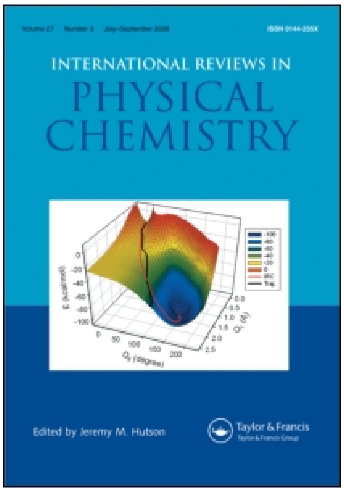

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Properties of the phosphorus oxide radical, PO, its cation and anion in their ground electronic states: comparison of theoretical and experimental data

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Experimental and theoretical data for the phosphorus oxide radical (PO), its cation (PO^+) and anion (PO^-) in their electronic ground states are reviewed. The internuclear distances, fundamental vibrational frequencies, bond orders, partial atomic charges, free valences, dipole moments, dissociation energies, ionization potential and electron affinity are discussed. The literature data are augmented by the results of a theoretical study including computations using restricted Hartree–Fock closed- and open-shell, generalized valence bond–perfect pairing, Møller–Plesset perturbation theory, complete active space self-consistent field, coupled-cluster with single and double substitutions up to the level augmented by a perturbative estimate of triple excitations and density functional theory methods.

Contents

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1. Introduction

The diatomic phosphorus oxide radical, its cation and anion, in their ground electronic states PO ($X\,^2\Pi_r$), PO^{1+} ($X\,^1\Sigma^+$) and PO^{1-} ($X\,^3\Sigma^-$), will be referred to as PO, PO^+ and PO^- respectively. They are very reactive and are observed as transient species under special experimental conditions (see below). They are of interest in interstellar space [1–3] although to our knowledge they have not been observed, even in oxygen-rich stellar atmospheres [1–3]. Phosphorus ranks 11th in abundance in the lithosphere. It is an essential ingredient of all cell protoplasm, nerve tissues, bones and DNA. This importance of phosphorus in life processes (biology) is easily surmised from its early preparations from animal and vegetable materials [4–7]. The alchemist Hennig Brand (Hamburg) first isolated phosphorus in its elemental form in 1669 by distillation of urine [4–7]. The residue he obtained glowed in the dark and ignited spontaneously on exposure to air. This was more than a century before oxygen, the most abundant element in the Earth's crust, was isolated and recognized as an element by Scheele (1772) and Priestley (1774) in independent work [7]. The multiple uses of phosphorus and its compounds in pharmacology, agriculture and industry have provoked numerous studies of their extraordinary properties [4–7].

According to Geuter [8] the study of the line spectra of phosphorus compounds was initiated by Plücker [9] in 1859 when he reported the emission from '*chlorphosphor*' in a Geissler tube. Band spectra in the ultraviolet (UV), near 3270 Å, were recorded by Hartley [10] in 1894. Geuter [8] reviewed the early literature on the luminescence of phosphorus compounds. He also presented the results of a comprehensive study on the emission spectra of phosphorus (in a hydrogen flame) and of phosphorus compounds (P_2O_5, K_2PO_3, Na_2PO_3, $NaNH_4PO_3$) under a variety of experimental conditions. The positions of more than 500 lines in the spectral region 2380–5730 Å were reported. Two groups of bands in the UV regions between 2370–2700 Å and 3100–3470 Å were observed in the emission from a carbon arc containing P_2O_5. The rotational line positions for the band situated between 3208 and 3246 Å were determined and a series sequence was established [8]. In 1909 de Gramont and de Watteville [11, 12] found that the bands observed by Geuter in the higher energy UV region extended from 2298 to 2789 Å and were also produced when a solution of either phosphoric acid or ammonium phosphate was dropped into a flame.

A number of other workers [13–21] observed bands in the emission spectra from phosphorus or its compounds under a variety of experimental conditions before 1930. However, the species responsible for the emission of the spectral bands in the UV, or for the broad continuous spectrum in the visible region, had not yet been identified.

In 1927 Emeléus and Purcell [15] deduced that the bands emitted in the UV by oxidizing phosphorus were due to a phosphorus oxide: the bands were observed both in the glow of phosphorus and in the emission from a discharge through P_2O_5 vapour at 200 °C, in the absence of air. They reported the positions of the violet edges of a large number of bands but did not perform an analysis. They also subjected P_2O_5 at −50 °C to UV irradiation and only observed emission in the visible region.

They thus concluded that the visible emission from oxidizing phosphorus was due to excitation of the pentoxide by UV radiation emitted as a consequence of the oxidation reactions.

Shortly thereafter, however, Petrikaln [18, 19] showed that P_2O_5 did not absorb in the UV region if it was highly purified: thus the visible emission observed by Emeléus and Purcell [15] was presumably due to an impurity in their sample. He also showed that when highly purified P_2O_5 vapour was excited, using discharges caused by external or internal electrodes, the band in the region 3200–3400 Å was absent: only bands corresponding to oxygen emission were observed [18, 19].

When Petrikaln [19] excited P_2O_3 in a Geissler tube, two series of bands were emitted in the UV region, one above 3000 Å, the other from 2366 to 2636 Å. The line positions of the latter were measured with an accuracy of 0.1 Å and analysed, leading to $\nu_0 = 1378$ and $1221\,\mathrm{cm}^{-1}$ for the vibrational frequencies of the excited and ground electronic state species respectively. Unfortunately, he attributed the bands to the P_2O_3 molecule [19]. In an important breakthrough in the identification of the PO radical, Ghosh and Ball [22] showed that PO was responsible for the spectral bands observed in the region 2280–2760 Å when P_2O_5 was placed in a carbon arc. Using a vibrational quantum mechanical interpretation [23] of the spectra obtained at moderate resolution, they attributed them to a $^2\Sigma \rightarrow {}^2\Pi$ transition (γ bands) of the PO radical and obtained $\omega_e'' = 1230.64\,\mathrm{cm}^{-1}$ and $\omega_e' = 1391.0\,\mathrm{cm}^{-1}$ for the ground and electronically excited states respectively, as well as an estimate of the dissociation energy of PO in its ground electronic state. Two years later Curry *et al.* [24] determined values for some molecular constants of PO from a study of the band system at 3260 Å (later to be known as the β-system). However, these constants were not as accurate as those reported by Ghosh and Ball [22]. In 1935 Sen Gupta [25] reported the first rotational interpretation of the (0, 0), (0, 1) and (1, 0) bands of PO at 2478, 2555 and 2396 Å respectively. These results confirmed that they were indeed part of the γ band system, corresponding to a $^2\Sigma \rightarrow {}^2\Pi$ electronic transition.

Since then the PO radical has been the object of numerous experimental studies ([26–64] and references cited therein). The emission spectrum of the PO molecule is very rich, and it has been studied over the range extending from 1825 Å in the vacuum UV (VUV) [26, 27] to 12000 Å in the infrared (IR [31]. It has been observed in absorption over an even larger range, from 1550 Å in the VUV [32] to the far IR and microwave regions [33]. The lifetimes of the A and B states of PO have been measured using laser-excited fluorescence [56–58].

The species responsible for the broadband luminescence over the range ~3500–6500 Å emitted on oxidation of phosphorus has not been elucidated satisfactorily. In 1968 Davies and Thrush [38] studied the chemiluminescence of the reaction of O atoms with phosphorus and with phosphine in a discharge flow system. They attributed the continuum to the addition of O atoms and OH radicals to PO. Later Van Zee and Khan [39] investigated the reaction of phosphorus burning in air with added water. They observed emissions from the γ- and β-systems (A and B states) of PO as well as the featureless continuum which was tentatively assigned to emission from a $(PO)_2{}^*$ excimer [39]. However, emission from $PO_2{}^*$ to explain the continuum chemiluminescence was preferred by Fraser *et al.* [40, 41], who carried out an extensive study of the reaction of O atoms and ozone with phosphorus.

Many different methods have been employed for producing the PO radical in its ground and excited states. Some of the classical methods have been mentioned above. The most novel methods involve dissociation of volatile organophosphorus molecules such as dimethyl methylphosphonate, $(CH_3O)_3(P{=}O)CH_3$ (DMMP). The CO_2 laser IR multiple-photon dissociation of DMMP leads to selective formation of PO in the $X^2\Pi_{1/2}$ ground electronic state, which lies only 224 cm^{-1} below the $X^2\Pi_{3/2}$ state [42]. Wong *et al.* [56] flowed an inert gas–DMMP mixture through a microwave discharge (2450 MHz) to produce PO. The two-photon excimer laser photofragmentation of DMMP yields at least 95% of the nascent PO radicals in the lowest vibrational state [58]. In contrast to the above laser IR multiple-photon results [42], the PO $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ populations are characteristic of 300 K [58].

Only a few experimental studies have been reported for PO^+ [27, 64, 65] and PO^- [66, 67]. Dressler reported the first evidence for the existence of the cation in 1955 [27]. He attributed eight red-shaded emission bands in the spectral region 1900–2200 Å to the A–$X^1\Sigma^+$ system of PO^+. In 1982, using VUV photoelectron spectroscopy, Dyke *et al.* (DMR) [64] observed the band associated with the first ionization potential (IP) of PO for the first time. They determined values for ω''_e, the interatomic distance and the dissociation energy of PO^+ in its ground electronic state. The most accurate data on the ground electronic state of PO^+ (see section 3) were obtained a decade ago by Petrmichl *et al.* (PPW) [65] from its microwave spectrum, detected at frequencies up to 467 GHz in discharges in mixtures of PF_3, O_2 and Ar.

In apparently the only reported experimental study on the bond length and spectroscopy of PO^-, Zittel and Lineberger [66] characterized it in 1976 using laser photoelectron spectrometry. According to Morris and Viggiano [67] PO^- is unreactive towards CO, N_2O and H_2O but it abstracts an oxygen atom from O_2, CO_2 , NO_2 and even from NO (NO bond strength, 6.5 eV). Note that, to the best of our knowledge, the isovalent anion, PS^-, has not been observed experimentally [68, 69].

There have been a number of theoretical studies on PO [64, 69–84] and fewer on PO^+ [64, 69, 84–89] and PO^- [69, 72, 83, 90–93]. The results of a preliminary investigation by one of us of the properties of the three species, at the same theoretical levels [69], are supplemented by additional computations and compared with the experimental and theoretical literature data.

2. Method

All computations were carried out at the ULB–VUB Computing Centre. The Monstergauss (MG) *ab initio* program package [94] was used for the VAO5AD method [95] optimizations of the equilibrium internuclear distances (r_e) and other properties at the restricted open-shell Hartree–Fock (ROHF) [96], restricted Hartree–Fock (RHF) [97] and generalized valence bond–perfect pairing (GVB–PP) [98] theoretical levels. Gamess (version of 6 June 1999 described in [99]) was also used to check some of the GVB–PP results. The valence–virtual orbital pairs used in the GVB–PP computations were identified by examination of the molecular orbitals generated by a single-configuration ROHF or RHF optimization. The computations designated by GVB(N) indicate that N correlated valence–virtual pairs were implicated.

The Gaussian 98 (G98) program package [100(a)] was used for the Møller–Plesset second-order perturbation theory (MP2) [101], complete active space self-consistent field (CASSCF) [102], coupled–cluster (CC; with single and double substitutions (CCSD) and augmented by a perturbative estimate of triple excitations (CCSD(T))) [103], and density functional theory (DFT: B3LYP, Becke's three-parameter non-local exchange functional [104, 105] with the non-local correlation functional of Lee *et al.* [106]) methods.

The basis sets used are the standard 6–31G*(6d) [107, 108], 6–31+G*(6d) [109] and Dunning's correlation-consistent polarized valence triple-zeta (cc–pVTZ(5d); 64 basis functions), quadruple-zeta (cc–pVQZ(5d); 114 basis functions) and quadruple-zeta augmentated by one diffuse function of each function type in use for each atom (aug-cc-pVQZ(5d); 164 basis functions) [77, 110, 111]. The notations (5d) and (6d) indicate that pure 5d (spherical) or Cartesian 6d functions are incorporated in the corresponding basis sets. The Cartesian 6d functions are the default for the 6–31G* and 6–31+G* basis sets in G98. Only 6d functions are available for the 6–31G* basis set in Gamess. The pure 5d functions are the default functions for the Dunning basis sets in G98. For MG the d function type must be specified and only the results with Cartesian 6d functions are reported in this work. The basis sets will be indicated without the (5d) or (6d) extensions in the tables and in the remainder of the text.

Theoretical ω_{e}'' can be calculated at the r_e optimized at the BASIS1 level, using either (a) the BASIS1//BASIS1 (recommended) or (b) the BASIS1//BASIS2 methods where BASIS2 is a basis set of lower quality. All the ω_{e}'' calculated in this work use method (a) either directly with G98 or Gamess or using the force constants determined with MG by numerical two-sided finite differences of 10^{-3} bohr. The CCSD(T)/aug-cc-pVQZ calculations of ω_{e}'' for PO and PO^- failed because of a bug in the G98 version. These two frequencies were obtained using Gaussian 2003 (G03) [100(*b*)]. (They each required just over 45 h of CPU time on a COMPAQ-DIGITAL GS160 server with a CPU performance of 2 Gflops.)

