

Supporting Information

Nonequilibrium Formation of Cyanophosphine (H₂PCN)—the Simplest Phosphorus-Containing Nitrile—in Interstellar Ice Analogues

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Methods

Experimental. Experiments were carried out in an ultrahigh vacuum chamber evacuated by magnetically suspended turbomolecular pumps (Osaka, TG420MCAB and TG1300MUCWB) backed by an oil-free scroll pump (BOC Edwards, XDS35i),^{1,2} which maintained pressures of a few 10^{-11} Torr. A polished silver substrate was coupled to a closed-cycle helium cryostat and mounted on a movable assembly that permitted vertical translation through an adjustable bellows and horizontal rotation through a rotatable flange.^{1,2} Phosphine (PH_3 , Sigma-Aldrich, 99.9995%) and hydrogen cyanide (HCN , 5% seeded in helium) were used without further purification. After the substrate was cooled to 5 K, the phosphine–hydrogen cyanide (PH_3 – HCN) ice mixtures were prepared by codepositing phosphine and hydrogen cyanide independently through separate glass capillary arrays. During deposition, the partial pressures of PH_3 and HCN samples were maintained at 5×10^{-9} and 1×10^{-7} Torr, respectively, for approximately 20 minutes. Ice growth was monitored in situ by laser interferometry, and the ice thickness was determined from the interference fringes produced by reflections of a 632.8 nm helium-neon laser beam at the vacuum–ice and ice–substrate interfaces.³ The thickness of the deposited ice was calculated to be 670 ± 80 nm (Table S1) using an average refractive index of 1.43 ± 0.12 ,⁴ determined from the refractive indices of phosphine ice at 5.5 K (1.51 ± 0.04)³ and hydrogen cyanide ice at 18 K (1.346).⁵ Infrared spectra of PH_3 – HCN ice mixtures were collected over the 6000–500 cm^{-1} range at a spectral resolution of 4 cm^{-1} using a Nicolet 6700 Fourier transform infrared (FTIR) spectrometer (Thermo Electron). The ratio of phosphine to hydrogen cyanide was determined to be 1.6 ± 0.4 : 1 (Table S1) from the integrated infrared absorptions of selected infrared bands and their corresponding absorption coefficients: the ν_1 band at 2315 cm^{-1} (7.0×10^{-18} cm molecule^{-1}), the ν_3 band at 2335 cm^{-1} (2.4×10^{-18} cm molecule^{-1}), and the ν_4 band at 1103 cm^{-1} (7.1×10^{-19} cm molecule^{-1}) for phosphine,³ and the ν_1 band at 3132 cm^{-1} (7.384×10^{-17} cm molecule^{-1}), and the ν_3 band at 2096 cm^{-1} (1.029×10^{-17} cm molecule^{-1}) for hydrogen cyanide.⁵

After deposition, the ice mixtures were irradiated with 5 keV electrons generated by an electron gun (SPECS, EQ PU-22) to mimic secondary electrons produced by galactic cosmic rays (GCRs) as they penetrate interstellar ices within cold molecular clouds.^{4,6,7} The 5 keV electrons employed here simulate GCR-induced energy deposition in interstellar ices because their linear energy transfer is comparable to that of 10–20 MeV GCR protons.^{2,8,9} The ices were irradiated with

electrons at a current of 28 nA for 5 minutes at an incidence angle of 70°. Monte Carlo simulations using the CASINO software suite¹⁰ yielded irradiation dose of 0.19 ± 0.03 eV per PH₃ and 0.18 ± 0.03 eV per HCN utilizing the densities of PH₃ ice (0.90 g cm^{-3})^{3,11} and HCN ice (0.85 g cm^{-3}).⁵ Notably, low dose electron irradiation was used here to minimize sequential reaction pathways and preferentially probe first-generation products, an approach validated in previous studies of electron-irradiated ices, in which only first-generation products were detected at comparably low irradiation doses.^{2,12-16} These doses correspond to $(7 \pm 2) \times 10^5$ years of GCR exposure, representative of an early stage of a cold molecular cloud.¹⁷ The simulations revealed an average penetration depth of 360 ± 50 nm for the incident electrons in the PH₃–HCN ice and indicated that 99% of the incident electron energy was deposited within the upper 570 ± 100 nm, which is less than the total thickness of 670 ± 80 nm, thereby minimizing interactions between the electrons and the underlying silver substrate. FTIR spectra were recorded *in situ* before, during, and after irradiation to monitor the chemical evolution of the irradiated ices.

Following irradiation, the ice mixtures were heated from 5 to 320 K at a rate of 1 K min^{-1} under temperature-programmed desorption (TPD) conditions. Molecules releasing into the gas phase were photoionized using pulsed (30 Hz) vacuum ultraviolet (VUV) light at photon energies of 11.10, 10.24, 10.52–10.74, and 10.78–10.87 eV. The tunable VUV light was generated by resonant four-wave mixing in a xenon or krypton gas jet through sum- and difference-frequency generation ($2\omega_1 \pm \omega_2$). Two independently tunable dye lasers (Sirah Lasertechnik, Cobra-Stretch), pumped by separate Nd:YAG lasers (Spectra-Physics, Quanta-Ray PRO 270-30 and PRO 250-30), produced the fundamental ω_1 and ω_2 laser beams; detailed parameters for VUV generation are provided in Table S6. A biconvex lithium fluoride lens mounted in an off-axis configuration separated the VUV light from the residual fundamental beams and directed to the photoionization region located 2.0 ± 0.5 mm above the ice surface to ionize molecules during TPD. The resulting ions were extracted into a reflectron time-of-flight mass spectrometer (Jordan TOF Products), separated according to their mass-to-charge ratios, and detected by a dual microchannel plate (MCP) detector. Following amplification and discrimination, the ion signals were recorded using a multichannel scaler (FAST ComTec, MCS6A). Each mass spectrum was acquired with a temporal resolution of 3.2 ns and was accumulated for 2 minutes, corresponding to 3600 cycles.

Computational. The Cartesian geometries of neutral and cationic H₂PCN isomers were optimized at the coupled cluster CCSD/cc-pVTZ level of theory,¹⁸⁻²¹ and harmonic vibrational frequencies and infrared intensities were calculated at the same level. The energies were computed separately with coupled cluster CCSD(T)/cc-pVDZ, CCSD(T)/cc-pVTZ, and CCSD(T)/cc-pVQZ methods, and then extrapolated to the completed basis set limits,²² CCSD(T)/CBS, with the CCSD/cc-pVTZ zero-point energy (ZPVE) corrections. Through taking the energy difference between the ionic and the neutral isomers of similar conformation, the adiabatic ionization energies (IEs) were computed.⁷ The Gaussian16 program is facilitated in the *ab initio* electronic structure calculations.²³ The uncertainty associated with the CCSD(T)/CBS energies is estimated to be within 8 kJ mol⁻¹.^{24,25} The IE ranges are corrected for the combined theoretical uncertainty of -0.03/+0.06 eV²⁶ and an additional correction of -0.03 eV to account for thermal and Stark effects.⁶ The optimized Cartesian coordinates (Table S7), harmonic vibrational frequencies and corresponding infrared intensities (Table S8) for the H₂PCN isomers and their cations are provided.

Vertical electronic excitation energies and oscillator strengths were calculated with time-dependent density functional theory (TD-DFT) using Gaussian 16.²³ TD-DFT calculations were performed at the B3LYP/cc-pVTZ²⁷⁻³⁰ level of theory. For each structure, the lowest 20 excited states were computed using the TD = (NStates = 20). Franck–Condon simulations were performed for the photoionization transition between the neutral molecule and the corresponding radical cation. Equilibrium geometries and harmonic vibrational frequencies for both charge states were obtained with CFOUR 2.1³¹ at the CCSD(T)/cc-pVTZ level of theory, using frozen-core correlation. The neutral state was treated as a closed-shell singlet, and the radical cation as a doublet. Analytical harmonic vibrational frequency calculations were carried out at the optimized geometries, and both structures were verified to have real vibrational frequencies only. Franck–Condon factors were evaluated with ezFCF v1.3³² using the harmonic approximation including Duschinsky rotation. The 0–0 ionization energy was calculated from the difference in final electronic CCSD(T) energies corrected by the harmonic zero-point vibrational energy difference. The ezFCF Duschinsky calculation was performed at 0 K with initial-state vibrational excitation restricted to $v = 0$. The final-state vibronic expansion was truncated at 12000 cm⁻¹ and allowed up to 10 vibrational quanta in the target state. The relative ezFCF stick energies were shifted by the calculated E_{00} value to obtain absolute ionization energies in eV. Stick spectra were then

convoluted with a Gaussian line shape using a full width at half maximum of 0.05 eV. The broadened spectra were normalized to a maximum intensity of unity for plotting. The plotted spectra therefore use absolute ionization energy in eV on the x-axis and normalized Franck–Condon intensity on the y-axis (Figure S6).

