Electronic Supplementary Information to

Photoelectron spectroscopy of low valent organophosphorus compounds, P-CH_3, H-P=CH_2 and P=CH_2

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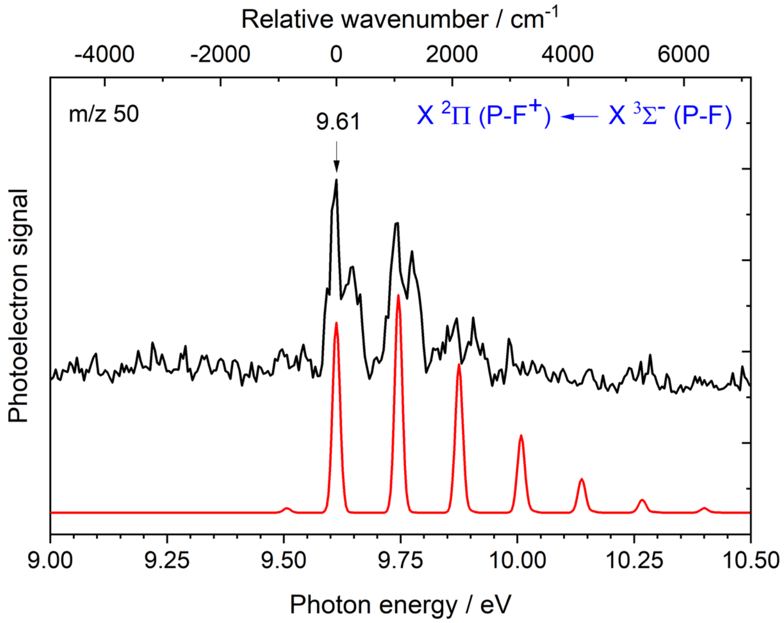
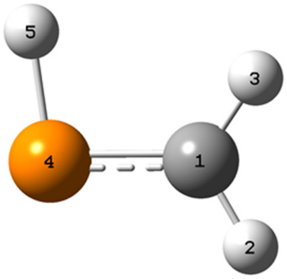


Figure S1 Recorded SPES considering mass channel 50. The spectrum is similar to the one reported by Dyke et al. for PF, but the current resolution is higher.[1] The spectral simulation is done by PGOPHER using geometry optimized in DFT/M06-2X/aug-cc-pVTZ level.[2] The extracted IE, 9.61 ± 0.01 eV, is very close to the reported value of 9.60 ± 0.01 eV. The spectral bands are split by about 280 cm^{-1} due to spin-orbit coupling and the value is also comparable to 316 ± 16 cm^{-1} reported by Dyke et al.[1]

Table S1 Comparison of the geometrical parameters and the computed harmonic frequencies of $HP{=}CH_2$ in neutral (singlet) and cation (doublet) calculated in DFT/M06-2X/aug-cc-pVTZ level. All bond lengths are in Å.

	Parameter	Neutral (s)	Cation (d)	Vibrational mode	Neutral (d) (cm^{-1})	Cation (s) (cm^{-1})
 IE: 9.82 eV	4-1	1.658	1.716	1	749	659
	5-4	1.421	1.421	2	875	676
	1-3	1.082	1.089	3	1045	735
	1-2	1.083	1.087	4	1031	913
	3-1-2	115.9°	116.6°	5	928	1012
	5-4-1	97.4°	97.6°	6	1458	1411
	5-4-1-3	0°	-38.4°	7	2359	2474
	5-4-1-2	-180°	150.9°	8	3147	3120
				9	3238	3224