Most of the bond orders (BOs) were calculated with MG according to Mayer's definition [112–116]. They agree with those obtained using Gamess [99]. (BOs are not available for the G98 computations.)

The r_e values, total energies, BOs, predicted Mulliken atomic charges on P (δx) and on O (δy), force constants (FCs) and ω_{e}'' for PO, PO^+ and PO^- are given in tables 1–3 respectively.

3. Results and discussion

The configurations of the ground electronic states for PO, PO^+ and PO^- are $(1\text{–}4)\sigma^2 1\pi^4 (5\text{–}6)\sigma^2 2\pi^4 7\sigma^2 3\pi^{*(x)}$, where $x = 1$, 0 and 2 respectively. Dissociation of these diatomic species in their ground electronic state yields the atoms and/or the ions in their ground electronic states according to the following steps [74, 75, 86, 90]:

$$\begin{aligned} PO &\rightarrow P(^4S_u) + O(^3P_g);\\ PO^+ &\rightarrow P^+(^3P_g) + O(^3P_g);\\ PO^- &\rightarrow P(^4S_u) + O^-(^2P_u). \end{aligned}$$

The dissociation energies will be discussed in section 3.5.

3.1. *Internuclear distances*

In the remainder of the text the equilibrium internuclear distances of the radical, cation and anion will be referred to as $r_{\mathrm{e}}(PO)$, $r_{\mathrm{e}}(PO^+)$ and $r_{\mathrm{e}}(PO^-)$ respectively. Non-equilibrium distances will be referred to without the '*e*' subscript.

Table 1. $^{31}P^{16}O$ ($X\,^2\Pi_r$): optimized internuclear distances (r_e, Å), total energies (hartree), BOs, Mulliken atomic charges (δ, they are positive on P and negative on O), free valences (FV(P) and FV(O)), harmonic vibrational frequencies (ω_e'', cm^{-1}) and dipole moments (μ, debye). Experimental values of r_e, ω_e'' and μ are given for comparison.

Method/basis set	r_e	Total energy	BO	δ	FV(P)	FV(O)	ω_e''	μ[a]
ROHF/6–31G*[b]	1.453 7	−415.542 321	1.82	0.56	1.14	0.21	1427	−2.62
ROHF/6–31G*[c]	1.454 6	−415.543 656	1.96	0.56	0.73	0.02	1419	−2.61
ROHF/6–31G*[d]	1.454 6	−415.543 656		0.56	0.85[e]	0.15[e]	1419	−2.61
GVB(2)/6–31G*[b]	1.454 1	−415.553 906	1.79	0.58	1.17	0.22	1420	−2.72
GVB(3)/6–31G*[b]	1.463 7	−415.568 175	1.78	0.57	1.20	0.25	1357	−2.71
CASSCF(11,8)/6–31G*[d]	1.512 4	−415.636 091		0.41			1165	−1.80
CASSCF(11,8)/6–31+G*[d]	1.511 0	−415.640 916		0.38			1163	−1.96
CASSCF/cc–pVDZ[77][f]	1.539 8	−415.664 18					1090	
CASSCF/cc–pV5Z [77][f]	1.496 7	−415.702 25					1157	
CCSD/6–31G*[d]	1.499 7	−415.833 910		0.50	1.39[e]	−0.39[e]	1243	−2.25
CCSD/6–31+G*[d, g]	1.500 0	−415.844 509		0.52	1.40[e]	−0.40[e]		−2.63
CCSD(T)/6–31+G*[d, g]	1.491 3	−415.855 536		0.55	1.21[e]	−0.21[e]		−2.84
CCSD/cc–pVTZ[d]	1.482 6	−415.982 699		0.45	0.79[e]	0.21[e]	1284	−2.63
CCSD/cc–pVQZ[d]	1.473 7	−416.018 848		0.52	0.80[e]	0.20[e]	1291	−2.59
CCSD(T)/aug–cc–pVQZ[d, g]	1.486 5	−416.043 950		0.90	0.82[e]	0.18[e]	1229	−2.63
CCSD/ [83][h]	1.474	−415.629 85					1286	−2.60
ROHF/MP2/6–31G*[d]	1.517 1	−415.828 141		0.58	0.85[e]	0.15[e]	1162	−2.88
ROHF/MP2/6–31+G*[d]	1.518 2	−415.839 397		0.59	0.90[e]	0.10[e]	1152	−3.11
MRD–CI [76]	1.491	−415.856 1					1240	−2.01 [87]
MR–CI/apVQZ [79][f]	1.480 8	−416.017 66					1253	−1.99[i]
MRCI/cc–pVQZ [84][f]	1.487 0	−416.002 9					1214	
MRCI+Q/cc–pVQZ [84][f]	1.489 1	−416.031 4					1215	
CMRCI/cc–pV5Z [77][f]	1.480 6	−416.019 67					1225	

(*continued*)

Table 1. *Continued.*

Method/basis set	r_e	Total energy	BO	δ	FV(P)	FV(O)	ω''_e	μ^a
B3LYP/6–31G* [d]	1.498 6	−416.530 558		0.41	0.76[e]	0.24[e]	1232	−2.00
B3LYP/6–31+G* [d]	1.498 8	−416.540 039		0.42	0.86[e]	0.14[e]	1226	−2.29
HCTH(AC)/D [84][f]	1.490 3	−416.616 5					1206	
Experimental								
Rotational analysis of γ system in UV [34]	1.473 0						1233.42	
IR laser spectroscopy	1.476 370(15) [36]						1233.37[j]	
Millimetre–wave spectroscopy	1.476 373 55 (10) [37]							
Microwave spectroscopy								$\lvert 1.88\pm0.07\rvert$ [59]

[a] The negative sign corresponds to $P^{\delta+}O^{\delta-}$.

[b] Computed with MG [94]. Only MG shares the unpaired electron between the equivalent p orbitals.

[c] Computed with Gamess [99].

[d] Computed with G98 [100(*a*)].

[e] Total atomic spin density.

[f] Results with other basis sets/methods are also reported.

[g] The frequency was computed with G03 [100(*b*)].

[h] Composite basis set.

[i] Calculated at the experimental bond length.

[j] Calculated using $\nu(v=1)=1220.25\,\text{cm}^{-1}$ [36, 60] $+\,2\,(\omega''_e x''_e)=6.56\,\text{cm}^{-1}$ [47, 48, 51]).

Table 2. $^{31}\mathrm{P}^{16}\mathrm{O}^{+}$ ($X\ ^{1}\Sigma^{+}$): optimized internuclear distances (r_e, Å), total energies (hartree), BOs, Mulliken atomic charges on the phosphorus (δx) and oxygen (δy) atoms, free valences (FV(P) and FV(O)), harmonic vibrational frequencies (ω_e'', cm^{-1}), and dipole moments (μ, debye). Experimental values of r_e and ω_e'' are given for comparison.

Method/basis set	r_e	Total energy	BO	δx	δy	FV(P)	FV(O)	ω_e''	μ [a]
RHF/6–31G* [b,c]	1.397 1	−415.255 410	2.37	1.29	−0.29	0.00	0.00	1659	−3.84
GVB(2)/6–31G* [b]	1.421 4	−415.309 582	2.29	1.18	−0.18	0.19	0.26	1507	
GVB(3)/6–31G* [b]	1.429 0	−415.323 029	2.27	1.17	−0.17	0.21	0.28	1471	
CASSCF(10,8)/6–31G* [d]	1.448 9	−415.396 396		1.14	−0.14			1389	−3.05
CASSCF(10,8)/6–31+G* [d]	1.448 9	−415.397 520		1.12	−0.12			1387	−3.13
CASSCF/6–311G(MC)(d) [86]	1.450	−415.434 51						1378	
CCSD/6–31G* [d]	1.441 4	−415.547 098		1.31	−0.31			1440	−4.05
CCSD/6–31+G* [d]	1.441 6	−415.550 391		1.32	−0.32			1437	−4.10
CCSD(T)/6–31G* [d]	1.453 8	−415.560 655		1.32	−0.32			1361	−4.10
CCSD(T)/6–31+G* [d]	1.453 8	−415.564 323		1.33	−0.33			1360	−4.19
CCSD/cc-pVTZ[d]	1.429 4	−415.679 523		1.16	−0.16			1470	−4.02
CCSD/cc-pVQZ[d]	1.421 2	−415.712 236		1.22	−0.22			1482	−4.06
CCSD(T)/aug-cc-pVQZ[d]	1.434 7	−415.736 790		1.63	−0.63			1401	−4.10
CI-SD/A [88][e]	1.417 0	−415.628 19						1518	−3.44
MP2/6–31G* [d]	1.470 4	−415.546 535		1.32	−0.32			1255	−4.26
MP2/6–31+G* [d]	1.470 7	−415.550 048		1.33	−0.33			1252	
MP4SDQ/A [88][e]	1.440 4	−415.659 52						1339	
CEPA-1/(B+C) [65][e]	1.427 6							1433	
MRCI/cc-pVQZ [84]	1.435 7	−415.518 9						1399	
MRCI+Q/cc-pVQZ [84]	1.437 0	−415.540 6						1392	
B3LYP/6–31G* [d]	1.440 1	−416.221 473		1.14	−0.14			1429	−3.29
B3LYP/6–31+G* [d]	1.440 0	−416.223 484		1.15	−0.15			1426	−3.43
HCTH/D [84]	1.434 9	−416.305 8						1394	
Experimental									
Photoelectron spectroscopy [64]	1.419(5)							1410(30)	
Microwave spectroscopy [65]	1.4249 92 7(4)							1411.5(3)	

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[a] The negative sign corresponds to $\mathrm{P}^{\delta+}\mathrm{O}^{\delta-}$.

[b] Computed with MG [94].

[c] Gamess [99] and G98 [100 (*a*)] give the same r_e, energy, charges and ω_e'' as MG in this closed-shell case.

[d] Computed with G98 [100 (a)].

[e] Results with other methods/basis sets are also reported.

Table 3. $^{31}P^{16}O^-$ ($X\,^3\Sigma^-$): Optimized internuclear distances (r_e, Å), total energies (hartree), BOs, Mulliken atomic charges on the phosphorus (*ch*(P)) and oxygen (*ch*(O)) atoms, free valences (*FV*(P) and *FV*(O)), harmonic vibrational frequencies (ω''_e, cm^{-1}) and dipole moments (μ, debye). Experimental values of the internuclear distance and fundamental frequency are given for comparison.

Method/basis set	r_e	Total energy	BO	*ch*(P)	*ch*(O)	*FV*(P)	*FV*(O)	ω''_e	μ[a]
ROHF/6–31G*[b, c]	1.5247	−415.548648	1.56	−0.18	−0.82	1.32	0.07	1173	−1.31
GVB(2)/6–31G*[b]	1.5259	−415.560864	1.50	−0.15	−0.85	1.42	0.09	1158	
GVB(3)/6–31G*[b]	1.5425	−415.576858	1.48	−0.15	−0.85	1.45	0.12	1086	
B3LYP/6–31G*[d]	1.5761	−416.551358		−0.36	−0.64	1.40[e]	0.60[e]	1001	
B3LYP/6–31+G*[d]	1.5666	−416.587321		−0.40	−0.60	1.71[e]	0.29[e]	1000	
CASSCF(12,8)/6–31G*[d]	1.5925	−415.598900		−0.35	−0.65			931	−0.41
CASSCF(12,8)/6–31+G*[d]	1.5801	−415.620041		−0.42	−0.58			934	−0.46
CASSCF[f]	1.5405	−415.75544						1047	−0.13
CCSD/6–31G*[d]	1.5699	−415.835868		−0.20	−0.80	1.53[e]	0.47[e]	1032	−1.41
CCSD/6–31+G*[d]	1.5647	−415.873241		−0.24	−0.76	1.91[e]	0.10[e]	1019	−1.41
CCSD(T)/6-31G*[d]	1.5794	−415.844166		−0.19	−0.81	1.52[e]	0.48[e]	994	−1.34
CCSD(T)/6-31+G*[d]	1.5735	−415.883256		−0.23	−0.77	1.90[e]	0.10[e]	985	−1.48
CCSD/cc-pVTZ[d]	1.5504	−416.004694		−0.29	−0.71	1.55[e]	0.45[e]	1071	−1.07
CCSD/cc-pVQZ[d]	1.5386	−416.050875		−0.20	−0.80	1.59[e]	0.41[e]	1079	−0.89
CCSD(T)/aug-cc-pVQZ[d,f]	1.5457	−416.084471		+0.04	−1.04	1.68[e]	0.32[e]	1034	−0.57
CI-SD[g]	1.5216	−415.99674						1121	−0.52
CEPA-1[g]	1.5421	−416.03611						1026	−0.22
MIDI![d]	1.5585	−413.474304		−0.35	−0.65	1.35[e]	0.65[e]	1165	−0.22
MP2/cc-pVDZ[d]	1.6026	−415.852417		−0.25	−0.75	1.49[e]	0.51[e]	965	−1.39
ROHF/MP2-FC/6–31G*[d]	1.5838	−415.828947		−0.15	−0.85	1.62[e]	0.38[e]	1004	−1.59
ROHF/MP2-FC/6–31+G*[d]	1.5772	−415.867317		−0.21	−0.79	1.82[e]	0.18[e]	1000	−1.65
UMP2-FC/6–31+G*[d]	1.5770	−415.864080		−0.23	−0.77	1.90[e]	0.10[e]	975	−1.45
MP4SDQ[g]	1.5388	−416.03291						1055	
Experimental									
Laser photoelectron spectroscopy [66]	1.540(10)							1000(70)	

[a] The negative sign corresponds to $P^{\delta+}O^{\delta-}$, i.e. a larger negative, partial charge on O than on P.

