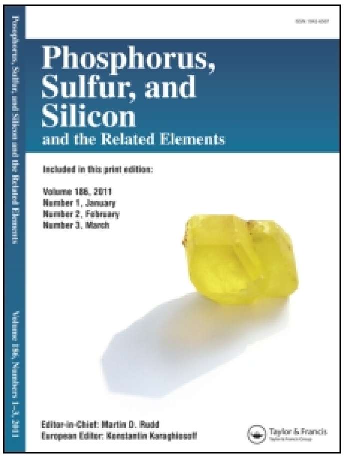

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THE P_4 MOLECULE AND P_4H ION

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THE P_4 MOLECULE AND P_4H^+ ION

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Experimental findings as well as quantum chemical calculations indicate that the P_4 molecule has a remarkably low nucleophilicity. The P_4H^+ ion is predicted to have a "proton at apex" configuration whereas a proton in the centre seems to be metastable. The influence of *d* orbitals on the stability of P_4 against 2 P_2 and 1/2 P_8, the photoelectron spectrum, and the valence electron density is discussed.

INTRODUCTION

The chemistry of elemental white phosphorus indicates that the molecule P_4 has a very low nucleophilicity. This behaviour is usually interpreted by the assumption that the lone electron pair on each phosphorus atom is to a first approximation located in the 3*s* orbital. It is therefore spherically distributed around the nucleus and does not outstretch towards the outer sphere. As a consequence the molecule of white phosphorus is found only sporadically as a ligand in coordination compounds. The only pieces of evidence for the presence of an intact P_4 molecule were found in rhodium complexes of the type $RhCl(P_4)L_2$ with L = $(C_6H_5)_3P$, $(p\text{-}CH_3C_6H_4)_3P$, $(m\text{-}CH_3C_6H_4)_3P$ and $(C_6H_5)_3As$ though no ^{31}P nmr signals due to P_4 in the complexes could be observed.[1] In agreement with the model mentioned above is the large chemical shift of elemental white phosphorus towards high field strengths in the ^{31}P nmr spectrum. Its chemical shift is 460.06 ppm in the condensed phase at 30°C referred to 85% aqueous orthophosphoric acid while phosphorus vapour has even a larger highfield shift of 553.5 ppm (extrapolated to zero pressure and bulk susceptibility corrected).[2]

The action of the phosphorus molecule as electron donor and acceptor was shown in a series of publications by Heckmann and Fluck[2–6] and by Krabbes and Großmann.[7–9]

Though several calculations on the P_4 molecule can be found in the literature, as is seen from the references in the next paragraph, a new approach on the basis of pseudopotentials should result in an improved model and should allow us to make predictions with respect to a protonated P_4 molecule, i.e. the P_4H^+ ion.

METHOD OF CALCULATION

To date, the *ab initio* calculation of the P_4 molecule has only been possible through the use of relatively small and strongly contracted basis sets. It has not been possible, however, to investigate the influence of 3*d*-type polarization functions on certain molecular properties, such as stability and nucleophilicity. Along with the use of a minimal STO-3G basis (9*s*,6*p*) contracted to [3*s*,2*p*],[10] there also exists a calculation with a (11*s*,7*p*) basis contracted to [4*s*,3*p*].[11]

Assuming that only the valence electrons are responsible for certain molecular properties, then the valence electron approximation not only allows the calculation of larger molecules but also the use of more extended basis sets than those employed in *ab initio* calculations. The electrons of the P atom can be unequivocally classified into core and valence ones. The so-called "Pauli forces" which prevent the valence electrons from collapsing into the core, can be described analytically through pseudopotentials which can be calibrated with the aid of experimental data. A model potential which seems to be particularly suitable for Gaussian basis sets and which has already been used successfully on the NaK molecule, is:[12]