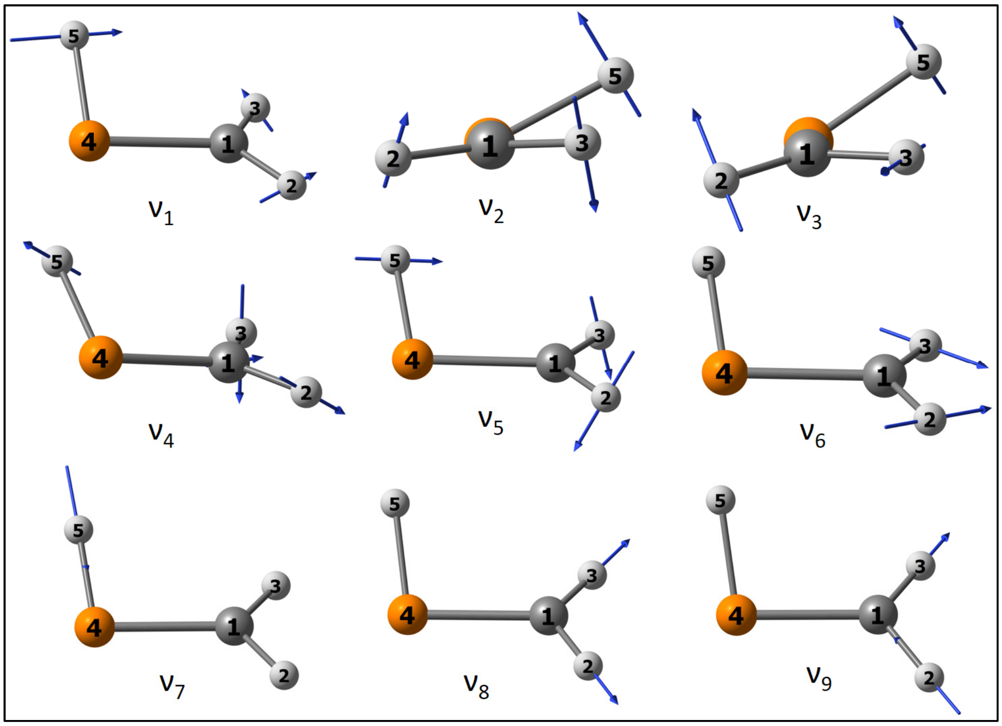
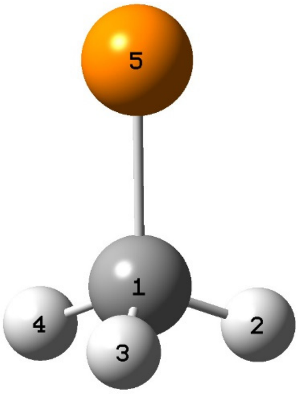


Figure S2 Normal mode description of the $H\text{-}P{=}CH_2^+$ computed in DFT/M06-2X/aug-cc-pVTZ

Table S2 Comparison of the geometrical parameters and the computed harmonic frequencies of P-CH$_3$ in neutral and cation calculated in DFT/M06-2X/aug-cc-pVTZ level. All bond lengths are in Å.

	Parameter	Neutral (t)	Cation (d)	Vibrational mode	Neutral (t) (cm^{-1})	Cation (d) (cm^{-1})
 IE: 8.86 eV	1-5	1.839	1.737	1	794	357
	1-2 1-4	1.091	1.092	2	788	754
				3	718	875
	1-3	1.091	1.132	4	1451	1154
	2-1-4	108°	114°	5	1301	1240
	4-1-3 3-1-2	108°	106°	6	1447	1393
				7	3114	2755
	5-1-3	111°	93°	8	3033	3051
	5-1-2 5-1-4	111°	117°	9	3111	3125

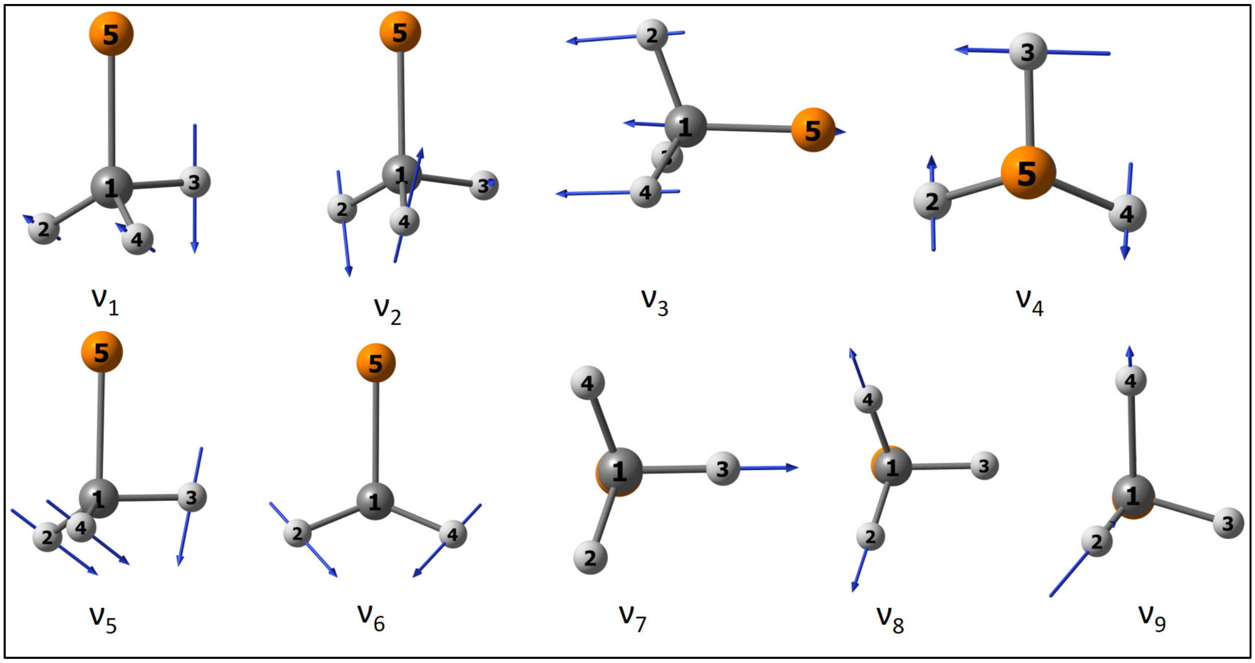
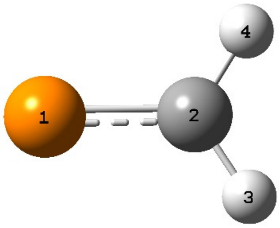