[b] Computed with Monstergauss [94].

[c] Gamess [99], G98 [100 (*a*)] and MG give the same r_e , energy, charges and frequencies. However, G98 gives a lower value of μ, 1.16 D.

[d] Computed with G98.

[e] Total atomic spin density.

[f] The frequency was obtained using G03 [100 (b)].

[g] The basis set consisted of 101 contracted Gaussian-type orbitals [91].

3.1.1. $r_e(PO)$

3.1.1.1. *Experiment.* Note that, as early as 1935, Sen Gupta [25] reported $r_e = 1.446$ Å and $r_e = 1.449$ Å for the lowest $X^2\Pi_{1/2}$ and $X^2\Pi_{3/2}$ states of the PO radical. These values were determined from a rotational analysis of UV emission bands at 2396, 2478 and 2555 Å (γ system). (It is remarkable that these r_e values are within 1.5% of the best experimental data available today; see table 1.) Over 20 years later, Rao [34] determined r_e(PO) = 1.4730 Å from the rotational analysis of the same emission system of PO over the region 2300–2380 Å. The following year a slightly higher value, 1.475 Å, was reported by Singh [35]. On the basis of a recalculation using the molecular rotational constant B_e in Rao's paper (0.7331 cm^{-1} [34]), Butler *et al.* [36] revised his r_e value upwards to 1.4765 Å [36]. Also, using $B_e = 0.7337\ \text{cm}^{-1}$, determined by Verma and Singhal [51] from the rotational analysis of 23 vibrational emission bands in the region 3000–3900 Å (β system, $B^2\Sigma^+ \rightarrow X^2\Pi$), Butler *et al.* [36] obtained $r_e = 1.4759$ Å. These values, considering the experimental uncertainties in the earlier work, are in agreement with their own high resolution value obtained in the first gas phase IR study of PO [36]. The analysis of the high resolution vibration–rotation spectra obtained with a tunable IR laser diode spectrometer led to the values $B_e = 0.733\,227\,3(18)\ \text{cm}^{-1}$ and $r_e(\text{PO}) = 1.476\,370(15)$ Å (the value in parentheses indicates the 3σ range and applies to the last digits [36]). While this paper was nearing completion, important work by Bailleux *et al.* [37] came to our attention. They report $r_e(\text{PO}) = 1.476\,373\,55(10)$ Å, obtained from millimetre wave absorption spectroscopy of the chemiluminescent reaction of oxygen with white phosphorus, P_4. This value is in excellent agreement with that of Butler *et al.* [36] and reduces the uncertainty on the last digits.

3.1.1.2. *Theory*

3.1.1.2.1. **Literature.** *Ab initio* self-consistent field (SCF) single-determinant computations, without configuration interaction (CI), have been reported by a number of workers [64, 69–73, 80]. Because of computational limitations, no optimizations of the internuclear distance of the radical were attempted in the earliest theoretical studies [71, 80]. Boyd and Lipscomb [80] used a minimal basis set of Slater-type functions (STFs) augmented by *3d* polarization functions on P. They found that using r(PO) = 1.474 Å (an average of the values in [34] and [35]), instead of r(PO) = 1.448 Å (an average of the earlier values in [25] and [117]), caused a lowering of the total energy, lending support to the longer experimentally determined internuclear distance. Nevertheless, some years later, Mulliken and Liu [71] used the shorter internuclear distance to investigate the effects of including or omitting *3d* and *4f* STFs in the basis set. Their results indicated, as expected, that, if polarization functions are included in the basis set, they must at least be included for the heavier atom.

In 1982 DMR [64] used a Clementi double-zeta quality Slater-type orbital basis set [118] augmented by *3d* functions on O and *3d*, *4s* and *4p* functions on P. By interpolation of the total energies obtained at five points within 0.02 Å of their theoretical energy minimum, they obtained r_e(PO) = 1.4601 Å which is 0.0163 Å less than the best experimental value. From an unrestricted Hartree–Fock (UHF) 6–31G* optimization, Lohr [72] obtained a lower value, r_e(PO) = 1.456 Å, which was confirmed in this work. Using a numerical HF (NHF) procedure, Adamowicz *et al.* [83] obtained an even shorter value, r_e(PO) = 1.433 Å, by interpolation of the energies at 12 internuclear distances.

Moussaoui [69] performed optimizations on PO, PN and PP and their mono cations and anions using the STO–3G*, 3–21G$^{(*)}$ (*d* functions in the basis set for both atoms) and 6–31G* basis sets to evaluate their potential use (error evaluation) for computations on larger molecules containing these moieties. Computations were carried out using both 5d and 6d functions in the basis sets and gave similar results. As is usually observed [93], the optimizations with the 5d functions required less time and memory, important considerations when the performance of 'supercomputers' was less than that of today's personal computers. Some of Moussaoui's 6–31G* (with Cartesian 6d functions) results are included in the tables without special notation.

Most of the CI and CC computations reported in the literature [74–79, 83, 84] have yielded r_e(PO) longer than experiment. In 1973 Roche and Lefebvre–Brion [74] performed CI computations on the ground and valence states of PO at nine different internuclear distances ranging from $2.5a_0$ to $4.3a_0$. The double-zeta STO basis set was augmented by *3d* polarization functions on P. Interpolation of the data for the ground electronic state yielded r_e(PO) = 1.536 Å. In the same year Tseng and Grein used a minimal basis set and full valence CI [75] in calculations on 57 electronic states of PO. Interpolation of the energies obtained for the ground state at 11 internuclear distances from $2.45a_0$ to $6.5a_0$ yielded r_e(PO) = 1.64 Å. Later Grein and Kapur [76] carried out multireference (MRD) CI computations with a double-zeta quality basis set, supplemented by polarization and diffuse functions (*d* functions and extra *s* and *p* functions on both atoms) 'over a wide range of internuclear distances' on eight states of PO. They found r_e(PO) = 1.491 Å for the ground electronic state, within 1% of the best experimental data.

With a hybrid NHF and Slater orbital basis set, Adamowicz *et al.* [83] obtained r_e(PO) = 1.474 Å and r_e(PO) = 1.490 Å from CCSD and CCSD(T) optimizations. Compared with experiment, these CCSD and CCSD(T) r_e values are thus about 0.002 Å too short and 0.014 Å too long respectively. These values compare favourably with the latest CI and CC results where large cc–pV basis sets have been used [77, 78, 84] to approach the experimental spectroscopic results and to provide benchmark data [77] for a series of diatomic molecules. At the present time such large computations are not generally feasible for large molecules containing the PO moiety.

Woon and Dunning [77] used cc–pV basis sets of double- to quintuple-zeta (cc-pVDZ to cc-pV5Z) quality to determine spectroscopic constants for PO with the CASSCF and internally contracted MR single and double-excitation CI (CMRCI) methods. With the CASSCF method, their r_e(PO) decrease from 1.53 Å (cc-pVDZ) to 1.4967 Å (cc-pV5Z). The latter are still 0.02 Å higher than the most accurate experimental value. Their best result, r_e(PO) = 1.4806 Å [77] (0.0042 Å above experiment) was obtained with a CMRCI/cc-pV5Z calculation.

de Brouckère [78] carried out MR–CI and MR–CI+Q (where Q signifies the Davidson correction for quadruple excitations) computations with a Dunning-type augmented correlation-consistent coupled-cluster polarized-valence quadruple-zeta (denoted by apVQZ) basis set. The MR–CI computations led to r_e(PO) = 1.4808 Å, close to the best value obtained by Woon and Dunning [77]. However, including the Davidson correction for quadruple excitations gave r_e(PO) = 1.4855 Å, thus further away from experiment.

Brinkmann *et al.* [82] carried out a series of DFT calculations on the oxides of P, Al, Si, S and Cl using six different functionals and a DZP++ basis set. The r_e(PO) they obtained ranged from 1.469 Å to 1.515 Å. Only the BHLYP functional yielded r_e(PO) below experiment.

Spielfiedel and Handy [84] investigated the ground state and the lowest singlet and triplet cationic states as well as many valence and Rydberg states of PO using DFT (with their HCTH(AC) functional) and multiconfigurational interaction (MRCI) methods. For the latter the cc-pVQZ basis set of Dunning was used. Their DFT computations with the largest basis set (D, with uncontracted diffuse functions on both P and O) included 114 basis functions. Their best result, $r_e(\mathrm{PO}) = 1.4870$ Å (0.0106 Å above experiment), was obtained at the MRCI/cc-pVQZ level (table 2 in [84]).

3.1.1.2.2. **This work.** The $r_e(\mathrm{PO})$ obtained from the ROHF/ and GVB(2)/6–31G* optimizations (table 1) are about 1.5% below the best experimental value. Including a σ^*–σ orbital pair in the GVB optimization (GVB(3)/6-31G*) results in a longer $r_e(\mathrm{PO})$, bringing the value closer to, but still about 0.01 Å below, experiment.

In contrast to the ROHF and GVB data, most of the $r_e(\mathrm{PO})$ obtained with the B3LYP, CASSCF, CCSD and MP2 methods are too long. The only exception is the present CCSD/cc-pVQZ result ($r_e(\mathrm{PO}) = 1.4737$ Å, 0.0027 Å below experiment). Indeed, for the remainder, $r_e(\mathrm{experiment}) < r_e(\mathrm{CCSD(T)}) < r_e(\mathrm{B3LYP}) < r_e(\mathrm{CCSD}) < r_e(\mathrm{CASSCF}) < r_e(\mathrm{MP2})$. Attempts to optimize the internuclear distance at the CCSD(T)/6–31G* level all led to convergence failure. Going from the CCSD to the CCSD(T) level with the 6–31 + G* basis set improved the agreement of the optimized $r_e(\mathrm{PO})$ with experiment. This is in contrast to the findings of Adamowicz *et al.* [83] (see above). (The divergence between the results of the two studies could be due to an effect of basis set size.) The MP2/6–31+G* $r_e(\mathrm{PO})$ is 0.0011 Å longer than that obtained from the MP2/6–31G* optimization. Here, as in general, increasing the basis set by including a diffuse function in the basis set for the MP2 optimization produced an increase in the internuclear distance. For an example of this effect, the reader is referred to table 1 in the excellent paper on the CO molecule by Peterson and Dunning [119].

For the B3LYP optimizations, increasing the basis set from 6–31G* (34 functions) to 6–31 + G* (42 functions) has only a minor effect, increasing $r_e(\mathrm{PO})$ by 0.0002 Å, thus a little further away from experiment. Nevertheless, these DFT results are nearly 1% closer to experiment than those obtained at the CASSCF level with the same basis set (table 1). The present $r_e(\mathrm{PO})$ obtained at the CCSD(T)/6–31+G* level is very close to those reported for MRD–CI [76] and HCTH(AC) [84] optimizations.

The CCSD(T)/aug-cc-pVQZ optimization, with the largest basis set (164 basis functions) used in this work, yields $r_e(\mathrm{PO})$ which is 0.004 Å further from experiment than the CCSD/cc-pVTZ result. These results are close to, but above, the MR–CI/apVQZ [79] and CMRCI/cc-pVQZ [77] results discussed above.

3.1.2. $r_e(PO^+)$

3.1.2.1. *Experiment.* Because of the absence of electrons in the antibonding 3π* orbital in the cation, $r_e(\mathrm{PO}^+)$ is expected to be shorter than $r_e(\mathrm{PO})$. This was confirmed in 1982 by DMR [64] who determined $r_e(\mathrm{PO}^+) = 1.419 \pm 0.005$ Å from a Franck–Condon analysis of the VUV photoelectron spectral intensities. More recently, PPW [65] detected the emission microwave spectrum of PO^+ produced by discharges in mixtures of PF_3, Ar and O_2. Analysis of 48 rotational transitions (including eight from the P $^{18}\mathrm{O}^+$ isotopomer) yielded $r_e(\mathrm{PO}^+) = 1.424\,992\,7(4)$ Å, which is 0.051 38 Å or 3.5% less than $r_e(\mathrm{PO})$.

3.1.2.2. *Theory*

3.1.2.2.1. **Literature.** In the first *ab initio* study of the cation, DMR [64] used the basis set and method described above for the PO radical (section 3.1.1) and obtained $r_e(PO^+) = 1.4093$ Å, about 1.1% below the best experimental value available today.

Wong and Radom [86] determined r_e for 20 isoelectronic species, including PO^+, using the 6–311G(MC)(d) basis set [120]. They obtained $r_e(PO^+) = 1.422$, 1.450 and 1.448 Å with the MP3, CASSCF and ST4CCD (CC theory with double substitutions and in which the effects of single and triple excitations are incorporated via fourth-order perturbation theory) methods respectively. Note that, whereas the MP3 value is very close to experiment, it is 0.013 Å higher than the MP3 $r_e(PO^+)$ reported by Peterson and Woods [87] using their basis set B (see next paragraph). This probably indicates an important basis set size effect with the MP3 method for this species.