$$V(r) = -Z/r + (B/r + C)\, e^{-\beta r^2}$$

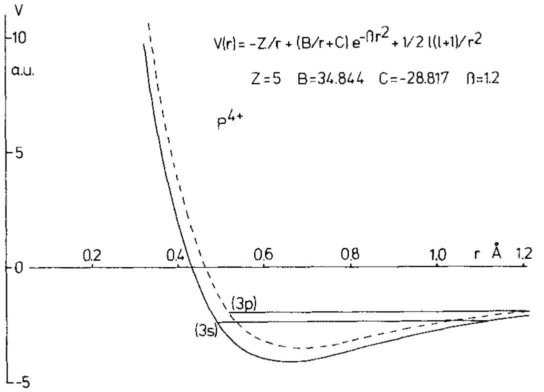

FIGURE 1 Pseudopotential $V(r)$ for the P atom. The parameters are given in atomic units.

Z is the number of valence electrons, while β, B, C are parameters which were calibrated with the aid of experimental ionization energies (here $3s$ and $3p$) of the one-valence-electron atom.[13] The parameters obtained for P^{4+} are shown in Figure 1. The pseudopotential for the s- as well as that for the p-terms together with the corresponding ground states are shown graphically in the same figure. Hartree–Fock–SCF–MO calculations have been performed in the usual way but with inclusion of the atomic one-electron potential $V(r)$.

The radial functions of the pseudo-orbitals ($3s$), ($3p$) which were obtained with the above described method are nodeless. For this reason the well-known *ab initio* basis functions cannot be used in the pseudopotential calculations. The Gaussian basis sets for the pseudo-orbitals of the valence shell were obtained through energy variation on the P atom (^4S).

In this work all basis sets were used uncontracted. The value of 0.35 for the exponent of the d-functions was obtained with the aid of an energy variational calculation on PH_3. The calculations could also be considered as a test for the method, since no general knowledge is available about the usefulness of the currently determined local pseudopotential in molecular calculations. According to our results so far, it seems that the chosen form of the pseudopotential is relatively successful for the M valence shell, while this is not the case for the L valence shell.[14]

TABLE I

Valence-electron energies and Gaussian basis sets for P (^4S)

Basis	E (a.u.)	s-				p-exponents		
$(2s,1p)$	−6.171	1.079	0.256			0.198		
$(3s,2p)$	−6.448	0.779	0.604	0.149		1.950	0.284	
$(4s,3p)$	−6.578	3.583	1.240	0.592	0.164	1.491	0.492	0.145

THE STABILITY OF THE P_4 MOLECULE

The calculation of the stabilization energy of a molecule is connected with the difficulty of finding the difference between two large and almost equal numbers as accurately as possible. In quantum chemical calculations which are based on the LCAO representation of the molecular orbitals, the fragmentation of a molecule results in a fragmentation of the basis set as well. The quality of the bond energies obtained in this way depends, in many cases, on a series of mutually cancelled errors:

1) As a consequence of the separation of a finite basis of functions, the molecular fragments are not as well described energetically as the molecule itself. It follows that the calculated bond energies are too large. This so-called basis superposition defect can be corrected if both the molecule and its fragments are calculated with the same superbasis.

2) The electronic correlation energy is inherently neglected in the one-determinant representation of the wave function of a closed-shell molecule. However, it is larger for the whole molecule than for the sum of the molecular fragments. Consequently, neglecting the correlation energy can lead to bond energies that are too small.

3) The use of polarization functions can be more important for the molecule than for the fragments. Here, two cases can be distinguished: (a) The polarization functions as an improvement of a finite basis set (Example: $2p\sigma$ orbitals in Li_2). (b) The polarization functions required by the symmetry of the molecule (Example: $3d$ orbitals in H_2O for the $1b_1$ orbital). The neglect of polarization functions usually results in excessively small bond energies.