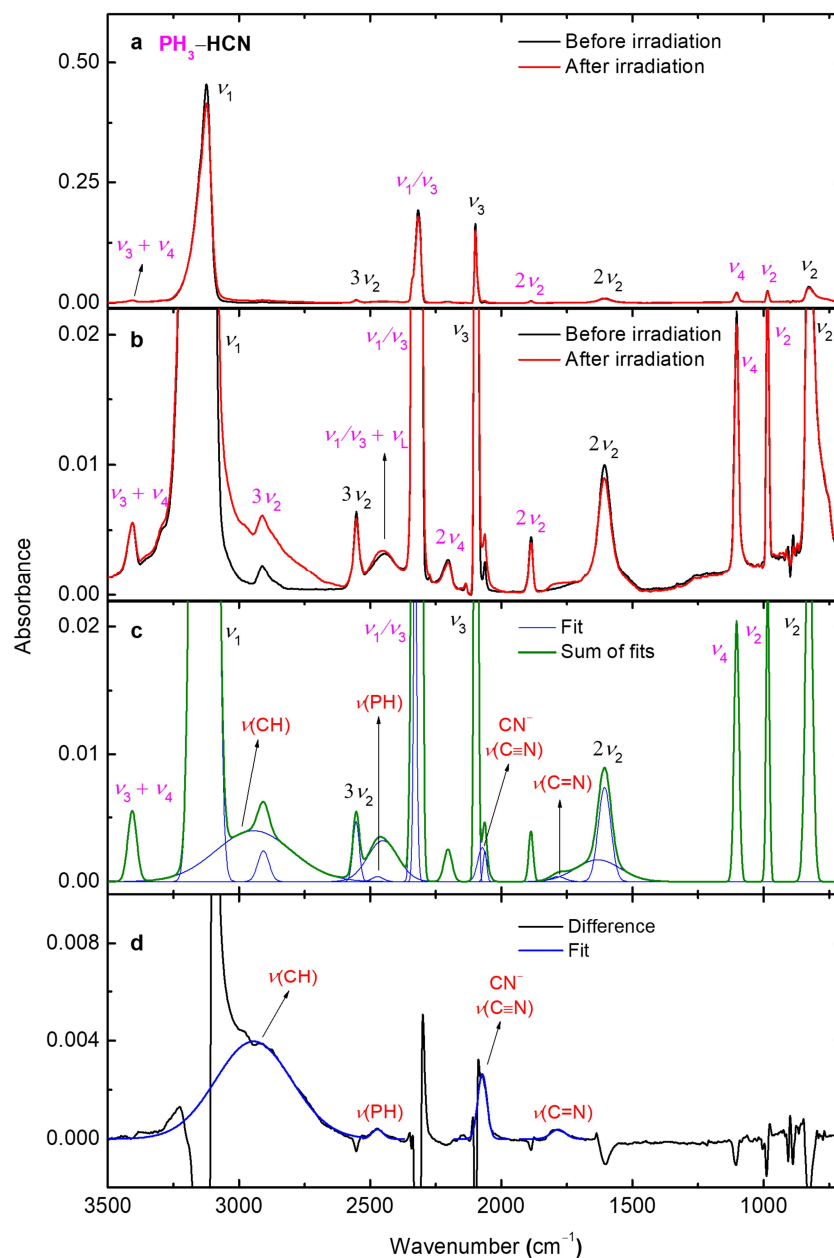


Figure S1. Infrared spectra of PH₃-HCN ice before and after irradiation at 5 K. (a) Comparison of the infrared spectra collected over the 3500–700 cm⁻¹ range before and after irradiation, and (b) a magnified view. (c) Spectrum after irradiation was deconvoluted using gaussian functions. (d) Difference IR spectrum between before and after irradiation, with new formed absorptions deconvoluted. Band assignments associated with PH₃ and HCN are indicated in magenta and black, respectively, whereas newly formed absorptions after irradiation are labeled in red. Detailed assignments are provided in Table S2.

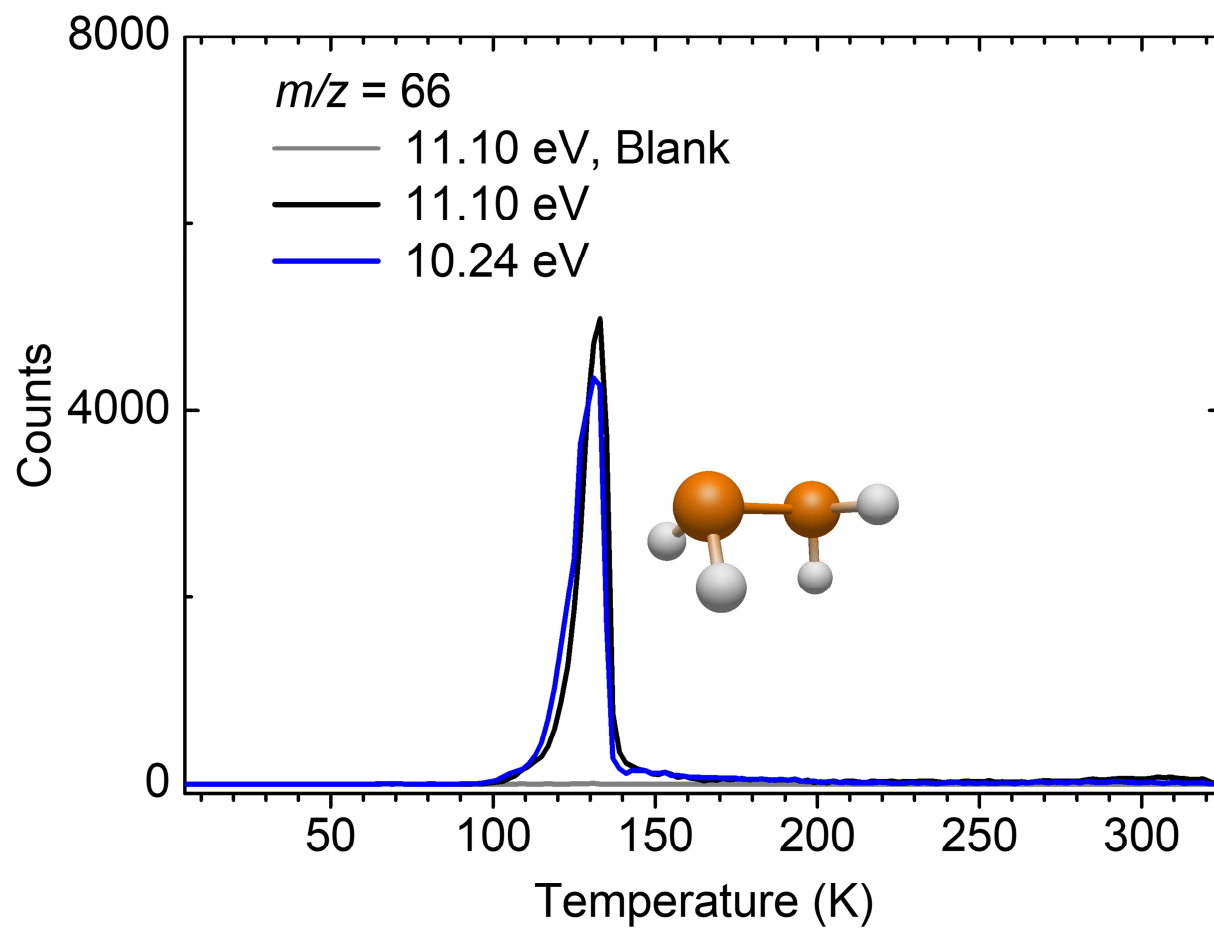


Figure S2. Ion signals recorded during TPD from PH_3 – HCN ices recorded at 11.10 and 10.24 eV. TPD profiles of $m/z = 66$ with a peak temperature of 132 K was assigned to diphosphane (P_2H_4).³