Peterson and Woods [87, 88] and PPW [65] determined $r_e(PO^+)$ using two large basis sets including *f* functions (basis A, 66 contracted Gaussian-type orbitals (cGTOs); basis B, 93 cGTOs) and SCF, MP2, MP3, MP4DQ, MP4 theory with single, double and quadruple substitutions (MP4SDQ) and CI–SD methods (see table IV in [87] and table V in [65]). The basis set used is indicated by placing either '(A)' or '(B)' after the method. The SCF optimizations with basis sets A and B yielded $r_e(PO^+) = 1.3877$ and 1.3884 Å respectively, which are shorter than experiment and shorter than the RHF/6–31G* results. (This is a typical effect of basis set size.) The $r_e(PO^+)$ values obtained with the MP and CI–SD methods are as follows: $r_e(\mathrm{MP3(B)}) = 1.4092$ Å $< r_e(\mathrm{CI\text{–}SD(B)}) < r_e(\mathrm{MP4DQ(B)}) < r_e(\mathrm{experiment}) < r_e(\mathrm{MP4SDQ(B)}) < r_e(\mathrm{MP4SDQ(A)}) < r_e(\mathrm{MP2(B)}) = 1.4481$ Å. When a size consistency correction was applied (denoted by an 's' subscript), the closest $r_e(PO^+)$ to experiment (1.4248 Å) was obtained with the CI–SD$_s$(B) method [65]. Note that the CEPA-1 (version 1 of the coupled-electron-pair approximation) method used with a larger basis set including both *f* and diffuse functions gave a satisfactory result: $r_e(PO^+) = 1.4276$ Å [65]. Finally, Spielfieldel and Handy [84] obtained $r_e(PO^+) =$ 1.4349, 1.4357 and 1.4370 Å (all about 0.01 Å above experiment) with the HCTH, MRCI and MRCI–Q methods respectively.

3.1.2.2.2. **This work.** In contrast to the results for the PO radical, where the optimized RHF and GVB $r_e(PO)$ are lower than experiment (table 1), here we find $r_e(\mathrm{RHF}) < r_e(\mathrm{GVB(2)}) < r_e(\mathrm{expt}) < r_e(\mathrm{GVB(3)})$ for the cation (table 2). The GVB $r_e(PO^+)$ values are satisfactory: the deviations from the best experimental value are −0.25% (GVB(2)) and +0.28% (GVB(3)). They are very close to those obtained with the larger (and more expensive) CCSD/cc-pVQZ and CCSD/cc-pVTZ optimizations respectively. The CCSD(T)/aug-cc-pVQZ $r_e(PO^+)$ is 0.010 Å (0.68%) too long and thus even further away from experiment. Similarly, the other CCSD and CCSD(T), B3LYP, CASSCF and MP2 optimizations all yielded $r_e(PO^+)$ that are too long. For these methods the smallest and largest deviations in $r_e(PO^+)$ from experiment are observed for the B3LYP and MP2 methods (0.015 and 0.046 Å respectively).

3.1.3. $r_e(PO^-)$

3.1.3.1. *Experiment.* In 1976, in apparently the only experimental study on PO^-, Zittel and Lineberger [66] produced it either by burning phosphine (PH_3) or phosphorus with N_2O in a low pressure discharge or in a high pressure, higher temperature Colutron source. Electron detachment from the anion was effected by crossing the ion beam (obtained by acceleration at 680 V) with a continuous wave Ar ion laser beam at 4880 Å. The resolution of the electrostatic monochromator used for the energy analysis was insufficient to separate individual rotational transitions. Nevertheless, a Franck–Condon factor analysis of the (v', v'') transition intensities [66] led to $r_e(PO^-) = 1.540 \pm 0.010$ Å for the ground electronic state, ($4.3 \pm 0.7\%$) longer than r_e(PO).

3.1.3.2. *Theory*

3.1.3.2.1. **Literature.** When Boyd and Lipscomb [80] studied PO (see above) and PO^- to obtain information on P–O bonds and the effect of a negative charge on the P–O moiety, PO^- had not been observed. A parabolic fit of the energies obtained at three internuclear distances led to $r_e(PO^-) = 2.859a_0$ (1.513 Å) '*appropriately longer than the distance in neutral PO*' [80]. In their work they found the energy of the anion to be 0.58 eV higher than that of the neutral radical, a result which they correctly predicted might be reversed on optimization or expansion of the basis set. From a UHF/6–31G* optimization, Lohr [72] obtained $r_e(PO^-) = 1.529$ Å, which is shorter than the experimental value. (This value has been confirmed in this work.)

Bruna and Grein [90] carried out large-scale MRD–CI computations on the $\pi^4\pi^{*2}$ electronic states of PO^-, NS^- and PS^- using extended atomic orbital basis sets. However, for PO^-, the computations were carried out only at the experimental internuclear distance for the ground electronic state. The most important conclusion of their work is that not only the ground triplet state but also at least one and perhaps both of the first electronically excited singlet states lie below the ground state of the parent radical.

With their NHF procedure, Adamowicz *et al.* [83] found $r_e(PO^-) = 1.493$ Å, which is approximately 0.05 Å too short. However, their CCSD and CCSD(T) calculations yielded $r_e(PO^-) = 1.536$ Å and $r_e(PO^-) = 1.548$ Å respectively, both within the experimental error limits [83].

Peterson and Woods [91] used a basis set of 101 cGTOs with the UHF, ROHF, MP4SDQ, CI–SD, CEPA-1 and CASSCF methods. They obtained $r_e(PO^-) = 1.5031$ (UHF), 1.4976 (ROHF), 1.5216 (CI-SD), 1.5388 (MP4SDQ), 1.5349 (CI–SD$_s$), 1.5421 (CEPA-1) and 1.5405 (CASSCF) Å. It can be seen that, except for the UHF and ROHF values, all these r_e are within the experimental error limits. Applying a correction based on the difference between the experimental and computed r_e for the neutral radical yielded lower $r_e(PO^-)$ in each case (see table III in [91]).

From DFT optimizations (see section 3.1.1.2) Brinkmann *et al.* [82] reported $r_e(PO^-)$ ranging from 1.525 to 1.577 Å, the smallest value being obtained from a BHLYP optimization. In their table 1, however, these data are assigned to a $^1\Sigma^+$ (excited) electronic state instead of the $X^3\Sigma^+$ ground electronic state. Their B3LYP energy, −416.5786 hartree, lies between those obtained in our B3LYP/6–31G* and B3LYP/6–31+G* optimizations (table 3).

3.1.3.2.2. **This work.** With the B3LYP, CASSCF, CCSD and MP2 methods, going from the 6–31G* to the larger 6–31+G* basis set results in a slight reduction in r_e. Nevertheless, all the $r_e(PO^-)$ obtained with these methods and basis sets lie above the upper limit of the experimental value by 0.015–0.043 Å.

The GVB(3)/6–31G* $r_e(PO^-)$ is only 0.0024 Å (0.15%) above the median experimental value and lies between those obtained with the CCSD/cc–pVQZ and

CCSD(T)/aug–cc–pVQZ methods. The ROHF/ and GVB(2)/6–31G* values lie just under the lowest experimental error bar (table 3).

The CCSD/cc–pVQZ value ($r_e(PO^-) = 1.5386$ Å) is 0.011 Å less than that obtained from the CCSD/cc–pVTZ optimization. Note that the MP4SDQ optimization in [91] yielded an almost identical value, $r_e(PO^-) = 1.5388$ Å.

The r_e(CO) values obtained using the CCSD method with the cc–pVDZ through cc–pV6Z basis sets are compared with experiment in figure 2 of [119]. The r_e values decrease sharply on going from the DZ to TZ to QZ levels, the last of these being under experiment. These CCSD TZ and QZ results for CO [119] and ours for PO and its ions (tables 1–3) indicate that 1.54 Å < $r_e(PO^-)$ < 1.55 Å. Only further experimental work can verify this supposition.

3.2. *Fundamental vibrational frequencies (ω_e'')*

3.2.1. ω_e''*(PO)*

3.2.1.1. *Experiment.* Experimental vibrational frequencies and molecular constants for the ground and a large number of electronically excited states of the PO radical have been reported [121]. In 1931, Ghosh and Ball [22] were the first to report vibrational constants for the PO radical. Their vibrational analysis of the UV bands in the region 2280–2760 Å gave $\omega_e'' = 1230.64\,\mathrm{cm}^{-1}$ and $\omega_e''x_e'' = 6.52\,\mathrm{cm}^{-1}$ for the anharmonicity constant. Twenty-four years later, Dressler and Miescher [26] reported slightly higher values, $\omega_e'' = 1233\,\mathrm{cm}^{-1}$ and $\omega_e''x_e'' = 7\,\mathrm{cm}^{-1}$, from a study of bands in the VUV (1820–1930 Å) and UV (3200–3560 Å) regions. In the same year Dressler [27] reported revised values, $\omega_e'' = 1232.5\,\mathrm{cm}^{-1}$ and $\omega_e''x_e'' = 6.5\,\mathrm{cm}^{-1}$. Using higher resolution (dispersion, 0.42–0.54 Å mm^{-1}), Verma [48] studied the emission spectrum from a flow of traces of $POCl_3$ in Ar, excited by a radio frequency discharge, in the region 3800–5300 Å and obtained $\omega_e'' = 1233.30\,\mathrm{cm}^{-1}$ and $\omega_e''x_e'' = 6.56\,\mathrm{cm}^{-1}$. Verma and Singhal [51] obtained $\omega_e'' = 1233.34\,\mathrm{cm}^{-1}$ and $\omega_e''x_e'' = 6.56\,\mathrm{cm}^{-1}$ from a rotational analysis of 23 bands in the spectral region 3000–3900 Å.

The experimental value of ω_e'' is calculated using the values of the frequency for the $v = 1$ level of the ground state ($\nu(v = 1)$) and $2(\omega_e''x_e'')$. The former has been determined at high accuracy by Butler *et al.* [36] ($\nu(v = 1) = 1220.249\,01(43)\,\mathrm{cm}^{-1}$) and by Qian [60] ($\nu(v = 1) = 1220.254\,61(33)\,\mathrm{cm}^{-1}$). Combining these values with the experimental $\omega_e''x_e'' = 6.56\,\mathrm{cm}^{-1}$ [47, 48, 51] one obtains $\omega_e'' = 1233.37\,\mathrm{cm}^{-1}$, for which the major, but rather small, error comes from the value of $(\omega_e''x_e'')$.

3.2.1.2. *Theory*

3.2.1.2.1. **Literature.** Lohr [72] used the UHF method with the 6–31G* basis set and obtained $\omega_e'' = 1406\,\mathrm{cm}^{-1}$. He proposed a scaling factor of 0.868 which would bring the theoretical frequency to $1220\,\mathrm{cm}^{-1}$. This is incorrect as the latter is the frequency of the $v = 1$ vibrational level (see above); a scaling factor of 0.877 would be more appropriate. (Note that Brinkmann *et al.* [82] give values ranging from 1158 to $1336\,\mathrm{cm}^{-1}$ for their six DFT results for the fundamental frequency of PO. However, they cite an experimental value of $1220.25 \pm 43\,\mathrm{cm}^{-1}$, attributed to Zittel and Lineberger [66]. This appears to be an error, or a combination of errors.) In 1973, for the first high level calculations on PO, Tseng and Grein [75] used a minimal basis, full valence CI wavefunction and obtained $\omega_e'' = 939\,\mathrm{cm}^{-1}$, a low value which reflected the long internuclear distance (1.64 Å). Ten years later Grein and Kapur [76] used an extended basis set (see section 3.1.1.2) for MRD–CI calculations and obtained $\omega_e'' = 1240\,\mathrm{cm}^{-1}$, close to experiment.

The NHF procedure of Adamowicz *et al.* [83] gave $\omega''_e = 1447\,\text{cm}^{-1}$, $214\,\text{cm}^{-1}$ (17%) too high. However, their CCSD and CCSD(T) calculations yielded $\omega''_e = 1186$ and $\omega''_e = 1197\,\text{cm}^{-1}$ respectively [83], both lower than experiment by $> 35\,\text{cm}^{-1}$.

All the ω''_e values reported by Woon and Dunning [77] with the CASSCF and CMRCI methods for ten diatomic species are lower than experiment. Better agreement with experiment was obtained with increasing basis set size. For PO, the largest and smallest deviations, 143 and $9\,\text{cm}^{-1}$, were observed for the CASSCF/cc-pVDZ and CMRCI/cc-pV5Z calculations, respectively [77]. de Brouckère [78] reported $\omega''_e = 1253.3$ and $1228.9\,\text{cm}^{-1}$ at the MR–CI/ and MR–CI+Q/apVQZ levels, higher and lower than experiment respectively. In contrast Spielfiedel and Handy [84] found that the ω''_e calculated at the MRCI/ and MRCI+Q/cc-pVQZ levels are both lower than experiment and only differ by $1.6\,\text{cm}^{-1}$ (see table 1). In both de Brouckère's [78] and Spielfiedel's and Handy's [84] work, including the correction for quadruple excitations in the CI improves ω''_e but the corresponding r_e are further away from experiment, reflecting both the strong interdependence of these parameters and their dependence on basis set size.