Figure S3 Normal mode description of the P-CH$_3^+$ computed in DFT/M06-2X/aug-cc-pVTZ

Table S3 Comparison of the computed harmonic frequencies of $P{=}CH_2$ in neutral and cation calculated in DFT/M06-2X/aug-cc-pVTZ level. Both neutral and cation are C_{2V} symmetric.

	Vibrational mode	Type of mode	Symmetry	Neutral (d) (cm^{-1})	Cation (s) (cm^{-1})
 IE: 8.78 eV	1	Symmetric stretching of H-C-H	A_1	3113	3039
	2	Scissoring of CH_2	A_1	1421	1297
	3	Stretching of P=C and Scissoring of CH_2	A_1	1054	1087
	4	Wagging of CH_2	B_1	893	852
	5	Asymmetric stretching of H-C-H	B_2	3190	3108
	6	Rocking of CH_2	B_2	733	229

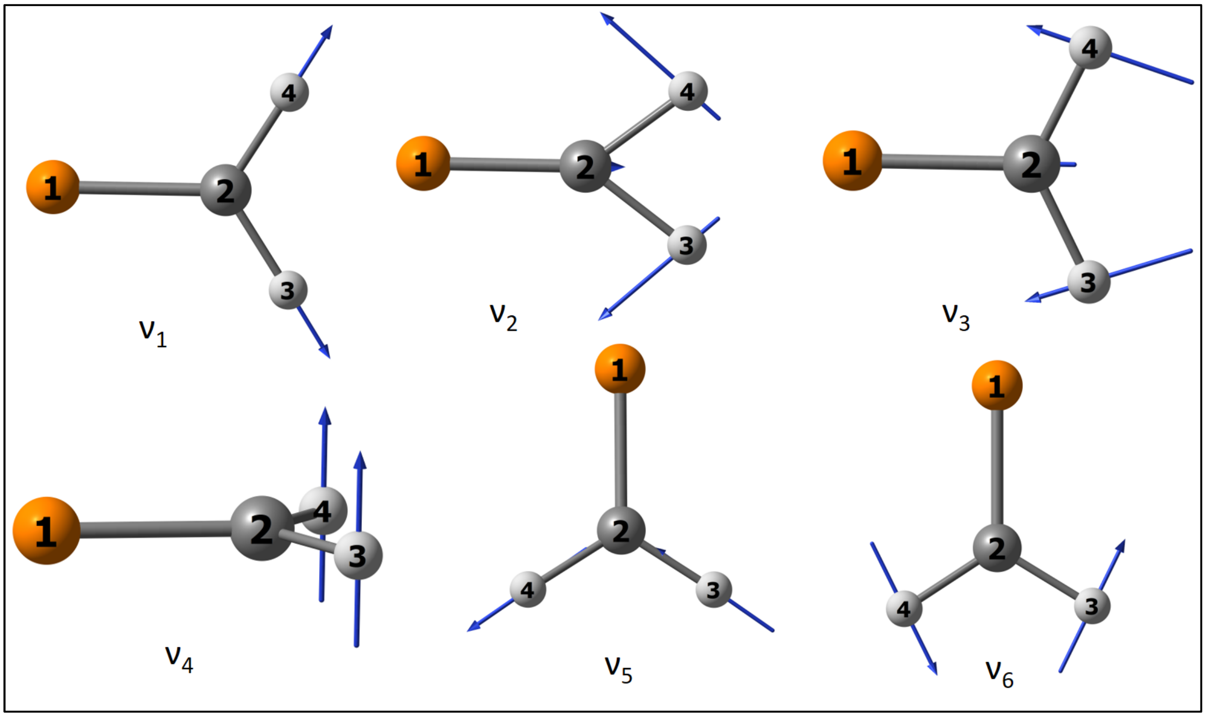
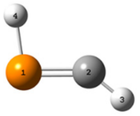
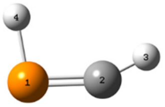
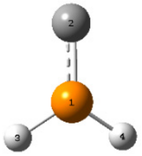


Figure S4 Normal mode description of the $P\text{-}CH_2^+$ computed in DFT/M06-2X/aug-cc-pVTZ

Table S4 Comparison of the geometrical parameters of different isomers of PCH_2 in neutral and cation calculated in DFT/M06-2X/aug-cc-pVTZ level. All bond lengths are in Å.