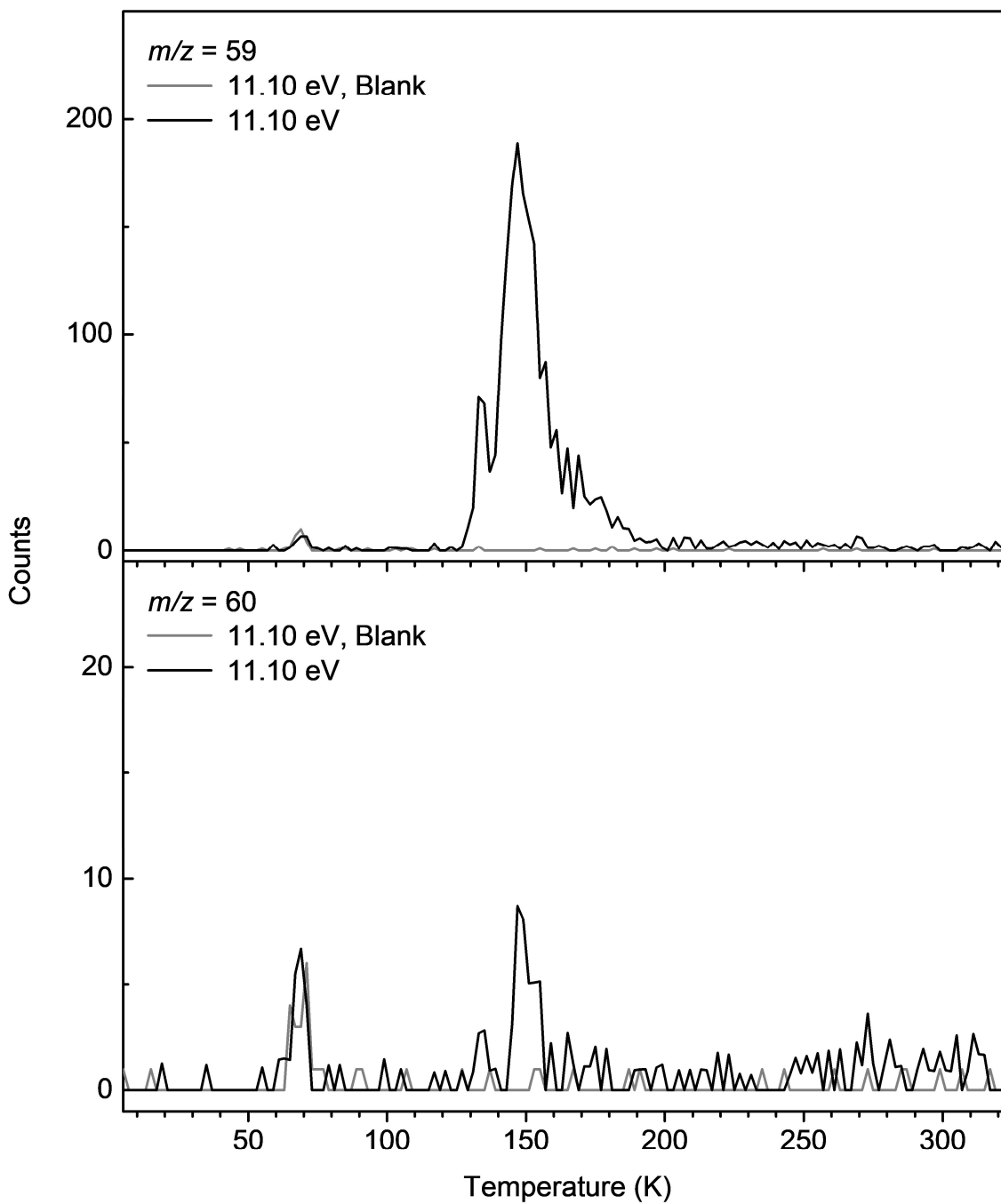


Figure S3. TPD profiles of $m/z = 59$ and 60 from phosphine–hydrogen cyanide ($\text{PH}_3\text{--HCN}$) ice recorded at 11.10 eV.

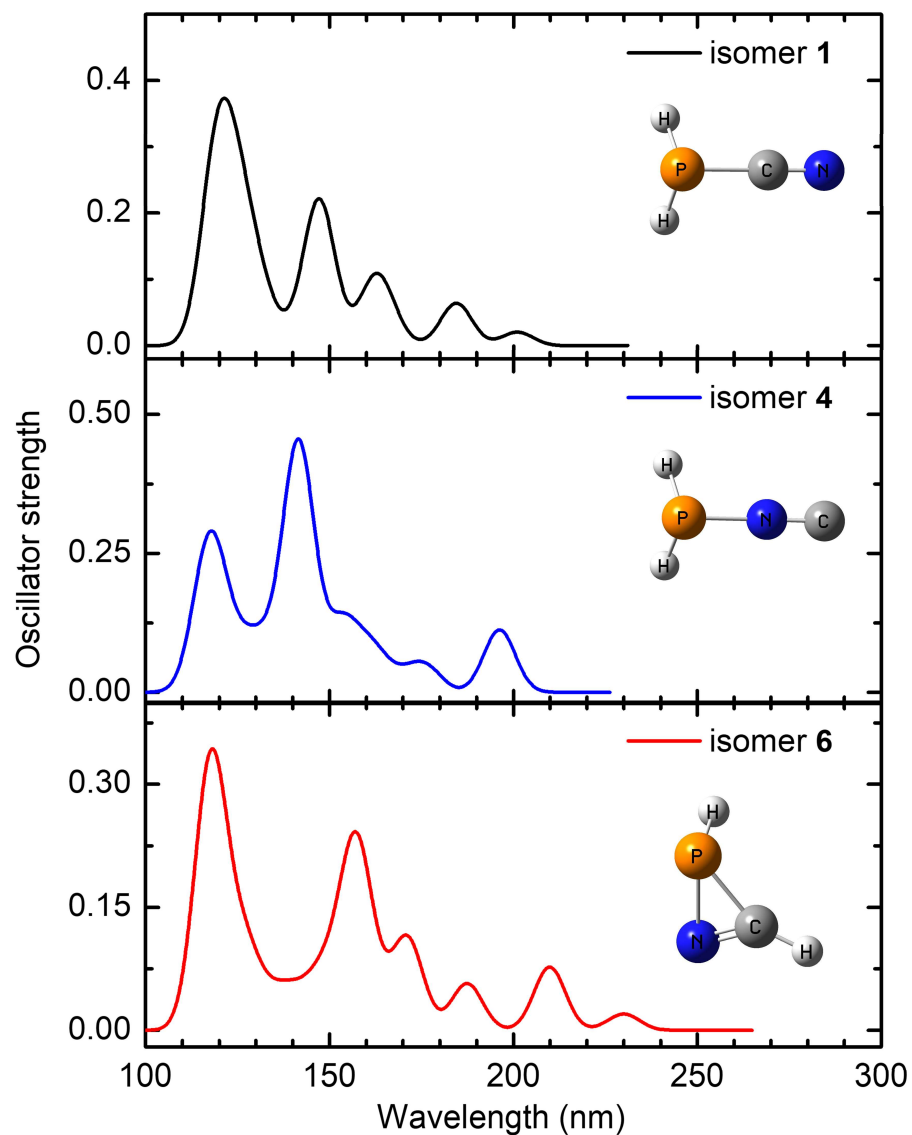


Figure S4. Simulated ultraviolet (UV) spectra of H₂PCN isomers **1**, **4**, and **6** computed at the TD-B3LYP/cc-pVTZ level of theory. The discrete electronic transitions were broadened using Gaussian line shape functions with a full width at half maximum (FWHM) of 10 nm.

