. T_1 diagnostic values for species in Figs. 1, 4, and 6.

		T_1 diagnostic		
		CCSD(T)/ cc-pVDZ	CCSD(T)/ cc-pVTZ	CCSD(T)/ cc-pVQZ
close-shell				
	1 ($C_1, ^1A_1$)	0.009966	0.010834	0.011321
	2 ($C_s, ^1A'$)	0.015498	0.014376	0.014000
	(E)-3 ($C_s, ^1A'$)	0.015686	0.016129	0.016064
	(Z)-3 ($C_s, ^1A'$)	0.015572	0.016028	0.016037
	4 ($C_{2v}, ^1A_1$)	0.029353	0.027809	0.027498
	5 ($C_{2v}, ^1A_1$)	0.019273	0.018007	0.017523
	6 ($C_s, ^1A'$)	0.009595	0.010554	0.011004
	ts (1-3+H₂) ($C_1, ^1A_1$)	0.017680	0.016237	0.015919
	ts (2-3+H₂) ($C_1, ^1A_1$)	0.020013	0.018104	0.017438

	ts (6-3+H₂) (C₁, ¹A)	0.054369	0.061301	0.063474
open-shell				
	1+ (C_s, ²A')	0.016338	0.017531	0.017641
	2+ (C_s, ²A'')	0.014171	0.014703	0.014980
	(E)-3+ (C_s, ²A')	0.057876	0.0569701	0.057386
	(Z)-3+ (C₁, ²A)	0.063102	0.062664	0.063196
	4+ (C_{2v}, ²B₂)	0.072590	0.072067	0.072529
	5+ (C_{2v}, ²B₂)	0.024127	0.023162	0.023150
	ts (2⁺-1⁺) (C₁, ²A)	0.025363	0.025945	0.026086
	ts (1⁺-3⁺+H₂) (C₁, ²A)	0.027859	0.029022	0.029692
	ts (1⁺-5⁺+H₂) (C₁, ²A)	0.017873	0.018728	0.018866

	ts (2⁺-3⁺+H₂) (C₁, ²A)	0.023505	0.025089	0.025806
	ts (2⁺-4⁺+H₂) (C₁, ²A)	0.028315	0.027243	0.027216
	HPNH₂ (C₁, ²A)	0.016420	0.017537	0.017954
	H₂PNH (C₁, ²A)	0.028877	0.031339	0.032808

Table S11. (a) MRCI/CBS//CCSD/cc-pVTZ ionization energies (IE) of H₂NP isomers depicted in Figure 1, and the activation energy of 6→3+H₂ in Figure 6. **(b)** Numbers of configuration state functions (CSFs) of MCSCF and MRCI in **(a)**.

(a)

	E_{zpc}^a	MCSCF (6,9)/(5,9)			MRCI				IE ^b (eV)	E_a^c (kJ mol ⁻¹)
		cc-pVDZ	cc-pVTZ	cc-pVQZ	cc-pVDZ	cc-pVTZ	cc-pVQZ	CBS		
(E)-3 (C _s , ¹ A')	0.022700	-396.400972	-396.441700	-396.452456	-396.639616	-396.793463	-396.851470	-396.885362	9.30	0
(E)-3 ⁺ (C _s , ² A')	0.020504	-396.072866	-396.112247	-396.122140	-396.311832	-396.455057	-396.509489	-396.541332		
(Z)-3 (C _s , ¹ A')	0.022227	-396.399009	-396.439570	-396.450182	-396.638070	-396.792229	-396.850171	-396.884008	9.49	2
(Z)-3 ⁺ (C ₁ , ² A)	0.018527	-396.065053	-396.105594	-396.115799	-396.300348	-396.444932	-396.499688	-396.531702		
4 (C _{2v} , ¹ A ₁)	0.019417	-396.355051	-396.399510	-396.412161	-396.572309	-396.728651	-396.788359	-396.823315	9.50	154
4 ⁺ (C _{2v} , ² B ₂)	0.018568	-396.038569	-396.077345	-396.088117	-396.248794	-396.387900	-396.441660	-396.473193		
										E_a^d (kJ mol ⁻¹)
6 (C _s , ¹ A')	0.047632	-397.529162	-397.570880	-397.580950	-397.808232	-397.973379	-398.032089	-398.066064		0
ts (6→3+H ₂) (C ₁ , ¹ A)	0.036260	-397.444859	-397.488248	-397.499067	-397.734213	-397.896305	-397.953317	-397.986248		180