3.2.1.2.2. **This work.** The RHF and ROHF methods used in this work are known to overestimate ω''_e and the deviations may be quite large, especially when small basis sets are used [69, 122]. Nevertheless, the main interest in using these methods lies in the possibility of applying scaling methods to the force constants. These methods are quite acceptable and permit transfer of the scaled force constant for a given molecular moiety to the force fields of larger molecules. The only requirements are that the calculations must be carried out at the same theoretical level, near the Hartree–Fock limit [123–125].

The ROHF/ and GVB(2)/6–31G* calculations (table 1) give $\omega''_e \sim 15\%$ above experiment, just below that obtained by Adamowicz *et al.* [83] with their NHF procedure (see above). The GVB(3)/6–31G* calculation gave a smaller deviation (+10%). In contrast, the ω''_e computed with the CASSCF method and both the 6–31G* and 6–31+G* basis sets are underestimated by ~6%. Note that they are closer to experiment than the CASSCF ω''_e reported by Woon and Dunning for cc–pV basis sets ranging from double- to quintuple-zeta size (see table XII in [77] and table 1). The ROHF/MP2 method also yielded ω''_e values that are underestimated by ~ 6%.

The B3LYP method gives excellent results, $1\,\text{cm}^{-1}$ and $7\,\text{cm}^{-1}$ below experiment with the 6–31G* and 6–31+G* basis sets. The CCSD/6–31G* result is only $\sim 10\,\text{cm}^{-1}$ above experiment. Note that the CCSD computations with the larger cc-pVTZ and cc-pVQZ basis sets yielded ω''_e approximately 51 and $58\,\text{cm}^{-1}$ above experiment respectively. The ω''_e value obtained with the costly CCSD(T)/aug-cc-pVQZ calculation is $4\,\text{cm}^{-1}$ below experiment.

3.2.2. $\omega''_e(PO^+)$

3.2.2.1. *Experiment.* In contrast to the extensive work concerning the parent radical, there have been only a few studies on PO^+, which is more difficult to produce and observe. In 1955, Dressler [27] reported ω''_e $(PO^+) = 1405\,\text{cm}^{-1}$ from a vibrational analysis of emission bands in the VUV region (1900–2200 Å). Next, in 1982, DMR [64] determined $\omega''_e(PO^+) = 1410 \pm 30\,\text{cm}^{-1}$ from the UV photoelectron band associated with the first ionization potential of the PO radical. PPW [65] calculated ω''_e $(PO^+) = 1408 \pm 7\,\text{cm}^{-1}$ from a refit of the band origin in Dressler's data [27]. Their emission microwave spectroscopy study in the range 140–470 GHz led to $\omega''_e = 1411.5 \pm 0.3\,\text{cm}^{-1}$, about 14% higher than that for the parent radical [65].

3.2.2.2. *Theory*

3.2.2.2.1. **Literature.** In the first *ab initio* computations on PO^+ (see section 3.1.2.1), DMR [64] reported $\omega_e'' = 1625\,cm^{-1}$. This value lies between those obtained by Moussaoui [69] from RHF ($1775\,cm^{-1}$) and GVB(2) ($1581\,cm^{-1}$) calculations with the STO–3G* basis set which is known to yield frequencies higher than experiment. Using their basis sets A and B (see section 3.1.2.2) at the SCF level, Peterson and Woods [87] obtained $\omega_e'' = 1672.4$ and $1676.5\,cm^{-1}$ respectively, both approximately 18% higher than experiment. As noted above for $r_e(PO^+)$, the different MP level calculations with basis set B gave oscillating results: $\omega_e''(MP2) < \omega_e''(MP4SDQ) < \omega_e''(expt) < \omega_e''(MP4DQ) < \omega_e''(MP3)$, the values ranging from 1309.3 to $1576.8\,cm^{-1}$ [87]. Wong and Radom [86] calculated the properties of 20 isoelectronic species, including PO^+, at the CASSCF/6-311G(MC) level. They obtained $\omega_e''(PO^+) = 1378\,cm^{-1}$, $33\,cm^{-1}$ below experiment. In a study of thirteen 22-electron diatomics Peterson and Woods [88] carried out CI–SD/A, CI–$SD_{(s)}$/A and CEPA-1/(B+C) calculations on PO^+. They obtained $\omega_e''(PO^+) = 1518.3\,cm^{-1}$ ($\sim 107\,cm^{-1}$ above experiment) for the CI–SD/A calculations, a value which was reduced to $1439.6\,cm^{-1}$ by the size consistency correction. The CEPA-1/(B+C) calculation gave $\omega_e''(PO^+) = 1433.1\,cm^{-1}$, only $22\,cm^{-1}$ above experiment [88]. Recently, Spielfiedel and Handy [84] obtained $\omega_e''(PO^+) = 1393.5$, 1398.7 and $1391.5\,cm^{-1}$ from HCTH, MRCI/cc-pvQZ and MRCI+Q/cc-pvQZ calculations respectively.

3.2.2.2.2. **This work.** With the 6–31G* basis set, we find ω_e'' (RHF) > ω_e''(GVB(2)) > ω_e''(GVB(3)) > ω_e''(expt) (table 2). The GVB(3)/6–31G* ω_e'' is about $50\,cm^{-1}$ closer to experiment than that reported for the CI–SD/A result in [88]. As was observed for ω_e''(PO) in table 1, the CASSCF method yields $\omega_e''(PO^+)$ which are below experiment. However, they are only $22\,cm^{-1}$ (1.7%) below experiment. The deviation of the MP2/6–31G* $\omega_e''(PO^+)$ from experiment is ~13% (too low) or twice that observed for the parent radical. The B3LYP results are close to experiment, being $\leq 18\,cm^{-1}$ above it.

Including the correction for triple excitations in the CCSD calculations (CCSD(T)) results in a very sharp decrease in ω_e'' from $\sim 30\,cm^{-1}$ above to $\sim 50\,cm^{-1}$ (3.5%) below experiment with both the 6–31G* and the 6–31+G* basis sets. The CCSD computations with the larger cc-pVTZ and cc-pVQZ basis sets both yield ω_e'' further away from experiment ($> +59\,cm^{-1}$). Thus the results with these large basis sets are no better than that obtained from the much less expensive CCSD/6–31G* optimization. However, the CCSD(T)/aug-cc-pVQZ frequency computation yielded $\omega_e'' = 1401\,cm^{-1}$, approximately $10\,cm^{-1}$ below experiment.

3.2.3. $\omega_e''(PO^-)$

3.2.3.1. *Experiment.* Apparently, the only experimental data on the spectroscopy of PO^- is from the fixed-frequency laser photoelectron spectrometry study by Zittel and Lineberger [66]. They determined $\omega_e''(PO^-) = 1000 \pm 70\,cm^{-1}$, a value which is, as expected, lower than that for the parent radical.

3.2.3.2. *Theory*

3.2.3.2.1. **Literature.** In the first theoretical determination of ω_e'' (PO^-) Lohr [72] obtained $1166\,cm^{-1}$ by use of analytical second derivatives of an optimized UHF/6–31G* wavefunction. On applying the scale factor determined for ω_e''(PO), the frequency is reduced to $1012\,cm^{-1}$, within experimental error. Peterson and Woods [91] determined ω_e'' at seven different levels of theory. The CASSCF and CEPA-1 methods gave $\omega_e'' = 1047.0$ and $1026.2\,\mathrm{cm}^{-1}$, respectively [91]. With the NHF, CCSD and CCSD(T) methods, Adamowicz *et al.* [83] obtained ω_e'' (PO^-) = 1190, 1076 and $1025\,\mathrm{cm}^{-1}$ respectively. Considering that their NHF and CCSD results overestimated ω_e'' (PO) by 214 and $53\,\mathrm{cm}^{-1}$, respectively (see above), one may reasonably infer that ω_e'' (PO^-) $< 1076\,\mathrm{cm}^{-1}$.

In spite of the reference to the $^1\Sigma^+$ (excited) state rather than to the $X\,^3\Sigma^+$ ground electronic state of PO^- in their table I, we mention here the DFT harmonic frequencies reported by Brinkmann *et al.* [82]. They range from 953 to $1116\,\mathrm{cm}^{-1}$. Except for the BHLYP value, $1116\,\mathrm{cm}^{-1}$, they lie within the experimental limits given by Zittel and Lineberger [66].

3.2.3.2.2. **This work.** The general trend, ω_e''(ROHF) > ω_e''(GVB(2)) > ω_e''(GVB(3)), is observed in table 3. The large error bars on the experimental value make it difficult to judge the exactness of the computed ω_e''. Indeed, the ω_e'' values calculated using the B3LYP, CASSCF, CCSD, CCSD(T) and MP2 methods with the 6–31G* and 6–31+G* basis sets all lie within the given experimental limits.

The CASSCF ω_e'' obtained for both PO and PO^+ in this work are underestimated (see tables 1 and 2). Also note that, in [86], the ω_e'' values obtained with the CASSCF method are too low for eight out of nine diatomics for which the experimental fundamental vibrational frequency is known. Thus one expects $\omega_e''(PO^-) > 931\,\mathrm{cm}^{-1}$, lending support to the lower limit given by Zittel and Lineberger [66].

The CCSD computations with the cc-pVTZ and cc-pVQZ basis sets give $\omega_e'' = 1071$ and $1079\,\mathrm{cm}^{-1}$ respectively, both just above the experimental error limit. Considering that the corresponding calculations for PO and PO^+ both gave ω_e'' more than $58\,\mathrm{cm}^{-1}$ above experiment, one would expect $\omega_e''(PO^-)$ to be above, but near, the mean experimental value. This supposition is reinforced by the value, $1034\,\mathrm{cm}^{-1}$, obtained with the CCSD(T)/aug-cc-pVQZ calculation.

3.3. *Bond order, Mulliken partial atomic charges, free valence and spin density*

The trends in the theoretically predicted values of these properties for the title species are of interest because they may give an indication of their stabilities and chemical reactivities.

3.3.1. *Bond order*

The trend in the 6–31G* BO values computed with MG at r_e is BO(R(O)HF) > BO(GVB(2)) > BO(GVB(3)). They range from 1.82 to 1.78 for PO (table 1), from 2.37 to 2.27 for PO^+ (table 2) and from 1.56 to 1.48 for PO^- (table 3). The BO calculated with Gamess using the 6–31G* basis set yielded BO(PO^+) = 2.37 (RHF), BO(PO) = 1.96 (ROHF) and BO(PO^-) = 1.56 (ROHF). The BOs for PO^+ and PO^- are in exact agreement with the MG data. However, the Gamess BO(PO) is higher than that obtained with MG, reflecting the fact that MG shares the unpaired electron equally between the equivalent π* (e_x, e_y) orbitals whereas Gamess does not. Note that, for the isovalent species PS^+, PS and PS^-, the corresponding BOs are 2.63, 1.88 and 1.41 respectively [68]. In both cases the BO may be considered as representing formal triple, double and single bonds for the cation, radical and anion respectively. For other examples of computed BO in diatomic species, the reader is referred to [126] where data on O_2, SO, S_2 and their mono- and dications are presented.

3.3.2. δx and δy

The computed Mulliken partial atomic charges (they are also denoted by total atomic charges) for the atoms in PO must of course be equal and opposite in sign, i.e. $\delta x = -\delta y$. Mulliken and Liu [71] showed that they depend strongly on the basis set used for each atom. With their full basis set (*3d* and *4f* STFs on both atoms), they obtained $\delta x = +0.45$. Omission of the *3d* and *4f* functions from the basis sets for both atoms yielded $\delta x = 0.66$. Most important, they found that deletion of the *3d* and *4f* functions from the basis set of only one atom strongly affected, and even reversed, the predicted atomic charges. Thus deletion of all the *3d* and *4f* functions from the basis set for P, or from the basis set for O, yielded $\delta x = 1.13$ and $\delta x = 0.12$ respectively [71].

The Mulliken population analyses calculated in this work for PO all predict positive partial charges on P. They are predicted to be near 0.6 by the ROHF, GVB, CCSD and ROHF/MP2 methods with the 6–31G* and 6–31+G* basis sets. The CASSCF and B3LYP computations yield lower values, i.e. $\delta x \cong 0.4$. The CCSD(T)/aug-cc-pVQZ computation predicts the highest Mulliken partial charges, $\delta x = 0.9$, for PO.

For PO^+, δx is predicted to be greater than unity and, correspondingly, the O atom carries a small partial negative charge. The Mulliken population analyses of the CCSD, CCSD(T) and ROHF/MP2 densities obtained from optimizations with the 6–31G* and 6–31+G* basis sets predict larger atomic charges ($\delta x \cong +1.3$ and $\delta y \cong -0.3$) than those from the analyses of the ROHF and GVB wave functions. The CCSD(T)/aug-cc-pVQZ computation yields the highest Mulliken total atomic charges with $\delta x = +1.63$ and $\delta y = -0.63$.

In contradiction with the report by Boyd and Lipscomb [80] that for PO^- the Mulliken charges on P and on O are −0.821 and −0.179 respectively, we find that the negative charge is predicted to be mainly on the O atom. (The highest level calculation carried out in this work, CCSD(T)/aug-cc-pVQZ, even predicts *a small positive charge* on P.) The highest predicted partial negative charges on the P atom, ~−0.4, are obtained with the B3LYP and CASSCF methods (table 3). Thus, although the theoretical free valence is mainly on the P atom, reaction of PO^- with an electrophilic species would probably occur via the O atom.