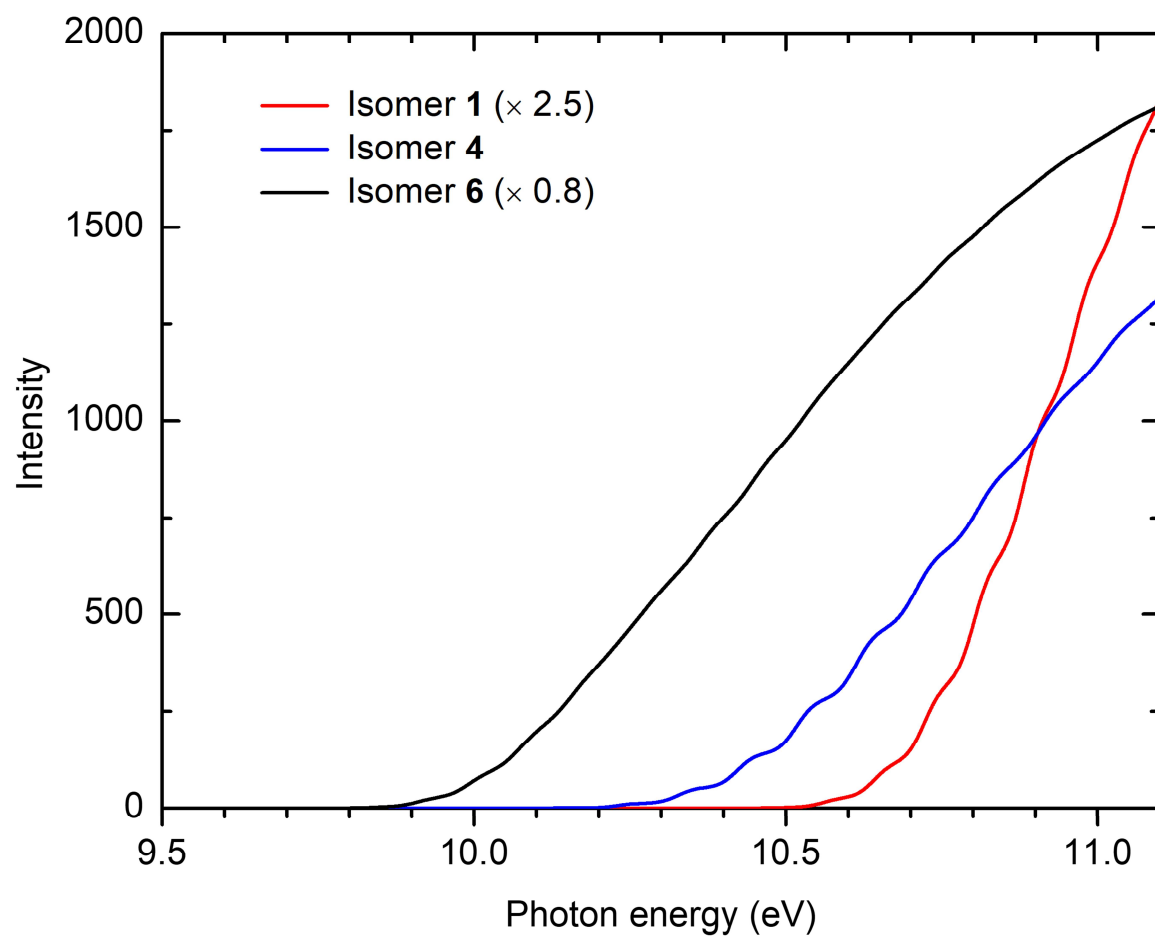


Figure S5. Simulated Franck-Condon photoionization efficiency (PIE) curves of isomers **1**, **4**, and **6**.

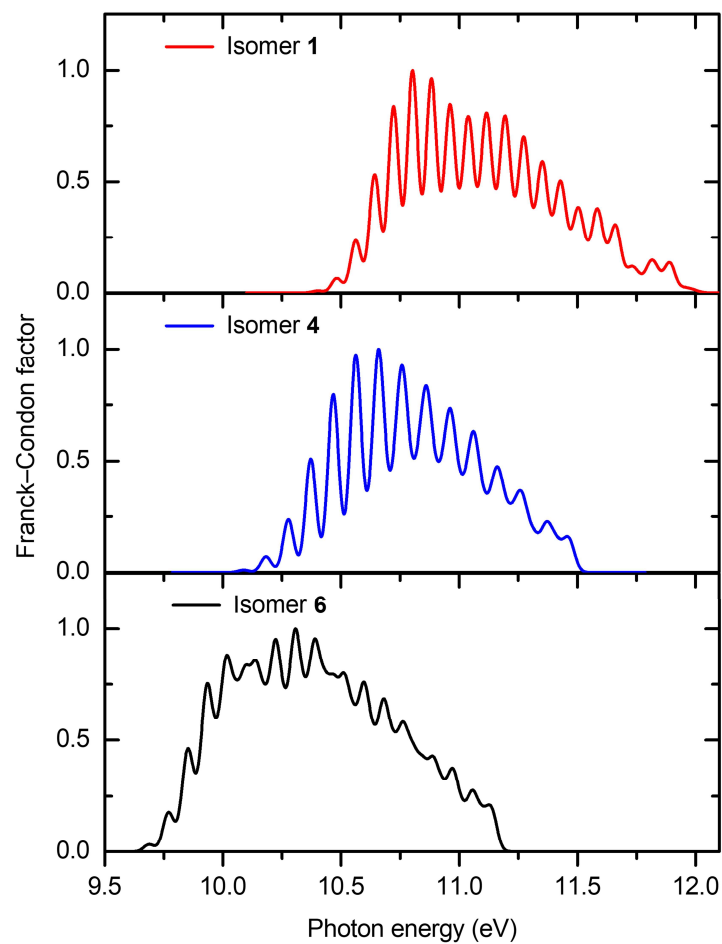


Figure S6. Computed Franck-Condon factors for isomers **1**, **4**, and **6** as a function of the energy.

Table S1. Experimental parameters for phosphine–hydrogen cyanide ices, including ice composition and ratio, thickness, irradiation current and time, and photoionization energy.

Ice composition	Ratio of phosphine to hydrogen cyanide	Thickness (nm)	Irradiation current (nA)	Irradiation time (s)	Dose (eV/phosphine)	Dose (eV/hydrogen cyanide)	Photon energy (eV)
PH ₃ –HCN	2.0 ± 0.5: 1	670 ± 80	–	–	–	–	11.10
PH ₃ –HCN	1.6 ± 0.4: 1	670 ± 80	28 ± 1	300 ± 10	0.19 ± 0.03	0.18 ± 0.03	11.10
PH ₃ –HCN	1.6 ± 0.4: 1	670 ± 80	31 ± 1	300 ± 10	0.21 ± 0.03	0.20 ± 0.03	10.78–10.87
PH ₃ –HCN	1.2 ± 0.3: 1	670 ± 80	32 ± 2	300 ± 10	0.22 ± 0.03	0.21 ± 0.04	10.67–10.74
PH ₃ –HCN	1.4 ± 0.3: 1	670 ± 80	28 ± 1	300 ± 10	0.19 ± 0.03	0.18 ± 0.03	10.52–10.66
PH ₃ –HCN	2.0 ± 0.5: 1	670 ± 80	31 ± 1	300 ± 10	0.21 ± 0.03	0.20 ± 0.03	10.24

Table S2. Infrared absorption features observed for PH₃–HCN ice before and after electron irradiation at 5 K.