^a zero-point energy by CCSD/cc-pVTZ in hartree,

^b ionization energy by MRCI/CBS with CCSD/cc-pVTZ zero-point energy correction in eV,

^c the relative energy of different isomer sets by MRCI/CBS with CCSD/cc-pVTZ zero-point energy correction in kJ mol⁻¹,

^d activation energy by MRCI/CBS with CCSD/cc-pVTZ zero-point energy correction in kJ mol⁻¹.

(b)

	MCSCF (6,9)/(5,9)			MRCI		
	cc-pVDZ	cc-pVTZ	cc-pVQZ	cc-pVDZ	cc-pVTZ	cc-pVQZ
<i>(E)</i> -3 (C_s , $^1A'$)	1,316	1,316	1,316	63,277,540	545,860,596	2,345,519,228
<i>(E)</i> -3 ⁺ (C_s , $^2A'$)	980	980	980	53,177,458	449,749,330	1,921,768,482
<i>(Z)</i> -3 (C_s , $^1A'$)	1,316	1,316	1,316	63,277,540	545,860,596	2,345,519,228
<i>(Z)</i> -3 ⁺ (C_1 , 2A)	1,890	1,890	1,890	176,854,500	1,582,487,100	6,926,064,660
4 (C_{2v} , 1A_1)	684	684	684	18,426,930	150,905,992	638,250,340
4 ⁺ (C_{2v} , 2B_2)	488	488	488	15,370,906	123,007,690	516,818,562
6 (C_s , $^1A'$)	1,316	1,316	1,316	137,250,912	1,195,242,982	5,297,582,236
ts (6-3+H₂) (C_1 , 1A)	2,520	2,520	2,520	482,909,400	4,366,584,900	19,608,107,310

