Infrared and electronic spectroscopy of small organo phosphorus molecules in rare gas matrices

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Abstract

Only a handful of phosphorus-containing species, namely PN, PO, CP, CCP, HCP, SiP, PO^+,PH_3[1] (and perhaps NCCP), already belong to the inventory of ca. 300 currently known inter- and circumstellar molecules. More will certainly be found. But the available spectroscopic information on many small, potentially astrochemical P-bearing compounds is scarce (often limited to microwave transitions). Our Warsaw group is trying to bridge that gap with the missing vibrational and electronic spectroscopy data.

Here we present recent results on characterization of photoproducts produced from UV irradiation of the P-containing precursors phosphaethyne (HCP), methylphosphine (CH_3-PH_2), phosphapropyne (CH_3-CP), and bisphosphinomethane (PH_2-CH_2-PH_2).The most important photodehydrogenation products were H_2C=PH (we provided the vibrational frequencies), CP (phosphorescence)[2], HCCP (IR and UV absorption spectra)[3], and PCP (optical absorption). We investigate these species, highly unstable at standard laboratory conditions, using the environment of cryogenic noble-gas solids ("matrices"). Spectral assignments are assisted with quantum chemical predictions.

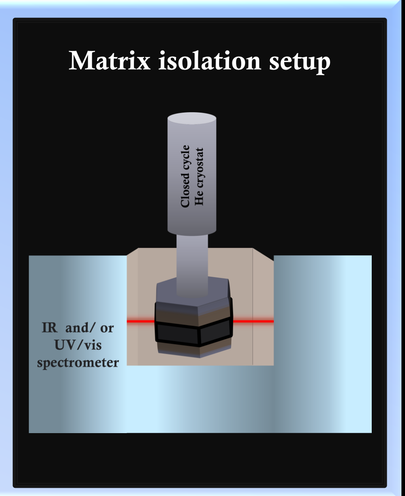
Motivation:

1. Compared to the available knowledge of photochemistry and spectroscopy of nitrogen-containing organic molecules, the phosphorous-containing molecules are not well studied.
2. Since 1975, nearly fifteen P-bearing molecules were detected in various extraterrestrial environments: planets, comets, meteorites, circumstellar envelopes, diffuse and molecular interstellar clouds[1].
3. The spectroscopy of many simple organo-phosphorous molecules remains unknown or poorly known.
4. This work focuses on exploring the spectroscopy of small organo-phosphorous compounds in argon matrices: from the diatomic CP radical to the polyatomic molecule H_2C=PH.
5. We have exploited infrared spectroscopy and electronic spectroscopy to study their vibrational and electronic energy states.

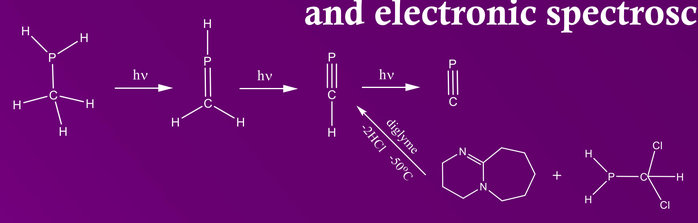
7	N 14.007
15	**P 30.973761998**
33	As 74.921595
51	Sb 121.760
83	Bi 208.98040

Experimental details:

1. The photo-precursors were synthesized in advance and stored at dry ice temperature (excluding HCP, prepared immediately before each experiment).
2. Guest-to-host ratio was approximately 1:1000. Precursor+Ar mixture was deposited onto a CsI or sapphire window (for IR and UV/Vis absorption measurements, respectively) at 10 K, in high vacuum.
3. A broad bandwidth far-UV Xe lamp and low-pressure Hg lamp were used as the photolyzing radiation sources.
4. Infrared frequencies and absorption intensities of photoproducts were predicted with DFT calculations (B3LYP/aug-cc-pVTZ)