Parameters	 ***trans*-H-P-CH**		 ***cis*-H-P-CH**		 **C=PH$_2$**	
	Neutral (d)	Cation (t)	Neutral (d)	Cation (t)	Neutral (d)	Cation (t)
1-2	1.627	1.727	1.621	1.726	1.685	1.634
4-1	1.426	1.424	1.436	1.428	1.403	1.404
3-1					1.403	1.404
2-3	1.078	1.085	1.076	1.084		
4-1-2	97.7°	94.8°	98.0°	95.5°	122.9°	115.4°
1-2-3	140.2°	139.6°	154.5°	149.1°		
3-1-4					107.2°	116.3°
4-1-2-3	180.0°	180.0°	0.00°	0.00°	146.8°	140.1°

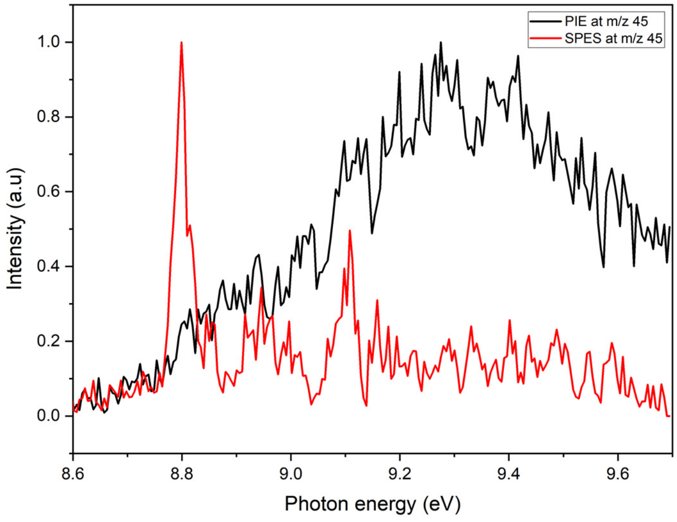
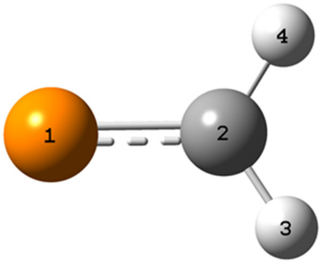
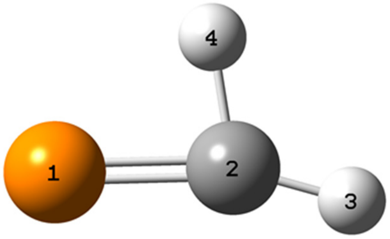


Figure S5 Photo-ion efficiency (PIE) curve at m/z 45 along with corresponding SPES. When molecules are small enough, the autoionization resonances in the PIE would be visible, but when the molecule has a certain size and the resolution of the photon source is not too good, they can be easily smeared out.

Table S5 Comparison of the geometrical parameters of two isomers of $P=CH_2$ in neutral and cation calculated in DFT/M06-2X/aug-cc-pVTZ level. All bond lengths are in Å. The Conformer-2 has no minimum in neutral state though the geometry is significantly changed. In cation the energy difference is only 0.01 eV.

<table>
<tr><td colspan="3">

$P=CH_2$</td><td>

$P=CH_2$ (Con-2)</td></tr>
<tr><td>Parameter</td><td>Neutral (d)</td><td>Cation (s)</td><td>Cation (s)</td></tr>
<tr><td>1-2</td><td>1.645</td><td>1.600</td><td>1.569</td></tr>
<tr><td>2-3</td><td>1.086</td><td>1.097</td><td>1.082</td></tr>
<tr><td>2-4</td><td>1.086</td><td>1.097</td><td>1.166</td></tr>
<tr><td>3-2-4</td><td>115.1°</td><td>115.3°</td><td>114.5°</td></tr>
<tr><td>1-2-3</td><td>122.5°</td><td>122.3°</td><td>163.1°</td></tr>
<tr><td>1-2-4</td><td>122.5°</td><td>122.3°</td><td>82.4°</td></tr>
</table>

References:

1. V. Butcher, J. M. Dyke, A. E. Lewis, A. Morris and A. Ridha, *Journal of the Chemical Society, Faraday Transactions 2*, 1988, **84**.
2. C. M. Western, *J. Quant. Spectrosc. Radiat. Transfer*, 2017, **186**, 221–242.