References

- 1 B. M. Jones and R. I. Kaiser, *J. Phys. Chem. Lett.*, 2013, **4**, 1965-1971.
- 2 C. Zhu, A. Bergantini, S. K. Singh, R. I. Kaiser, A. K. Eckhardt, P. R. Schreiner, Y.-S. Huang, B.-J. Sun and A. H. H. Chang, *ChemComm.*, 2021, **57**, 4958-4961.
- 3 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.
- 4 M. Bouilloud, N. Fray, Y. Benilan, H. Cottin, M. C. Gazeau and A. Jolly, *Mon. Not. R. Astron. Soc.*, 2015, **451**, 2145-2160.
- 5 S. A. Sandford and L. J. Allamandola, *Astrophys. J.*, 1993, **417**, 815.
- 6 R. I. Kaiser and K. Roessler, *Astrophys. J.*, 1997, **475**, 144.
- 7 D. Drouin, A. R. Couture, D. Joly, X. Tastet, V. Aimez and R. Gauvin, *Scanning*, 2007, **29**, 92-101.
- 8 A. G. Yeghikyan, *Astrophysics*, 2011, **54**, 87-99.
- 9 M. D. Francia and E. R. Nixon, *J. Chem. Phys.*, 1973, **58**, 1061-1065.
- 10 J. Wang, J. H. Marks, A. M. Turner, A. A. Nikolayev, V. Azyazov, A. M. Mebel and R. I. Kaiser, *Phys. Chem. Chem. Phys.*, 2023, **25**, 936-953.
- 11 G. D. Purvis III and R. J. Bartlett, *J. Chem. Phys.*, 1982, **76**, 1910-1918.
- 12 C. Hampel, K. A. Peterson and H.-J. Werner, *Chem. Phys. Lett.*, 1992, **190**, 1-12.
- 13 P. J. Knowles, C. Hampel and H. J. Werner, *J. Chem. Phys.*, 1993, **99**, 5219-5227.
- 14 M. J. Deegan and P. J. Knowles, *Chem. Phys. Lett.*, 1994, **227**, 321-326.
- 15 K. A. Peterson, D. E. Woon and T. H. D. Jr., *J. Chem. Phys.*, 1994, **100**, 7410-7415.
- 16 T. J. Lee and P. R. Taylor, *Int. J. Quantum Chem.*, 1989, **36**, 199-207.
- 17 J. C. Rienstra-Kiracofe, W. D. Allen and H. F. Schaefer, *J. Phys. Chem. A*, 2000, **104**, 9823-9840.
- 18 G. W. T. M. J. Frisch, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, D. J. Fox, Gaussian 16, Revision C.1, Gaussian Inc. Wallingford, CT, 2019.
- 19 P. J. K. H.-J. Werner, G. Knizia, F. R. Manby, M. Schütz, P. Celani, W. Györffy, D. Kats, T. Korona, R. Lindh, A. Mitrushenkov, G. Rauhut, K. R. Shamasundar, T. B. Adler, R. D. Amos, S. J. Bennie, A. Bernhardsson, A. Berning, D. L. Cooper, M. J. O. Deegan, A. J. Dobbyn, F. Eckert, E. Goll, C. Hampel, A. Hesselmann, G. Hetzer, T. Hrenar, G. Jansen, C. Köppl, S. J. R. Lee, Y. Liu, A. W. Lloyd, Q. Ma, R. A. Mata, A. J. May, S. J. McNicholas, W. Meyer, T. F. Miller III, M. E. Mura, A. Nicklass, D. P. O'Neill, P. Palmieri, D. Peng, T. Petrenko, K. Pflüger, R. Pitzer, M. Reiher, T. Shiozaki, H. Stoll, A. J. Stone, R. Tarroni, T. Thorsteinsson, M. Wang, M. Welborn, and B. Ziegler, MOLPRO, 2024.1, a package of ab initio programs, University of Cardiff: Cardiff, U.K., 2024.
- 20 J. Wang, C. Zhang, A. K. Eckhardt and R. I. Kaiser, *Chem. Sci.*, 2025, **16**, 21111-21120.

- 21 Y. Mo, J. Yang and G. Chen, *J Chem Phys*, 2004, **120**, 1263-1270.
- 22 W. Zheng and R. I. Kaiser, *J. Phys. Chem. A*, 2010, **114**, 5251-5255.
- 23 W. Zheng and R. I. Kaiser, *Chem. Phys. Lett.*, 2007, **440**, 229-234.
- 24 J. H. Teles, G. Maier, B. Andes Hess Jr. and L. J. Schaad, *Chem. Ber.*, 1989, **122**, 749-752.
- 25 G. Socrates, *Infrared and raman characteristic group frequencies: Tables and charts*, 3rd edn., John Wiley & Sons, Ltd., New York, 2004.
- 26 D. E. Milligan and M. E. Jacox, *J. Chem. Phys.*, 1965, **43**, 4487-4493.
- 27 W. Zheng, D. Jewitt, Y. Osamura and R. I. Kaiser, *Astrophys. J.*, 2008, **674**, 1242.
- 28 R. Frigge, C. Zhu, A. M. Turner, M. J. Abplanalp, B.-J. Sun, Y.-S. Huang, A. H. Chang and R. I. Kaiser, *ChemComm.*, 2018, **54**, 10152-10155.
- 29 R. I. Kaiser, S. P. Krishtal, A. M. Mebel, O. Kostko and M. Ahmed, *Astrophys. J.*, 2012, **761**, 178.