Photochemistry of methylphosphine (CH_3PH_2) and electronic spectroscopy of CP



Infrared absorption spectrum of the CH_3PH_2 photolysis products

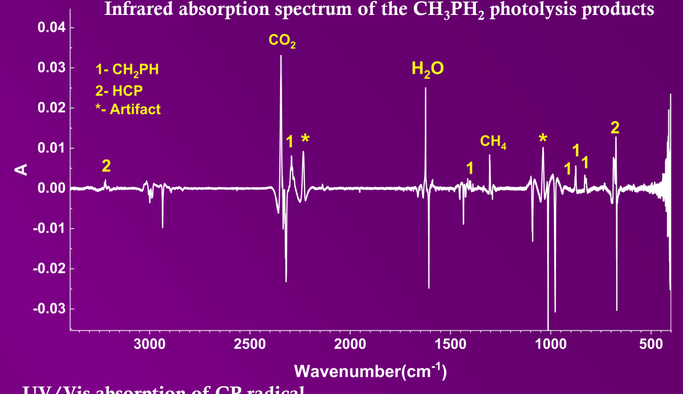


Table 1- IR absorption of H_2C=PH: Experiment vs. theory

Mode of vibration	RCCSD(T)[4] anharm. cm^{-1}	Theory B3lyp/aug-cc-pvtz Frequencies cm^{-1}	Theory B3lyp/aug-cc-pvtz Absolute intensity	Ar matrix, 6 K cm^{-1}	Ar matrix, 6 K Relative intensity	KBr pellet, 77 K[7] (tentative)
ν_1	3100	3085	0.5	-	-	
ν_2	3009	3007	4.4	-	-	
ν_3	2279	2237	94	2287 2292	2	2260
ν_4	1411	1395	2.4	1400	1	
ν_5	1020	994	23	903	2	
ν_6	976	961	1.9	-	-	
ν_7	741	718	0.7	-	-	
ν_8	881	878	44	875	10	860 (broad)
ν_9	831	826	24	830	10	

Table 2- IR absorption of HCP: Ar matrix vs. gas phase

Vibrations	Ar matrix (this work) cm^{-1}	Gas phase[5] cm^{-1}
ν_1 C-H (str)	3225	3217
ν_2 C≡P (str)	-	1278
ν_3 H-C≡P (def)	675	672
$2\nu_3$	1335	1334

UV/Vis absorption of CP radical

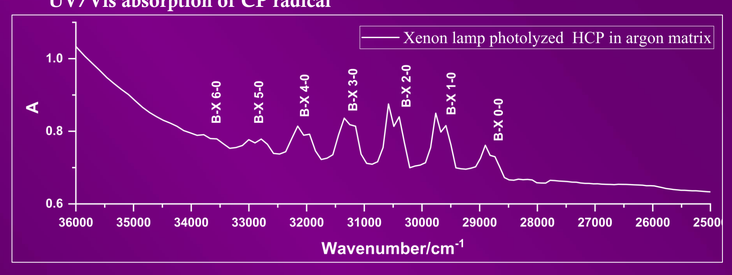
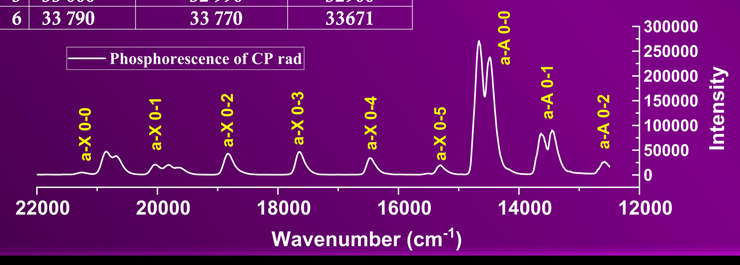