Infrared absorptions before irradiation (cm ⁻¹)	
PH ₃	Assignment ³
4553	2ν ₁
3407	ν ₃ + ν ₄
2907	3ν ₂
2452	ν ₁ /ν ₃ + ν _L
2335	ν ₃ (PH stretch)
2315	ν ₁ (PH stretch)
2203	2ν ₄
2062	ν ₂ + ν ₄
1887	2ν ₂
1103	ν ₄
984	ν ₂
HCN	Assignment ⁵
3960	ν ₁ + ν ₂
3695	2ν ₂ + ν ₃
3132	ν ₁ (CH stretch)
2554	3ν ₂
2096	ν ₃ (CN stretch)
1606	2ν ₂
827	ν ₂ (HCN bend)
New infrared absorptions after irradiation (cm ⁻¹)	
	Assignment ³³⁻³⁵
2944	ν(C–H)
2472	ν(P–H)
2073	ν(C≡N) (CN ⁻)
1784	ν(C=N)

Table S3. Error analysis of the adiabatic ionization energies (IEs) and relative energies (ΔE) of H₂PCN isomers computed at the CCSD(T)/CBS//CCSD/cc-pVTZ level of theory, including zero-point vibrational energy (ZPVE) corrections obtained at the CCSD/cc-pVTZ level (Table S4). The IE ranges are corrected for the combined theoretical uncertainty of $-0.03/+0.06$ eV²⁶ and an additional correction of -0.03 eV accounting for thermal and Stark effects.⁶

Isomers	Structure	ΔE (kJ mol ⁻¹)	Computed IE (eV)	Corrected IE ranges (eV)
1 (C _s , ¹ A')		0	10.51	10.45–10.54
2 (C ₁ , ¹ A)		73	8.36	8.30–8.39
3 (C _s , ¹ A')		67	8.59	8.53–8.62
4 (C _s , ¹ A')		64	10.17	10.11–10.20
5 (C ₁ , ¹ A)		362	9.05	8.99–9.08
6 (C ₁ , ¹ A)		117	9.86	9.80–9.89
7 (C ₁ , ¹ A)		200	7.69	7.63–7.72
8 (C _s , ¹ A')		131	9.28	9.22–9.31
9 (C ₁ , ¹ A)		158	7.60	7.54–7.63
10 (C _{2v} , ¹ A ₁)		116	7.73	7.67–7.76

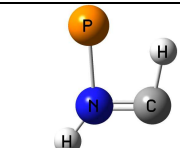
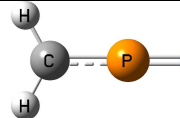
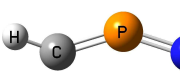
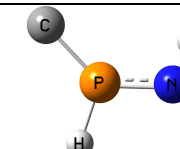
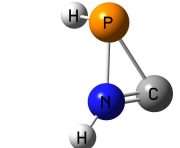
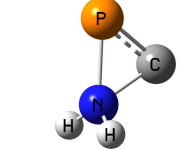
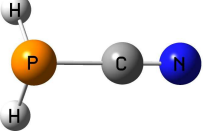
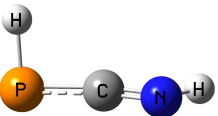
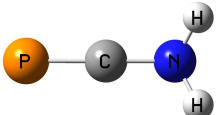
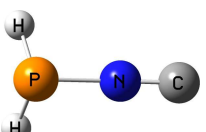
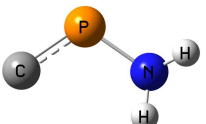
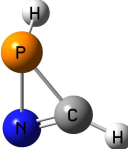
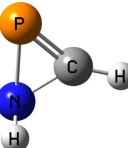
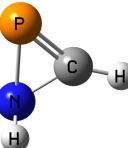
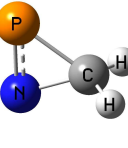
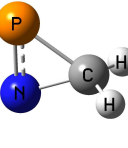
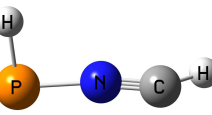
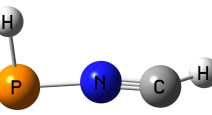
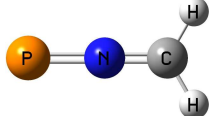
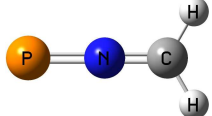
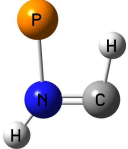
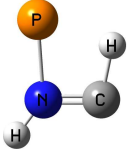
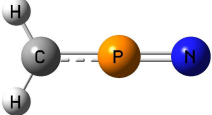
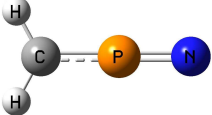
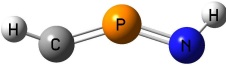
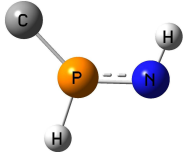
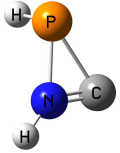
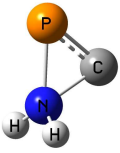
11 (C_1 , ^1A)		387	7.61	7.55–7.64
12 (C_{2v} , $^1A_1$)		274	9.58	9.52–9.61
13 (C_1 , ^1A)		286	9.67	9.61–9.70
14 (C_1 , ^1A)		513	9.16	9.10–9.19
15 (C_1 , ^1A)		226	8.91	8.85–8.94
16 (C_s , $^1A'$)		287	9.44	9.38–9.47

Table S4. Calculated parameters for CCSD(T)/CBS//CCSD/cc-pVTZ adiabatic ionization energies and relative energies of H₂PCN isomers.

		CCSD/ cc-pVTZ ^a	E _{zpc} ^b	CCSD(T)/ cc-pVDZ	CCSD(T)/ cc-pVTZ	CCSD(T)/ cc-pVQZ	CCSD(T)/ CBS
	1 (C_s, ¹A')	-434.732877	0.025855	-434.649669	-434.785051	-434.825995	-434.848984
	1⁺ (C_s, ²A')	-434.352426	0.025024	-434.275908	-434.402153	-434.440499	-434.462048
	2 (C₁, ¹A)	-434.701048	0.027356	-434.619196	-434.757880	-434.799368	-434.822610
	2⁺ (C_s, ²A'')	-434.406026	0.026750	-434.328854	-434.456759	-434.493927	-434.514621
	3 (C_s, ¹A')	-434.703399	0.031603	-434.624714	-434.764282	-434.805831	-434.829083
	3⁺ (C_s, ²A')	-434.398566	0.031678	-434.328268	-434.455505	-434.492760	-434.513536
	4 (C_s, ¹A')	-434.708771	0.025511	-434.620071	-434.759379	-434.800956	-434.824236
	4⁺ (C_s, ²A')	-434.339867	0.024894	-434.256005	-434.388051	-434.427640	-434.449828
	5 (C₁, ¹A)	-434.591358	0.028892	-434.503442	-434.647781	-434.690386	-434.714186
	5⁺ (C_s, ²A'')	-434.270217	0.029056	-434.189981	-434.322213	-434.360436	-434.381692
	6 (C₁, ¹A)	-434.684274	0.027784	-434.600979	-434.741202	-434.782917	-434.806258

	6⁺ (C₁, ²A)^c	-434.307300	0.028861	-434.251548	-434.384068	-434.4231969	-434.4450568
	7 (C₁, ¹A)	-434.650048	0.030205	-434.569985	-434.711940	-434.753894	-434.777336
	7⁺ (C_s, ²A'')	-434.381132	0.030708	-434.305164	-434.436212	-434.474139	-434.495238
	8 (C_s, ¹A')	-434.676915	0.030968	-434.596156	-434.739321	-434.780990	-434.804198
	8⁺ (C_s, ²A')^c	-434.325690	0.031244	-434.273008	-434.404736	-434.442529	-434.463513
	9 (C₁, ¹A)	-434.666534	0.025979	-434.583297	-434.724608	-434.765955	-434.789011
	9⁺ (C₁, ²A)	-434.402569	0.026526	-434.323812	-434.452438	-434.489581	-434.510232
	10 (C_{2v}, ¹A₁)	-434.684462	0.030211	-434.603582	-434.745402	-434.786432	-434.809255
	10⁺ (C_{2v}, ²B₁)	-434.411826	0.030005	-434.336666	-434.466591	-434.504204	-434.525128
	11 (C₁, ¹A)	-434.582559	0.026720	-434.498562	-434.639231	-434.679948	-434.702599
	11⁺ (C_s, ²A'')	-434.320899	0.029656	-434.249497	-434.371653	-434.406519	-434.425856
	12 (C_{2v}, ¹A₁)	-434.616134	0.026723	-434.530084	-434.677170	-434.720949	-434.745448
	12⁺ (C_s, ²A')	-434.277782	0.025691	-434.204954	-434.333534	-434.371273	-434.392330