A referee has pointed out that higher partial negative charges on P in PO^- (−0.5) have been reported by Easton *et al.* [93] and has asked us to justify our results. Easton *et al.* report this value for MP2/cc-pVDZ, AM1 and PM3 optimizations and −0.4 from an optimization with their new MIDI! basis set (table 18 in [93]). However, the MP2/cc-pVDZ result they report is a ChelpG partial charge which is calculated by fitting point charges to the electrostatic potential. It is therefore very likely that it is different from the Mulliken partial atomic charge calculated at the same theoretical level. Moreover, the AM1 and PM3 results can be unreliable. (It is pointed out by Easton *et al.* [93] that the semi-empirical AM1 and PM3 methods give very different Mulliken charge distributions in phosphorus-containing compounds. This is not surprising: there is a caveat in the G98 AM1 output that 'AM1 has been requested along with some elements for which only MNDO parameters are available. *Such mixtures of methods are very risky and have not been fully tested.*' (italics ours).)

Rounding off of the partial charges to one significant figure can hide significant differences in the values (in this case > ± 10% or up to 20%). For this reason we have repeated the four optimizations to obtain the Mulliken (default in G98 output) and ChelpG partial charges on the P atom in PO^-. The Mulliken partial charge is given first and the ChelpG partial charge second in the parentheses: MP2/cc-pVDZ (−0.25, −0.46), MIDI! (−0.35, −0.60), AM1 (−0.44, −0.60) and PM3 (−0.51, −0.55). Thus the *apparent* large difference between our results and those of Easton *et al.* [93] is indeed only *apparent*. The MP2/cc-pVDZ Mulliken partial charge on P is close to a number of the CCSD and MP2 values we report in table 3. The MIDI! partial charge on P is actually equal to, or lower than, those we report for the B3LYP and CASSCF results. The ChelpG partial charges obtained with the MIDI!, AM1 and PM3 methods all place a larger percentage of the charge on phosphorus. This seems rather unlikely in view of the difference in electron affinities of O and P [7, 127, 128].

3.3.3. *Free valence and spin density*

Of the three programs used in this work, only MG and Gamess give free valence (FV) values in the output. G98 gives total atomic spin densities (SDs); these are reproduced in tables 1–3 with appropriate notations.

3.3.3.1. *PO*. For the ROHF and GVB calculations MG predicts FV(P) to be greater than unity; the values ranging from 1.14 to 1.20. The FV(O) values are much smaller, lying in the range 0.21–0.25. At the ROHF/6–31G* level of theory and r_e(PO), Gamess predicts FV(P) = 0.73 and FV(O) = 0.02, thus lower than the corresponding MG values. This is probably caused by the equal sharing of the unpaired electron by the equivalent $\pi^*(e_x, e_y)$ orbitals in the MG calculations and not in those with Gamess.

The sum of the SDs is unity and, at the same theoretical level, G98 predicts SD(P) = 0.85 and SD(O) = 0.15. Slightly smaller SD(P) are predicted by the CCSD/cc-pVTZ, CCSD/cc-pVQZ and CCSD(T)/aug-cc-pVQZ calculations (0.79–0.82, table 1).

3.3.3.2. *PO^+*. The RHF/6–31G* computations with both MG and Gamess predict the FV to be zero on both atoms. The GVB computations predict a small FV (≤ 0.3) on each atom (table 2). For PS^+ a similar, small FV on each atom was predicted by the GVB/6–31G* calculations [68]. There are no SD results in the G98 outputs but they should be zero.

3.3.3.3. *PO^-*. The ROHF/6–31G* FVs calculated by MG and Gamess are identical and predict FV(O) = 0.07 and FV(P) = 1.32. (A similar result was obtained for PS^- [68].)

G98 predicts that SD(P) is greater than unity at all levels investigated (table 3). The largest values of SD(P), 1.90, are obtained with the UMP2–FC/6–31+G* and CCSD(T)/6–31+G* computations.

3.4. *Dipole moments $\mu(D)$*

In the outputs of G98, μ are given only as absolute values, without indication of their polarity. However, the Mulliken partial atomic charges obtained in this work all indicate polarities $P^{\delta+}$ $O^{\delta-}$ for PO and PO^+ and a larger negative charge on the O atom in PO^-. Thus with the O atom on the positive z axis, μ for the three species are negative, as obtained by Gamess. Whereas MG also gives negative μ, those obtained for the ions are not calculated from the centre of mass and they are not reported in tables 2 and 3.

3.4.1. *PO*

Using microwave spectroscopy, Kanata *et al.* [59] measured the electric dipole moment of PO, $\mu = |1.88 \pm 0.07|$D. It is much larger than that of the isovalent NO (0.158 72 D [121]) owing to the larger difference in electron affinities for P and O compared with N and O [59]. This difference is also evidenced by the theoretical polarities in these neutral species: $P^{\delta+}$ $O^{\delta-}$ and $N^{\delta-}$ $O^{\delta+}$ [90].

The theoretical values of μ(PO) depend strongly on the method and basis set used [69, 72, 78, 80, 90]. Early theoretical values range from much lower than experiment (0.22 D and 0.70 D for SCF calculations with a minimal basis set augmented by *d* functions [80]), to higher than experiment (2.76 D from an HF/6–31+G*//HF/6–31G* calculation [72]). Before the value of the dipole moment was known experimentally Bruna and Grein [90] reported μ(PO) = 2.01 D from MRD–CI calculations at the experimental r_e, for an $O^{\delta-}$ $P^{\delta+}$orientation. Recently, de Brouckère [78] obtained μ(PO) = −1.993 D at the MR–CI/apVQZ level and experimental r_e. He points out that the result might not be improved by going to larger basis sets.

At the ROHF/6–31G* level, G98 and Gamess both yield μ(PO) = −2.610 D, close to the value calculated with MG (μ(PO) = −2.622 D) . The small difference is caused mainly by the equal sharing of the unpaired electron by the degenerate $\pi^*(e_x, e_y)$ orbitals in the MG calculations and not in those with G98 and Gamess.

Urban *et al.* [129] have investigated the accuracy of CCSD(T) calculations of 11 small radicals including PO. We find that the CCSD and CCSD(T) values of μ(PO) are all at least 20% and up to 50% higher than experiment. Even the large CCSD(T)/aug-cc-pVQZ calculation yields μ(PO) essentially equal to that obtained from the less expensive ROHF/6–31G* optimization. The best agreement between theory and experiment is found at the CASSCF/6–31G* and 6–31+G* levels for which the μ(PO) values are only 0.01 D (0.5%) below and above the experimental error limits respectively.

3.4.2. *PO*$^+$ *and PO*$^-$

There do not seem to be any experimental dipole moment data for these species. The theoretical dipole moments for charged species depend on the choice of origin [86] and they should be calculated relative to the centre of mass.

Martin and Feher [85] used the convention that a positive dipole is associated with the polarity $P^{\delta+}$ $O^{\delta-}$. They reported values of μ_z (PO) for r_z ranging from 1.5 to 10.0 au. The highest μ_z, 3.29 D, was obtained at a rather high value of r_z, 3.2 au or 1.64 Å [85]. Peterson and Woods [88] reported $\mu(PO^+) = -3.441$ D from a CI–SD calculation. Maroulis *et al.* [89] studied the effect of electron correlation on the dipole moment and polarizability of CP^-, BCl, CCl^+ and PO^+. They found that including electron correlation in the calculations decreased $\mu(PO^+)$ from, for example, −1.5886 D (SCF) to −1.2698 D (CCSD(T)). That their $\mu(PO^+)$ values for calculations including electron correlation are all lower than those obtained in [88] and in this work could be due to a basis set effect.

The theoretical literature values for $\mu(PO^-)$ differ sharply, from -0.13 ± 0.20 D (CASSCF), -0.22 ± 0.20 D (CEPA-1) and -0.52 ± 0.20 D (CI–SD) in [91] to 4.67 D (MRD–CI at the experimental r_e) in [90]. However, the latter was calculated from the O atom and the polarity appears to be reversed compared with that in PO. Similarly, although Boyd and Lipscomb [80] reported $\mu(PO^-) = 1.50$ D, the Mulliken populations in their paper appear to be reversed with $\delta x = -0.821$ and $\delta y = -0.179$.

The RHF/ and ROHF/6–31G* values of $\mu(\mathrm{PO}^+)$ and $\mu(\mathrm{PO}^-)$ obtained with Gamess and G98 are somewhat different, i.e. $\mu(\mathrm{PO}^+) = -3.84$ D and $\mu(\mathrm{PO}^-) = -1.31$ D (Gamess) and $\mu(\mathrm{PO}^+) = -3.89$ D and $\mu(\mathrm{PO}^-) = -1.16$ D (G98) (tables 2 and 3). The reason for the small difference in the absolute values is unknown. All the $\mu(\mathrm{PO}^+)$ values obtained with the CCSD and CCSD(T) methods in this work lie in the rather narrow range from −4.02 to −4.19 D. Using the larger cc-pVTZ, cc-pVQZ or aug-cc-pVQZ basis sets for the computations has little effect on $\mu(\mathrm{PO}^+)$. If the corresponding results for PO (table 1) are considered, these CCSD and CCSD(T) results for $\mu(\mathrm{PO}^+)$ are probably about 40% too high.

The $\mu(\mathrm{PO}^-)$ values obtained in this work cover the range from −0.41 D (CASSCF/6–31G*) to −1.65 D (ROHF/MP2–FC/6–31+G*). Even the CCSD and CCSD(T) values are rather dispersed, from −0.57 to −1.48 D (the lowest value is from the CCSD(T)/aug-cc-pvQZ calculation).

With the 6–31G* basis set and the appropriate ROHF or RHF method one obtains $\mu(\mathrm{PO}^+)$, $\mu(\mathrm{PO})$ and $\mu(\mathrm{PO}^-) = -3.89, -2.61$ and -1.26 D respectively. If it is assumed that the relative error is the same for all three species, the experimental $\mu(\mathrm{PO}^+)$ and $\mu(\mathrm{PO}^-)$ are expected to be -2.8 ± 0.7 and -0.9 ± 0.7 D respectively. The latter could thus be very near zero and PO^- may be very difficult to detect by microwave spectroscopy.

3.5. *Dissociation energies, $D_e = D_0^0 + 0.5\omega_e''$*

For PO and its ions $D_\mathrm{e} > D_0^0$ by < 0.1 eV, or less than the usual experimental error. D_0^0 refers to the dissociation energy of PO (or its ions, as specified) from the lowest vibrational level of its ground electronic state to the atoms (or neutral atom and ion; see equations at the beginning of section 3) in their ground electronic state at 0 K. Except where indicated otherwise in the original papers, D will be used to designate the dissociation energy, which can be either D_e or D_0^0.

3.5.1. *Experiment*

The literature values of $D(\mathrm{PO})$, ranging from 5.4 to 7.1 eV, are based mainly on spectroscopic and/or thermochemical data [52, 53, 121, 130]. The mean of the extreme values, 6.1 eV, is remarkably close to the upper limit, D_0^0 (PO) = 49 536 cm^{-1} (6.16 eV), determined from pre-dissociation in the rotational emission attributed to the $D'\ \Pi_\mathrm{r}$ state of PO (later described as the $B\,^2\Pi$ state [74]) which is presumed to lead to the atoms in their ground electronic states [49, 121]. A slightly lower upper limit, 49 090 cm^{-1} (6.09 eV), was determined by Ghosh and Verma [52] from pre-dissociation of the electronically excited state leading to the first excited state products ($\mathrm{P}(^2\mathrm{D}) + \mathrm{O}(^3\mathrm{P})$). These upper limits are very close to the thermochemical value, D_0^0 (PO) = 593 ± 8 kJ mol^{-1} (6.15 ± 0.08 eV), reported by Drowart *et al.* [53]. The latter is the weighted average of three D_0^0 values obtained using the D_0^0 values of the molecules YO, GdO, SnO and P_2 and the enthalpies of the reactions of PO(g) with Y(g), Gd(g) and Sn(g), determined by mass spectrometry [53].

An estimate of D_0^0 (PO^+) = 8.41 eV, based on Dressler's work [27], is given in the compilation by Huber and Herzberg [121]. Combining the adiabatic first IP of PO and the first IP of atomic phosphorus, DMR [64] obtained a lower upper limit for $D_\mathrm{e}(\mathrm{PO}^+)$, 8.25 ± 0.01 eV. It is based on their determination of the first IP of PO and the error bar may be underestimated.

Huber and Herzberg [121] also give an estimate of D_0^0 (PO^-), 5.78 eV, calculated using D_0^0 (PO) and the electron affinities (EAs) of PO and O in their ground electronic states.

From the above data, one finds $D_0^0(PO^-) < D_0^0(PO) < D_0^0(PO^+)$. This order is of course expected from the effect of removal of the electrons from anti-bonding orbitals as one goes from the anion to the cation.