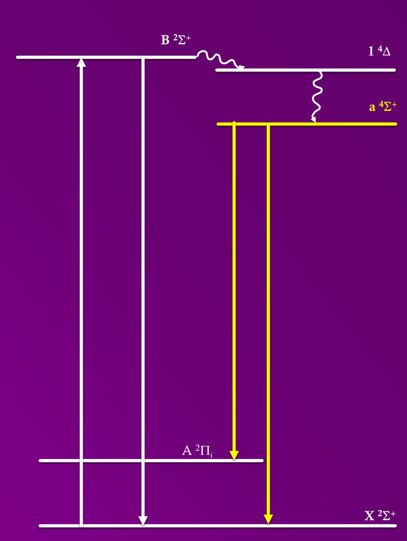
Table 3- UV absorption band wavenumbers of CP compared to those observed in phosphorescence excitation spectrum and in gas-phase fluorescence

v'	Ar matrix $X^2\Sigma^+$-$B^2\Sigma^+$ absorption	Ar matrix Phosphorescence excitation	Gas phase[6] $B^2\Sigma^+$- $X^2\Sigma^+$ fluorescence
0	28 900	28 930	28900
1	29 760	29 795	29722
2	30 580	30 660	30538
3	31 350	31 430	31337
4	32 150	32 240	32126
5	33 000	32 990	32900
6	33 790	33 770	33671

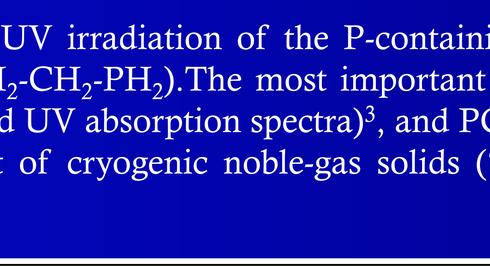
Table 4- Fluorescence of CP: Ar matrix vs. gas phase (cm^{-1})

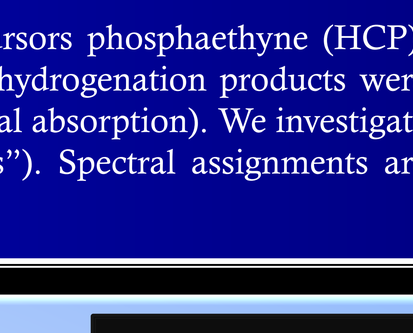
v''	Ar matrix	Gas phase[6]
0	28 900	28 900
1	27 520	27 675
2	26 360	26 462
3	25 140	25 264
4	23 910	24 079
5	22 750	

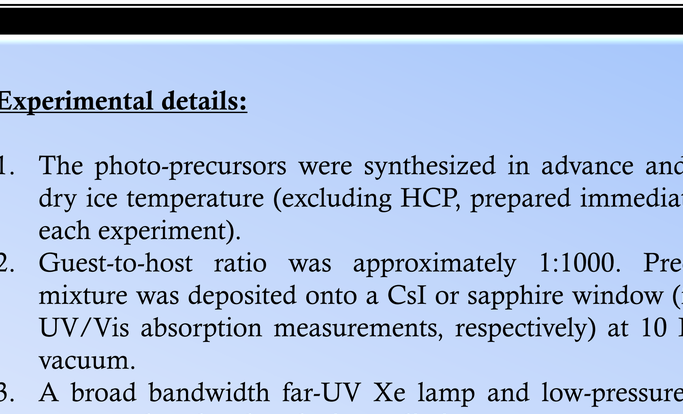




Photochemistry of phosphapropyne (CH_3CP); IR and UV/Vis characterization of HCCP

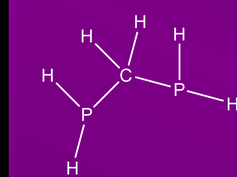






UV/Vis absorption spectrum of HCCP

UV/Vis absorption spectroscopy of PCP



Conclusions

1. Upon UV irradiation, methylphosphine undergoes dehydrogenation to H_2C=PH, HCP and CP.
2. Quartet-doublet phosphorescence of CP was observed for the first time.
3. A phosphinidene HCCP (analogous to the nitrene HCCN) was photochemically obtained in an inert cryogenic matrix from H_3CCP. IR and UV absorption spectroscopy of HCCP was studied.
4. The biradical PCP molecule, formed via photo-dehydrogenation of a diphosphine $H_2PCH_2PH_2$, was observed for the first time. Its UV/Vis triplet-triplet absorption transitions were detected, while the IR bands were too weak to be measured (as anticipated based on DFT predictions).

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