	13 (C₁, ¹A)	-434.608664	0.026671	-434.517892	-434.670224	-434.715488	-434.740809
	13⁺ (C_s, ²A'')	-434.270238	0.024980	-434.188045	-434.322169	-434.361607	-434.383620
	14 (C₁, ¹A)	-434.532934	0.025151	-434.439012	-434.584648	-434.628406	-434.652942
	14⁺ (C₁, ²A)	-434.204863	0.024525	-434.121430	-434.254010	-434.293509	-434.315617
	15 (C₁, ¹A)	-434.644459	0.027598	-434.559337	-434.700315	-434.741695	-434.764784
	15⁺ (C₁, ²A)	-434.324358	0.026173	-434.248177	-434.376812	-434.414696	-434.435849
	16 (C_s, ¹A')	-434.618646	0.031642	-434.537717	-434.680511	-434.722131	-434.745319
	16⁺ (C_s, ²A'')	-434.283787	0.030664	-434.208545	-434.339507	-434.376867	-434.397584

^a CCSD/cc-pVTZ energy with zero-point energy correction in hartree.

^b Zero-point energy by CCSD/cc-pVTZ in hartree.

^c The geometries are optimized at MP2/cc-pVTZ level.

Table S5. Proposed molecular formulae and isomers assigned to the ion signals detected at individual mass channels during TPD of the irradiated phosphine–hydrogen cyanide ices. Sublimation events observed are indicated by plus signs (+). The detected fragment ions are shown in italics. Blue and red labels indicate ion signals that were detected in electron-irradiated PH₃ ices³ and HCN ices,⁴ respectively.

PH ₃ –HCN				Proposed formula	Possible isomers, assigned from references ^{3,4}
<i>m/z</i>	Blank, 11.10 eV	Irradiation, 11.10 eV	Irradiation, 10.24 eV		
1	+	+	+	<i>H⁺</i>	
17		+		<i>NH₃^a</i>	
30		+	+	<i>N₂H₂⁺</i>	HNNH
31		+	+	<i>CH₅N⁺</i>	CH ₃ NH ₂
34	+	+	+	<i>PH₃⁺</i>	PH ₃
42		+	+	<i>CH₂N₂⁺</i>	NH ₂ CN
43		+	+	<i>C₂H₅N⁺</i>	CH ₃ CHNH
44		+	+	<i>CH₄N₂⁺</i>	NH ₂ CHNH, <i>c</i> -NHCH ₂ NH, CH ₃ NNH, CH ₂ NNH ₂
45		+	+	<i>N₃H₃⁺</i>	NH ₂ NNH, <i>c</i> -N ₃ H ₃
48		+		<i>PH₃N⁺</i> , <i>CH₅P^{+b}</i>	
49		+		<i>PH₄N^{+c}</i>	
50		+	+	<i>C₄H₂⁺</i>	HCCCCH
51		+	+	<i>¹³CC₃H₂⁺</i>	
55		+		<i>C₂H₃N₂⁺</i>	
59		+		<i>CH₂PN⁺</i>	H ₂ PCN
60		+		<i>¹³CH₂PN⁺</i>	
61		+	+	<i>CH₄NP⁺</i>	PH ₂ CHNH, PH ₂ NCH ₂
64		+	+	<i>P₂H₂⁺</i>	HPPH
65		+		<i>C₃HN₂⁺</i>	
66		+	+	<i>P₂H₄⁺</i>	PH ₂ PH ₂
67		+	+	<i>P₂H₅⁺</i>	Protonated parent of P ₂ H ₄ and/or fragment from P ₅ H ₇ isomers
80		+		<i>C₃H₂N₃⁺</i>	
81		+	+	<i>C₃H₃N₃⁺</i>	<i>c</i> -C ₃ H ₃ N ₃ (Triazine)
82		+	+	<i>C₂H₂N₄⁺</i> , <i>C₄H₆N₂⁺</i>	<i>c</i> -C ₂ H ₂ N ₄ (Tetrazine) <i>c</i> -C ₄ H ₆ N ₂ (Methyl imidazole)

96		+	+	$P_3H_3^+$	Fragment from P_4H_6 isomers
97		+	+	$P_3H_4^+$	Fragment from P_4H_6 isomers
98		+	+	$P_3H_5^+$	PH_2PHPH_2
112		+	+	$CH_7P_3^+$	$(PH_2)_2CHPH_2$, $(PH_2)_2PCH_3$, $PH_2PHPHCH_3$
113		+	+	$P_3H_6N^+$	$(PH_2)_2NPH_2$, $NH_2PHPHPH_2$, $(PH_2)_2PNH_2$
114		+	+	$P_3H_7N^+$	
126		+	+	$P_4H_2^+$	Fragment from P_6H_8 isomers
127		+	+	$P_4H_3^+$	Fragment from P_6H_8 isomers
128		+	+	$P_4H_4^+$	Fragment from P_5H_7 isomers
129		+	+	$P_4H_5^+$	Fragment from P_5H_7 isomers
130		+	+	$P_4H_6^+$	$(PH_2)_2PPH_2$, $PH_2PHPHPH_2$
159		+	+	$P_5H_4^+$	Fragment from P_7H_9 isomers
160		+	+	$P_5H_5^+$	Fragments from P_6H_8 and/or P_7H_9 isomers
161		+	+	$P_5H_6^+$	Fragments from P_6H_8 isomers
162		+	+	$P_5H_7^+$	$(PH_2)_2PPHPH_2$, $PH_2PHPHPHPH_2$
191		+	+	$P_6H_5^+$	Fragments from P_7H_9 and/or P_8H_{10} isomers
192		+	+	$P_6H_6^+$	<i>c</i> - P_6H_6 , $PH_2PHPHPPPH_2$
193		+	+	$P_6H_7^+$	Fragment from P_7H_9 isomers
221		+	+	$P_7H_4^+$	
223		+	+	$P_7H_6^+$	Fragment from P_8H_{10} isomers

^a No sublimation event is observed at 10.24 eV, which is above the ionization energy of ammonia (NH_3 , IE = 10.070 ± 0.020 eV),³⁶ indicating the event at 11.10 eV originates from a fragment ion.

^b No sublimation event is observed at 10.24 eV, which is above the ionization energy of methylphosphine (CH_3PH_2 , IE = 9.12 ± 0.07 eV),³⁷ indicating the event at 11.10 eV originates from a fragment ion.

^c No sublimation event is observed at 10.24 eV, which is above the ionization energy of phosphine imide ($NHPH_3$, IE = 8.89 ± 0.07 eV) and its phosphinous amide (NH_2PH_2 , IE = 8.57 ± 0.07 eV) isomer,³⁸ indicating the event at 11.10 eV originates from a fragment ion.

Table S6. Experimental parameters employed for the generation of vacuum ultraviolet (VUV) light, an uncertainty in photon energy of less than 0.001 eV.

Photon energy (eV)	Nonlinear medium in four- wave mixing	Laser wavelength for ω_1 (nm)	Laser dye for ω_1	Laser wavelength for ω_2 (nm)	Laser dye for ω_2
11.10 ($2\omega_1+\omega_2$)	Xenon	249.628	Coumarin 503	1064	–
10.78–10.87 ($2\omega_1-\omega_2$)	Krypton	202.316	Rhodamine 610 and 640	840–895	LDS 867
10.67–10.74 ($2\omega_1-\omega_2$)	Krypton	202.316	Rhodamine 610 and 640	780–820	LDS 798
10.52–10.66 ($2\omega_1-\omega_2$)	Krypton	202.316	Rhodamine 610 and 640	715–775	LDS 751
10.24 ($2\omega_1-\omega_2$)	Krypton	212.556	Stilbene 420	869.435	LDS 867

Table S7. CCSD/cc-pVTZ optimized Cartesian coordinates (Å) on the adiabatic singlet and doublet ground state potential energy surface of H₂PCN and H₂PCN⁺ isomers, respectively.