3.5.2. *Theory* (D_e)

Although a united species can often be described satisfactorily by a single-determinant wavefunction at or near the equilibrium geometry, when the distance between two moieties is increased, breaking the bond, the wavefunction will be unsatisfactory. For instance, for C–H bond rupture in ethylene, single-determinant computations at large C–H separations show a plateau but it is much too high energetically [131]. There is a very large dipole moment, indicating that, for this computation, the separated species constitute an ionic pair [131]. However, if one does not wish to follow the reaction coordinate for dissociation (or equivalently, that for the combination of the moieties), it is possible to obtain a reasonable estimate of D_e from the difference between the total energy at r_e and that computed either (i) for the sum of the energies of the isolated moieties [62, 68, 86, 87] or (ii) for the 'molecule' with the molecular moieties separated by a sufficient distance (i.e. ≥ 7 Å). (It is of course imperative that the proper multiplicities be used.) Both methods should give the same result and, used together, they are a good check on the results obtained. Examples of such computations can be found in [131–133]. The use of the GVB–PP method with basis sets larger than minimal gave energies in good agreement with experiment for ethylene → vinyl + H [131, 134] and propylene → $CH_3\text{–}CH = \dot{C}H$ (or $CH_3\text{–}\dot{C} = CH_2$) + H [132, 133].

The ROHF and GVB(1) energies computed for the P and O atoms and their ions are given in table 4.

3.5.2.1. *$PO(X\,^2\Pi_r) \rightarrow P(^4S_u) + O(^3P_g)$.* There have been only a few previous theoretical determinations of D_e(PO) [62, 69, 72, 75–77, 80] and, with the exception of some estimates of the atomization energies for the complete basis set (CBS) limit in [62], they are all lower than the experimental values (table 5). In their very early SCF study, Boyd and Lipscomb [80] obtained a rather low value, $D_e(PO) = 0.70$ eV. Lohr [72] determined $D_e(PO) = 4.70$ eV from ΔMP3/6–31+G*//HF/6–31G*

Table 4. ROHF, GVB(1) and CCSD energies (hartree) of the dissociation products.

Method/basis	$P(^4S_u)$	$P^{(1+)}(^3P_g)$	$O(^3P_g)$	$O^{(1-)}(^2P_u)$
ROHF/6–31G* [a]	−340.689 986 [b]	−340.320 826 [b]	−74.778 966	−74.715 457
GVB(1)/6–31G* [a]	−340.619 602 [b]	−340.269 231 [b]	−74.696 855	−74.716 158
CCSD/cc-pVTZ [c]	−340.817 237	−340.434 394	−74.971 050	−74.976 598
CCSD/cc-pVQZ [c]	−340.823 390	−340.439 619	−74.989 878	−75.014 790
CCSD(T)/aug-cc-pVQZ [c]	−340.828 267	−340.442 378	−74.995 268	−75.046 676

[a] Computed with MG [94].
[b] Reference [68].
[c] Computed with G98 [100 (*a*)].

Table 5. The computed and experimental dissociation energy (D_e) of PO in its ground electronic $X^2\Pi_r$ state to $P(^4S_u) + O(^3P_g)$. The theoretical values are obtained in this work from the difference between the appropriate ROHF, GVB(2) or CCSD energy at r_e (table 1) and (a) the ROHF, GVB(2) or CCSD energies for ^{6}PO calculated at $r = 20$ Å and (b) the sum of the corresponding ROHF, GVB(1) or CCSD energies given in table 4 for $P(^4S_u) + (^3P_g)$.

Method/basis set	E (^{6}PO) (hartree)	$\Sigma(E$, atoms) (hartree)	D_e (eV)
ROHF/6–31G*[a]	−415.468 952	−415.468 952	2.00
GVB/6–31G*[a]	−415.316 456	−415.316 457	6.46
CCSD/cc-pVTZ[a]	−415.788 288	−415.788 287	5.29
CCSD/cc-pVQZ[a]	−415.813 268	−415.813 268	5.59
CCSD(T)/aug-cc-pVQZ[a]	−415.823 535	−415.823 535	6.00
CASSCF/cc-pVDZ[b]			4.04
CASSCF/cc-pVTZ[b]			4.58
CASSCF/cc-pVQZ[b]			4.67
CASSCF/cc-pV5Z[b]			4.72
CRMCI/cc-pVDZ[b]			4.62
CRMCI/cc-pVTZ[b]			5.52
CRMCI/cc-pVQZ[b]			5.79
CRMCI/cc-pV5Z[b]			5.92
ΔMP3/6–31+G*//HF/6–31G*[72]			4.70
MRD-CI [76]			4.99
			D_0^0
Thermochemical cycle[c]			6.15 ± 0.08
Pre-dissociation[d]			6.15
Pre-dissociation[e]			6.09

[a] This work.

[b] Reference [77].

[c] The weighted average of three D_0 values obtained from the enthalpies of the reactions of PO(g) with Y(g), Gd(g) and Sn(g) determined by a mass spectrometric study and combined with D_0 of the molecules YO, GdO, SnO and P_2 [53].

[d] The rotational structure of emission from the D' state (later described as $B\,^2\Pi$), which is assumed to lead to the ground state atoms, breaks off at 49 536 cm^{-1} above the ground state of PO [49, 121].

[e] Analysis of the UV absorption spectrum in the region 2100–1550 Å. The pre-dissociation of the $A\,^2\Sigma^+$ state is presumed to lead to the first excited state products $P(^2D) + O(^3P)$ [52].

calculations. MRD–CI studies by Tseng and Grein [75] and Grein and Kapur [76] led to $D_e(PO) = 2.59$ and 4.99 eV respectively. As mentioned above, Grein and Kapur [76] used a much larger basis set in their computations. Woon and Dunning [77] used the cc-pVDZ to cc-pV5Z basis sets and obtained D_e(PO) ranging from 4.04 to 4.72 eV with the CASSCF method and from 4.62 to 5.92 eV with the CMRCI method. They estimate the CBS limits for D_e(PO) with the CASSCF and CMRCI methods to be 4.74 and 6.00 eV respectively [77]. Fast *et al.* [62] determined the CBS limits for the atomization energies of 29 molecules at the HF, MP2, MP4, CCSD and CCSD(T) theoretical levels. For PO they obtained 2.31, 6.55, 6.37, 5.63 and 6.07 eV respectively. The HF value is much too low [62].

In this work, for each theoretical level, the energy obtained for $PO(^6\Sigma^+)$ at $r = 20$ Å is equal, within 1×10^{-6} hartree, to the sum of the appropriate energies obtained for $P(^4S_u)$ and $O(^3P_g)$ (table 5). Compared with experiment, the theoretical ROHF D_e(PO) is much too low. This is in agreement with results of Fast *et al.* [62]

where all of the HF atomization energies are lower than those determined with four other methods. The D_e(PO) value determined with the GVB method in this work is ~5% too high. Nevertheless, it compares favourably with the CBS limits for the atomization energies for PO obtained with the MP2 and MP4 methods (table II in [62]). It is interesting to note that, with the cc-pVTZ and cc-pVQZ basis sets, D_e(CASSCF) < D_e(CRMCI) < D_e(CCSD). The CCSD(T)/aug-cc-pvQZ calculation gives the highest value, $D_e = 6.00$ eV, equal to the estimated CMRCI CBS limit in [77].

3.5.2.2. *$PO^+(X^1\Sigma^+) \rightarrow P^+(^3P_g) + O(^3P_g)$.* From MP4SDQ calculations, Peterson and Woods [87] obtained $D_e(PO^+) = 8.34$ eV, about 0.1 eV above experiment. Using five different methods, Wong and Radom [86] calculated $D_e(PO^+)$ ranging from 6.65 to 8.36 eV. Compared with DMR's experimental estimation [64], their best result, $D_e(PO^+) = 8.21$ eV, was obtained from MP4/6–311+G(MC)(2df) calculations using $r_e(PO^+)$ determined at the MP3/6–311G(MC(d)) level [86].

Again, as for PO, comparison of the RHF/6–31G* result with experiment shows that $D_e(PO^+)$ is too low (49%) whereas that determined by the GVB–PP method is 17% too high (table 6). However, the advantage of using the 6–31G* basis set with these methods is the considerable reduction in computer time compared with MP, CASSCF or CCSD calculations. Our best result $D_e = 8.14$ eV, or 0.1 eV below experiment, was obtained with the CCSD(T)/aug-cc-pVQZ calculations.

3.5.2.3. *$PO^-(X^3\Sigma^-) \rightarrow P(^4S_u) + O^-(^2P_u)$.* Peterson and Woods [91] obtained $D_e(PO^-) = 130\ \mathrm{kcal\,mol^{-1}}$ (5.64 eV) from MP4SDTQ calculations with the basis set described in [87].

The agreement between the energies obtained for the 'molecule' at 20 Å and the sum of the energies of $P(^4S_u)$ and $O^-(^2P_u)$ (table 7) is not as good as those obtained for PO and PO^+ (tables 5 and 6 respectively). The $D_e(PO^-)$ values obtained from the CCSD/cc-pVTZ, CCSD/cc-pvQZ and CCSD(T)/aug-cc-pVQZ calculations are very close to that (5.78 eV) obtained using D_0^0 (PO) and the electron affinities of PO and O [121].

3.6. *Ionization potential of PO*

3.6.1. *Experiment*

From extrapolation of its Rydberg spectral series, the first IP of PO was estimated to be 8.37 eV (67 570 cm^{-1} [49] and 67 532 cm^{-1} [52]). Drowart *et al.* [53] obtained 8.5 ± 1 eV from mass spectral data, using Sn for calibration of the energy scale. DMR [64] calculated IP(PO) = 8.39 ± 0.01 eV from VUV photoelectron spectral data. The latter, and most recent, value dates from just over 20 years ago and it would be interesting to have a new determination of IP(PO). However, note that an almost identical value, 8.38 eV, is obtained from the thermochemical cycle, $IP(PO) = D_e(PO) + IP(P) - D_e(PO^+)$, where $IP(P) = 10.484$ eV [7] and the D_e values are the experimental values for PO [53] and PO^+ [64] (see tables 5 and 6).

3.6.2. *Theory*

There have been few theoretical determinations of the first IP of PO. Ackermann *et al.* [73] calculated the Rydberg states of PO and their extrapolation led to an IP of 8.23 eV. DMR [64] used a double-zeta quality STO basis set augmented by *3d* functions on O and *3d*, *4s* and *4p* functions on P and obtained 8.22 eV for the vertical IP. These values are quite close to experiment.

Table 6. The computed and experimental dissociation energy (D_e) of PO^+ in its ground electronic $X\,^1\Sigma^+$ state to $\mathrm{P}^{(1+)}(^3\mathrm{P}_g)+\mathrm{O}(^3\mathrm{P}_g)$. The theoretical values are obtained in this work from the difference between the appropriate ROHF, GVB(2) or CCSD energy at r_e (table 2) and (a) the ROHF, GVB(2) or CCSD energy of PO^+ ($^5\Sigma^+$) calculated at 20 Å or (b) the sum of the corresponding ROHF, GVB(1) or CCSD energies given for $\mathrm{P}^{(1+)}(^3\mathrm{P}_g)$ and $\mathrm{O}(^3\mathrm{P}_g)$ in table 4.

Method/basis set	$E[\mathrm{PO}^+(^5\Sigma^+)]$ (hartree)	$\Sigma(E,\text{atoms})$ (hartree)	D_e(eV)
ROHF/6–31G*[a]	−415.099 81	−415.099 79	4.23
GVB/6–31G*[a]	−414.966 10	−414.966 09	9.35
CCSD/cc-pVTZ[a]	−415.405 44	−415.405 44	7.46
CCSD/cc-pVQZ[a]	−415.429 49	−415.429 50	7.69
CCSD(T)/aug-cc-pVQZ[a]	−415.437 64	−415.437 65	8.14
SCF[b]			4.46
MP2[b]			8.58
MP3[b]			7.46
MP4SDQ[b]			7.74
MP4SDTQ[b]			8.35
CASSCF[c]			7.54
MP3[c]			6.65
ST4CCD[c]			7.29
MP4/6–311G(MC)(2df)[d]			8.21
MP4/6–311+G(MC)(3d2f)[d]			8.36
Experimental			
Thermochemical cycle[e]			8.41
Photoelectron spectroscopy [64]			8.25(1)

[a] This work.
[b] Basis set B [87].
[c] Basis 6–311G(MC)(d) [86].
[d] At the MP3/6–311G(MC)(d) optimized internuclear distance [86].
[e] From $D_0^0(\mathrm{PO})+\mathrm{IP(P)}-\ \mathrm{IP(PO)}$ [121].

Table 7. The computed dissociation energy (D_e) of PO^- in its ground electronic $X\,^3\Sigma^-$, state to $\mathrm{P}(^4\mathrm{S}_u)+\mathrm{O}^-(^2\mathrm{P}_u)$ in comparison with experimental data. The ROHF and GVB values are obtained from the difference between the appropriate ROHF or GVB(2) energy at r_e (table 3) and (a) the ROHF and GVB(2) energies for $^5\mathrm{PO}^-$ calculated at $r=20$ Å or (b) the sum of the corresponding ROHF and GVB(1) energies given for $\mathrm{P}(^4\mathrm{S}_u)$ and $\mathrm{O}^-(^2\mathrm{P}_u)$ in table 4.