Atom	X	Y	Z	Atom	X	Y	Z
1				1⁺			
P	-0.095991	-1.037945	0.000000	P	-0.033994	-0.981098	0.000000
H	0.849393	-1.206857	1.037496	H	0.506337	-1.509596	1.179236
H	0.849393	-1.206857	-1.037496	H	0.506337	-1.509596	-1.179236
C	0.000000	0.760209	0.000000	C	0.000000	0.738364	0.000000
N	-0.036988	1.917376	0.000000	N	-0.071824	1.900782	0.000000
2				2⁺			
N	-1.763025	-0.000617	-0.120332	N	-0.055478	1.774444	0.000000
C	-0.554808	0.014838	-0.003471	C	0.000000	0.628867	0.000000
P	1.118269	-0.094105	0.009650	P	-0.058670	-1.184927	0.000000
H	1.238190	1.320553	0.006752	H	1.361453	-1.201530	0.000000
H	-2.342207	0.006316	0.711649	H	-0.093057	2.781125	0.000000
3				3⁺			
H	-0.265404	2.144201	0.842201	H	-0.000058	2.187522	0.868389
H	-0.265404	2.144201	-0.842201	H	-0.000058	2.187522	-0.868389
P	0.015262	-1.211921	0.000000	P	0.000030	-1.220473	0.000000
N	0.043125	1.688683	0.000000	N	-0.000047	1.660276	0.000000
C	0.000000	0.344938	0.000000	C	0.000000	0.385019	0.000000
4				4⁺			
N	0.000000	0.754745	0.000000	N	0.000000	0.711160	0.000000
C	-0.100539	1.925540	0.000000	C	-0.153816	1.900127	0.000000
P	-0.075982	-0.967623	0.000000	P	-0.015112	-0.905453	0.000000
H	0.871478	-1.161056	1.031978	H	0.574792	-1.398547	1.171779
H	0.871478	-1.161056	-1.031978	H	0.574792	-1.398547	-1.171779
5				5⁺			
C	1.472988	0.646564	0.015355	C	1.570950	-0.301805	0.000000
P	0.230472	-0.476236	0.000856	P	0.000000	0.599587	0.000000
N	-1.281347	0.311831	-0.091666	N	-0.968022	-0.704789	0.000000
H	-2.017312	-0.202709	0.364886	H	-1.973554	-0.573476	0.000000
H	-1.308276	1.284042	0.171804	H	-0.675993	-1.675974	0.000000
6				6⁺			
N	0.896793	0.721617	0.019868	N	0.789509	0.768367	-0.028898

C	0.909002	-0.527642	0.005861	C	0.959285	-0.478551	0.055196
P	-0.819753	-0.034753	-0.099991	P	-0.764642	-0.111607	-0.087851
H	1.673882	-1.290903	0.030219	H	1.705500	-1.252301	0.198310
H	-1.109148	-0.073272	1.295396	H	-1.518147	0.419142	0.990562
7				7⁺			
N	-0.992464	-0.596611	0.141659	N	-0.596282	-0.823831	0.000000
C	-0.557192	0.761311	-0.006866	C	0.670980	-0.771600	0.000000
P	0.849526	-0.075592	-0.008922	P	0.000000	0.896744	0.000000
H	-1.121387	1.677092	-0.057614	H	1.461616	-1.511167	0.000000
H	-1.331108	-0.934792	-0.758969	H	-1.313521	-1.543571	0.000000
8				8⁺			
N	0.827579	-0.573390	0.000000	N	0.736965	-0.517619	0.000000
C	-0.627300	-0.900176	0.000000	C	-0.546453	-1.104701	0.000000
P	0.000000	0.805472	0.000000	P	0.000000	0.879051	0.000000
H	-1.014626	-1.333646	0.913381	H	-0.940018	-1.467110	0.942026
H	-1.014626	-1.333646	-0.913381	H	-0.940018	-1.467110	-0.942026
9				9⁺			
N	-0.586879	0.026359	-0.000767	N	0.650812	0.023025	-0.012060
C	-1.767585	-0.001281	-0.117469	C	1.794896	-0.006659	0.000232
P	1.072455	-0.098072	0.009802	P	-1.131755	-0.095125	0.002765
H	-2.616195	-0.016470	0.545880	H	2.869852	-0.013939	0.036694
H	1.243038	1.310729	0.017279	H	-1.218589	1.319603	0.004857
10				10⁺			
N	0.000000	0.000000	-0.399456	N	0.000000	0.000000	-0.385576
C	0.000000	0.000000	-1.669418	C	0.000000	0.000000	-1.671050
P	0.000000	0.000000	1.148458	P	0.000000	0.000000	1.141786
H	0.000000	0.937831	-2.207087	H	0.000000	0.945822	-2.200722
H	0.000000	-0.937831	-2.207087	H	0.000000	-0.945822	-2.200722
11				11⁺			
C	1.227608	0.641916	0.000000	C	1.242224	1.024285	0.000000
H	-0.379559	1.888433	0.000000	H	-0.640008	1.614882	0.000000
P	-0.544292	-0.788249	0.000000	P	-0.593113	-0.922462	0.000000
N	0.000000	0.957136	0.000000	N	0.000000	0.820375	0.000000
H	1.178297	-0.616152	0.000000	H	2.083357	0.333720	0.000000
12				12⁺			
N	0.000000	0.000000	1.623828	N	0.012698	1.651534	0.000000
C	0.000000	0.000000	-1.518966	C	-0.010139	-1.574375	0.000000

P	0.000000	0.000000	0.120866	P	0.000000	0.136335	0.000000
H	0.000000	0.945648	-2.032999	H	-0.014026	-2.079756	0.959796
H	0.000000	-0.945648	-2.032999	H	-0.014026	-2.079756	-0.959796
13				13⁺			
N	1.451277	-0.279189	0.043485	N	-1.464739	-0.217893	0.000000
C	-1.533149	-0.250354	-0.089961	C	1.567399	-0.256952	0.000000
P	-0.036298	0.197226	0.023531	P	0.000000	0.273255	0.000000
H	-2.502891	0.086910	0.220258	H	2.563721	0.176114	0.000000
H	2.087319	0.411147	-0.337850	H	-1.714942	-1.207974	0.000000
14				14⁺			
N	1.409423	-0.246691	0.000000	N	1.362305	-0.302162	0.000000
C	-1.646552	-0.476781	0.000000	C	-1.686938	-0.521270	0.000000
P	-0.093491	0.278246	0.000000	P	-0.053742	0.322178	0.000000
H	-0.032551	1.678497	0.000000	H	-0.100988	1.723794	0.000000
H	1.448277	-1.264664	0.000000	H	1.492610	-1.313707	0.000000
15				15⁺			
N	-0.878679	-0.474868	0.005472	N	-1.063304	-0.391716	0.003063
C	-0.977928	0.794722	0.014393	C	-0.843742	0.806843	0.011417
P	0.830264	-0.012197	-0.098217	P	0.880090	-0.056963	-0.094714
H	1.083279	-0.008311	1.302625	H	1.032608	-0.083356	1.315120
H	-1.518920	-1.252989	0.045959	H	-1.728372	-1.161249	0.015653
16				16⁺			
C	0.982949	-0.558109	0.000000	C	0.958622	-0.695455	0.000000
P	0.000000	0.820557	0.000000	P	0.000000	0.854430	0.000000
N	-0.578915	-0.897614	0.000000	N	-0.552119	-0.864238	0.000000
H	-0.922647	-1.338200	0.838326	H	-0.943449	-1.297026	0.839440
H	-0.922647	-1.338200	-0.838326	H	-0.943449	-1.297026	-0.839440

Table S8. CCSD/cc-pVTZ vibrational frequencies (cm^{-1}) and infrared intensities (km mol^{-1}) on the adiabatic singlet and doublet ground state potential energy surface of H_2PCN and H_2PCN^+ isomers, respectively.

1			1⁺	
Normal modes	Frequency (cm^{-1})	IR intensity	Frequency (cm^{-1})	IR intensity
1	296.4906	2.7299	243.106	0.0282
2	322.0531	2.5183	261.7303	0.0234
3	623.2637	22.6219	666.1552	3.1649
4	877.1332	25.3889	716.514	51.1258
5	909.4745	14.8138	776.0094	18.1763
6	1123.8219	18.3476	1042.3027	20.6212
7	2297.1053	4.7266	2214.9755	248.1346
8	2446.5532	20.3532	2505.9194	33.896
9	2453.1722	30.8538	2557.5803	64.5549
2			2⁺	
1	368.034	1.5209	321.408	6.0491
2	417.1764	36.1961	338.1567	7.6904
3	739.7468	51.1291	540.9322	0.9754
4	778.3799	62.4682	599.3457	125.484
5	873.396	211.5297	620.8474	127.3515
6	917.5502	197.7782	927.7554	25.3985
7	1946.3563	518.7329	2268.1454	36.3192
8	2407.8587	37.5224	2421.2038	0.9168
9	3559.2609	68.7512	3703.9241	801.7332
3			3⁺	
1	336.4887	16.8766	321.1523	26.4919
2	409.543	120.3397	367.0667	11.7456
3	491.1955	198.4568	780.0867	177.0553
4	831.1324	5.8957	807.923	0.452
5	1173.0368	1.8585	1134.8407	0.0062
6	1640.1894	17.6443	1627.3052	23.9881
7	1702.2753	297.9142	1785.3898	110.7537
8	3593.3381	61.2528	3487.2995	332.2453
9	3694.7852	48.966	3593.7682	186.4623

	4		4 ⁺	
1	209.4753	0.092	159.7718	4.0353
2	237.1702	0.1097	186.24	3.0659
3	667.4466	69.8807	778.2513	3.5487
4	943.5102	17.3698	819.2394	26.4145
5	946.333	42.6355	828.2195	54.0513
6	1133.7115	21.3956	1058.3481	36.6727
7	2177.1974	250.3348	2051.4263	743.6592
8	2438.5613	33.8442	2494.284	19.9657
9	2444.5251	50.4205	2551.4113	36.8618
	5		5 ⁺	
1	149.8106	48.1822	201.6307	14.6147
2	271.3224	27.0245	431.6942	8.6817
3	512.3262	186.0058	697.035	196.1944
4	843.6928	42.7599	714.9457	16.8096
5	992.9104	9.5109	951.4811	13.9001
6	1023.4927	23.8717	989.0995	12.648
7	1619.0602	29.5005	1634.4459	64.7992
8	3582.556	34.1448	3514.0457	218.6107
9	3687.0793	37.4078	3619.57	171.0795
	6		6 ⁺	
1	560.1016	13.1712	568.1094	0.9958
2	718.0864	2.7	683.5771	40.514
3	761.0359	10.45	793.3988	3.7697
4	800.0114	13.3387	937.7027	10.6765
5	986.2971	19.2545	1010.1196	34.9084
6	1094.8384	47.4713	1305.8932	443.2157
7	1700.1527	26.7208	1755.1905	269.9326
8	2352.6063	122.516	2374.9279	41.1295
9	3222.7505	0.519	3239.7053	102.2902
	7		7 ⁺	
1	447.6191	8.5087	571.4285	134.9759
2	667.8121	38.5845	587.8607	48.975
3	854.4615	111.7921	699.8315	5.5524
4	1003.8148	41.3408	995.4761	0.1316
5	1099.4131	12.2667	1013.8111	19.5256
6	1211.5589	0.5428	1190.4679	95.4237

7	1277.3857	26.2624	1628.6294	16.6531
8	3272.808	1.1467	3243.5104	51.3413
9	3423.5006	0.1743	3548.044	317.483
8		8⁺		
1	636.5999	11.8291	590.4955	23.2874
2	891.1346	7.2076	715.5045	5.0414
3	903.6971	15.59	1057.6767	37.0692
4	1053.9492	27.0001	1109.7283	0.8745
5	1105.4459	1.1039	1137.728	11.8231
6	1136.8199	0.4924	1171.107	13.1748
7	1524.3182	5.0688	1505.2264	7.0114
8	3127.5778	20.6571	3142.822	30.1717
9	3213.7027	11.2621	3284.2341	24.8228
9		9⁺		
1	313.6829	9.9645	268.4079	22.1465
2	400.581	133.6714	281.2868	26.8665
3	483.4699	690.4471	513.2019	18.4199
4	779.1097	161.552	765.8273	22.6361
5	807.1341	18.1212	790.0692	23.5792
6	976.8476	34.2966	972.1135	33.312
7	1961.4344	509.4653	2238.2555	56.3925
8	2401.516	73.8051	2435.939	4.2794
9	3279.7741	30.1071	3378.4308	252.8321
10		10⁺		
1	304.1805	10.9822	305.7399	24.1889
2	441.1469	16.8893	340.118	21.8692
3	845.1381	52.6781	909.1485	0.1933
4	898.0339	0.1864	1010.0708	24.2158
5	1156.9874	10.5354	1144.9815	11.7054
6	1507.1906	0.0001	1496.4135	1.526
7	1692.8981	310.2456	1559.2705	60.0705
8	3155.7968	4.5535	3139.6271	66.5946
9	3259.7274	3.1916	3265.4118	21.6959
11		11⁺		
1	372.0191	49.9346	201.552	6.4817
2	517.8047	13.2532	588.4031	7.329
3	598.4024	10.1281	590.2197	38.1198

4	820.7399	79.0731	978.8778	109.7662
5	914.1763	65.6066	986.1593	65.5256
6	1185.7842	20.7698	1340.2305	13.2064
7	1623.1734	19.3001	1665.2339	39.7229
8	2030.0641	65.7	3183.5056	36.627
9	3666.4832	118.8093	3483.1128	167.3537
12		12⁺		
1	110.8893	42.8004	13.0235	3.057
2	153.1662	4.7452	78.6118	0.7434
3	463.377	69.7925	638.5951	31.1351
4	772.7582	0.067	765.8962	6.4707
5	932.369	13.7905	813.8243	0.0698
6	1359.6119	5.7872	1206.9945	94.1438
7	1395.036	17.5493	1354.3951	7.2039
8	3206.8104	17.6418	3128.9179	99.3042
9	3336.2299	13.0158	3276.948	87.876
13		13⁺		
1	188.635	17.0814	194.884	39.6655
2	316.343	6.3048	297.6151	20.9373
3	466.3953	108.6865	477.7483	43.0082
4	619.6845	81.1318	508.5293	102.2599
5	834.4213	172.2116	783.9851	31.8304
6	1019.6372	3.9669	876.8197	33.2245
7	1314.5211	18.3013	1091.4839	68.1199
8	3350.4117	31.7835	3219.5644	114.2338
9	3597.1294	68.0087	3514.5186	225.9184
14		14⁺		
1	264.6697	44.3218	175.7845	29.0049
2	266.5884	30.9578	323.5813	15.324
3	759.1165	86.0597	617.5	34.3671
4	834.3459	27.8531	742.6434	111.1286
5	861.7338	44.1143	824.7068	97.1491
6	957.7464	1.3999	920.1278	1.3848
7	1057.3684	42.9079	1111.9043	28.9571
8	2507.471	17.5451	2513.4835	26.6557
9	3530.7855	32.819	3535.341	180.1068
15		15⁺		

1	512.1074	16.6798	324.367	5.7953
2	541.162	31.4427	443.2081	46.91
3	700.3707	10.794	564.8043	18.8437
4	736.9353	37.1837	580.322	115.624
5	987.2372	16.054	848.723	70.4191
6	1098.3943	35.7883	947.8201	17.6383
7	1575.2073	50.7912	1799.6581	50.399
8	2366.1442	118.0132	2431.4825	6.0474
9	3596.629	71.8846	3548.3605	484.9124
16		16⁺		
1	521.3875	2.7048	560.6373	8.7426
2	744.0271	65.3909	728.401	32.6403
3	860.0096	70.9528	795.209	2.6738
4	865.6877	14.4453	919.9824	22.6969
5	987.999	4.965	965.7046	62.1148
6	1043.8258	37.5152	995.1773	161.2664
7	1646.6681	7.2679	1575.1701	55.1905
8	3560.6724	32.766	3414.605	236.9549
9	3659.1691	47.368	3504.9364	73.3494

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