Method/basis set	$E(^5\mathrm{PO}^-)$ hartree	$\Sigma(E,\text{atoms})$ hartree	D_e(eV)
ROHF/6–31G*[a]	−415.405 44	−415.405 44	3.30
GVB(2)/6–31G*[a]	−415.335 06	−415.335 76	5.22
CCSD/cc-pVTZ[a]	−415.793 839	−415.793 835	5.74
CCSD/cc-pVQZ[a]	−415.818 385	−415.838 180	5.79
CCSD(T)/aug-cc-pVQZ[a]	−415.874 949	−415.874 943	5.70
MP4SDTQ[b]			5.64
Thermochemical cycle[c]			5.78

[a] This work.
[b] The basis set is described in [87, 93].
[c] Calculated from $D_0^0(\mathrm{PO})$ and the electron affinities of PO and O [121].

Table 8. The IP and electron affinity EA of PO (eV).

Method/basis set	IP (vertical)	IP (adiabatic)	EA (adiabatic)
ROHF/6–31G*[a]	7.96	7.81	0.172
GVB(2)/6–31G*[a]	6.69	6.65	0.189
GVB(3)/6–31G*[a]	6.72	6.67	0.236
CASSCF/6–31G*[a]		6.52	−1.012
CASSCF/6–31+G*[a]		6.62	−0.568
CCSD/6–31G*[a]		7.81	0.053
CCSD/6–31+G*[a]		8.00	0.782
CCSD(T)/6–31+G*[a]		7.92	0.754
CCSD/cc-pVTZ[a]		8.25	0.599
CCSD/cc-pVQZ[a]		8.34	0.872
CCSD(T)/aug-cc-pVQZ[a]		8.36	1.103
MP2/6–31G*[a]		7.66	0.022
MP2/6–31+G*[a]		7.87	0.760
B3LYP/6–31G*[a]		8.41	0.566
B3LYP/6–31+G*[a]		8.61	1.287
MRD-CI(MO)[b]			0.88
B3LYP, B3P86, BHLYP, BLYP, BP86, LSDA[c]			0.43, 0.92, 0.22, 0.94, 1.15, 1.51
Experiment		8.39(1)[d]	1.092(10)[e]

[a] This work.

[b] Reference [91]. Basis set B, molecular orbitals. A lower value is obtained with natural orbitals.

[c] Reference [82]. Correction for the difference in zero-point energies increases the EA by about 0.02 eV. The basis set used is described as DZP++.

[d] Determined from the laser photoelectron spectrum band attributed to the process PO^+ $(X^1\Sigma^+)+$ e $\leftarrow PO(X^2\Pi)$ [64].

[e] Best literature value, obtained from the laser photoelectron detachment peak for the process $PO(X^2\Pi,\ \nu'=0)+e \leftarrow PO^-(X^3\Sigma^-,\ \nu''=0)$ [66].

The IPs reported in table 8 were calculated (neglecting the relatively small differences in the zero-point energies) using the equation $IP(PO)=E(PO^+)-E(PO)$, where, for the adiabatic IP, $E(PO)$ and $E(PO^+)$ refer to the energies given in tables 1 and 2 respectively. The energies from single-point calculations for PO^+ at $r_e(PO)$ were used to calculate the vertical IP. The differences between the vertical and adiabatic IP obtained with the ROHF and GVB methods are ≤ 0.1 eV. Except for the IP obtained with the B3LYP method, all of the values calculated in this work are lower than experiment (table 8). It is probably a coincidence that the B3LYP/6–31G* IP is closest to experiment. The CCSD(T)/aug-cc-pVQZ value is just below experiment; however, the optimizations required to obtain this IP are rather expensive.

3.7. *Electron affinity of PO*

3.7.1. *Experiment*

Apparently the only experimental value of EA(PO) in the literature is 1.092 ± 0.010 eV determined by Zittel and Lineberger [66] from the photoelectron detachment peak for the process $PO(X^2\Pi,\ \nu'=0)+e^- \leftarrow PO^-(X^3\Sigma^-,\ \nu''=0)$.

Because the centre of the peak does not necessarily correspond to the transition between the lowest rotational levels, EA(PO) was corrected according to Kasdan *et al.* [135].

3.7.2. *Theory*

Most of the previous theoretical determinations of EA(PO) are lower than experiment [72, 82, 83, 90, 91]. They are usually determined from the difference in the energies of PO and PO^- at their corresponding r_e, i.e. $EA(PO) = E(PO) - E(PO^-)$. Lohr [72] obtained 0.84 and 0.80 eV from frozen core MP3 and CISD computations with the 6–31+G* basis set at the HF/6–31G* optimized internuclear distances. Adamowicz *et al.* [83] determined EA(PO) = 0.70 eV and 0.91 eV (NHF and CCSD methods respectively). Including the linear correction for triple excitations (CCSD(T)) gave a slightly lower value, 0.88 eV [83]. Peterson and Woods [91] also obtained 0.88 eV from MP4SDTQ calculations. Bruna and Grein [90] found that their MRD–CI results underestimated EA(PO) by 0.24 eV compared with experiment. They pointed out that the discrepancies between their theoretical EAs for PO and NS and experiment are due mainly to incompleteness of basis sets: comparable discrepancies were also obtained for the EA of the atoms [90].

Brinkmann *et al.* [82] calculated the adiabatic EA of PO using six different DFT methods. The EAs obtained depend strongly on the method used, the values ranging from 0.22 eV to 1.53 eV.

The EA(PO) determined in this work also depend strongly on both the basis set and the method used (table 8). The ROHF/ and GVB/6–31G* vertical EA(PO) obtained in this work (not given in table 8) are all very low (0.016–0.067 eV). Allowing the anion to relax to its r_e (table 3) increases the predicted EA(PO) at both the ROHF/ and the GVB/6–31G* levels of theory but they are still < 25% of experiment.

The worst results are obtained with the CASSCF method: the ground electronic state of PO^- is predicted to lie more than 0.5 eV above that of PO. The inclusion of diffuse functions in the basis set (6−31 + G* instead of 6–31G*) has a marked effect, increasing the predicted adiabatic EA at the B3LYP, CCSD, CCSD(T) and MP2 levels of theory. The CCSD/, CCSD(T)/ and MP2/6–31+G* computations yield EA(PO) which are about 20% below experiment and thus lie just below the best previous theoretical literature results. Note, however, that only the B3LYP/ 6–31+G* method yields EA(PO) which is greater than experiment by 0.2 eV. The result closest to experiment is obtained from the CCSD(T)/aug-cc-pVQZ calculations.

4. Summary

The r_e values of PO and PO^+ in their ground electronic states are known with high accuracy (i.e. 1.476 373 55(10) Å [37] and 1.424 992 7(4) Å [65] respectively), permitting critical comparison of the optimized theoretical values. Although the error bar on $r_e(PO^-)$ is much larger (0.01 Å), it is low enough to permit useful comparison between results obtained using different theoretical methods and/or basis sets for the computations.

The optimized $r_e(PO)$ obtained in this work with the 6–31G* and 6–31+G* basis sets, using the ROHF (without electron correlation) and GVB methods lie in the range 0.8–1.5% below the best experimental value. In sharp contrast, with the same basis sets, the B3LYP, CASSCF, CCSD and MP2 methods all yielded r_e(PO) longer than experiment. The theoretical literature value of r_e(PO) closest to experiment (only 0.28% higher) was reported by Woon and Dunning [77] with their CMRCI/cc-pV5Z computations. In this work, the CCSD/cc-pVQZ optimization gave a satisfactory value (0.003 Å below experiment) whereas the CCSD(T)/aug-cc-pVQZ value is 0.01 Å (0.68%) higher than experiment.

Our RHF/ and GVB(2)/6–31G* values for $r_e(PO^+)$ are lower than experiment. The latter (1.4214 Å) is fortuitously equal to that obtained from the much larger CCSD/cc-pVQZ optimization. The other methods used in this work all yield r_e which are longer than experiment. The MP2 results deviate most from experiment (+3.2% longer) as was observed for r_e(PO). The best theoretical result reported in the literature, $r_e(PO^+) = 1.4248$ Å, was obtained with the CI–SD$_s$(B) method [65].

Because of the larger error bars on the experimental value of $r_e(PO^-)$, many theoretical values fall within or very close to them. The $r_e(PO^-)$ result closest to the mean experimental value was obtained from the CCSD/cc-pVQZ optimization. It would be very interesting to have new, more precise data on this elusive species.

The Hartree–Fock (ROHF and RHF) and GVB methods used in this work are known to overestimate the fundamental vibrational frequencies, ω_e''. The deviations may be quite large, especially when small basis sets are used [69, 122]. Nevertheless, the main interest in using these methods lies in the possibility of calculating a scale factor to correct the force constant, obtained at a given theoretical level for one of the title species, and using this scale factor to correct the force field of a larger molecule with the same molecular moiety. The only requirements are that the calculations must be carried out at the same theoretical level, preferably near the Hartree–Fock limit [123–125]. Transferring scale factors to the force fields of larger molecules should not be used for methods which underestimate the vibrational frequencies, requiring scale factors greater than unity.

Considering only the closeness of ω_e''(PO) to experiment, the best results obtained in this work are the B3LYP/6–31G* ($-1\,\mathrm{cm}^{-1}$) and CCSD(T)/aug-cc-pVQZ ($-4\,\mathrm{cm}^{-1}$) frequencies. These results are closer to experiment than the best results reported in the literature for computations with large basis sets and more extensive methods (see table 1 and [77, 78, 84]). However, there is a strong interdependence of ω_e'' and r_e: changing the basis set and/or theoretical method often leads to better agreement of one of them with experiment and a concurrent, further disagreement of the other with its experimental counterpart. Examples of this interdependence are found in both de Brouckère's [78] and Spielfieldel and Handy's [84] work: including the correction for quadruple excitations in the CI improves ω_e'' but the corresponding r_e values are further away from experiment.

The best experimental value for $\omega_e''(PO^+)$, $1411.5 \pm 0.3\,\mathrm{cm}^{-1}$, is approximately 14% higher than that for the parent radical. The CCSD(T)/aug-cc-pVQZ result for $\omega_e''(PO^+)$ is the closest to experiment ($-10\,\mathrm{cm}^{-1}$). The CCSD/cc-pVTZ and cc-pVQZ results are further away by more than $40\,\mathrm{cm}^{-1}$. Note that the high level computations of Spielfiedel and Handy [84] yielded $\omega_e''(PO^+)$ which are also lower than experiment (by -12 to $-19\,\mathrm{cm}^{-1}$ (see table 2).

Zittel and Lineberger [66] determined the only available experimental value of $\omega_e''(PO^-)$, $1000 \pm 70\,\mathrm{cm}^{-1}$. As expected, this value is lower than that for the parent radical. Note that the ω_e'' (CASSCF) values are near the lower experimental limit (table 3). In [86], the ω_e'' values obtained with the CASSCF method are too low for eight out of nine diatomics for which the experimental fundamental vibrational frequency is known. The B3LYP $\omega_e''(\mathrm{PO}^-)$ are fortuitously equal to the mean experimental value (table 3). Considering the B3LYP results for $\omega_e''(\mathrm{PO})$ and $\omega_e''(\mathrm{PO}^+)$, these data lend support to ω_e'' (PO^-) being $\leq 1000\,\mathrm{cm}^{-1}$. However, the predicted frequency from the CCSD(T)/aug-cc-pVQZ calculation is $1034\,\mathrm{cm}^{-1}$ and it is likely that the true experimental $\omega_e''(\mathrm{PO}^-)$ is close to this value.

The bond orders $\mathrm{BO(PO^+)} = 2.37$, $\mathrm{BO(PO)} = 1.82$ and $\mathrm{BO(PO^-)} = 1.56$, obtained using the 6–31G* basis set, may be considered as representing formal triple, double and single bonds in these species.

The Mulliken population analyses calculated in this work predict that the phosphorus and oxygen atoms in PO have partial positive and negative charges respectively (table 1). The positive charge on P in PO^+ is predicted to be greater than unity, compensated by a small partial negative charge on the O atom.

For PO^- we find that the negative charge is predicted to be mainly on the O atom. The highest partial negative charge on the P atom (up to 0.42) is obtained with the B3LYP and CASSCF methods (table 3). Only the CCSD(T)/aug-cc-pVQZ computation predicts that the total negative charge on O is greater than unity.

The predicted μ obtained in this work for all three title species are negative, corresponding to the polarity $\mathrm{P}^{\delta+} \rightarrow \mathrm{O}^{\delta-}$. Assuming that the relative error in the R(O)HF/6–31G* values is the same for the three species, the experimental $\mu(\mathrm{PO}^+)$ and $\mu(\mathrm{PO}^-)$ are expected to be -2.8 ± 0.7 and -0.9 ± 0.7 D respectively. The latter could thus be very near zero and PO^- may be very difficult to detect by microwave spectroscopy.

The trend $D_e(\mathrm{PO}^-) < D_e(\mathrm{PO}) < D_e(\mathrm{PO}^+)$ is expected from the effect of removal of electrons from the antibonding orbitals. The ROHF (PO^- and PO) and RHF (PO^+) methods yield D_e which are much lower than experiment (or those obtained from thermochemical cycles). With the ROHF method, even the experimental trend is not respected: $D_e(\mathrm{PO}^-)$ is predicted to be higher than $D_e(\mathrm{PO})$.

Considering only the predicted D_e for the three species and the IP and EA for PO, the CCSD(T)/aug-cc-pVQZ computations give the best results (tables 5–8).

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