Guest *et al.*[10] attempted to derive theoretically the stability of P_4 against 2 P_2. *Ab initio* calculations using the experimentally derived equilibrium geometry and a minimal STO-3G basis, while neglecting the effects 1 to 3, gave a stabilization energy of 35 kcal/mole. However, this energy lies in the uncertainty region created by the above described effects. The same situation arose when Osman *et al.*[15] using a minimal STO-3G basis for the valence electrons in the frame of a pseudopotential method obtained a stabilization energy of 25 kcal/mole. That these results are accidental can be clearly shown in the case of the presently most sophisticated *ab initio*

TABLE II

Calculated stabilization energies (kcal/mole) of P_4 with respect to 2 P_2 with different basis sets

	Basis separation	Superbasis
(2*s*,1*p*)	96	61
(2*s*,1*p*,1*d*)	119	103
(3*s*,2*p*)	98	11
(3*s*,2*p*,1*d*)	110	58
(4*s*,3*p*)	−2	−23

calculation with a (11*s*,7*p*) basis contracted to (4*s*,3*p*). The result of this calculation was the wrong prediction that P_4 is 42 kcal/mole less stable than 4 P.[11] Semi-empirical INDO calculations yielded an excessively large stabilization energy of 162 kcal/mole.[10] Archibald and Perkins reported CNDO calculations which showed a stabilization for P_4 only after the introduction of 3*d* functions.[16] Unfortunately no quantitative results were given.

In calculating stabilization energies, one should always attempt to approach the Hartree–Fock limit as closely as possible, to enable a subsequent correction of the obtained energies with the correlation energy. However, as the basis sets used must necessarily be finite, additional effects appear which will shortly be discussed.

Table II helps one to realize that the basis superposition effect is of the order of the stabilization energy under investigation for the basis sets used. Because of this effect the introduction of *d* functions in the calculation of P_4 results in a stabilization energy which is again of the order of the measured value. The correlation energy calculated within the framework of the density functional formalism[17] is relatively independent of the employed basis set and should, with 5 kcal/mole, play no important role on the stabilization energy of the P_4 molecule.

Concerning the significance of the *d* functions it should perhaps be emphasized here that the use of an adequately large (*s*,*p*) basis for P_4 could, in principle, obviate the use of *d* functions. It is, however, important to note that P_4 is found to be unstable when it is calculated with medium size (*s*,*p*) basis sets, so that now the addition of *d* functions is more efficient than bigger (*s*,*p*) basis sets. At this point it should be clear that there exists a certain amount of arbitrariness in all stability calculations. By a critical consideration of the results shown in Table II one can conclude that unambiguous theoretical evidence for the stability of P_4 has not yet been offered, although the largest basis set employed so far (3*s*,2*p*,1*d*) reproduces almost exactly the experimental stabilization energy of 55 kcal/mole.

It appears to be simpler, however, to prove the instability of P_8 compared with 2 P_4 rather than the latter's stability against 2 P_2. The electronic structure in a P_8 hexahedron should be energetically more favourable compared with that in a P_4 tetrahedron. The contribution of nuclear repulsion to the total energy in the case of P_8 is much more unfavourable compared with those of P_4. The evidence for the instability of the P_8 molecule arose from calculations carried out with the aid of the small basis set (2*s*,1*p*), which, due to the lack of *d* functions and neglect of the basis superposition effect, brings the P_4 system to an energetical disadvantage. Despite this, the energy of P_8 is 47 kcal/mole higher than that of 2 P_4, when a P–P distance of 2.21 Å is used for both molecules.

The calculated atomic distances in the P_4 molecule show a relationship to the calculated stabilization energies, when different basis sets are employed. A series of (*s*,*p*) basis sets yields an excessively large P–P distance of 2.36 Å,[10,15] while the inclusion of *d* functions results in the shortening of this distance to 2.25 Å. The measured distance is 2.21 Å.

THE PHOTOELECTRON SPECTRUM OF THE P_4 MOLECULE

The photoelectron spectrum of P_4 has been a subject of almost all theoretical investigations of this molecule. These calculations reproduce the orbital sequence; furthermore the three highest orbitals $5a_1$, $6t_2$ and $2e$ deviate energetically from the measured data by less than 1 eV. Table III shows that even with the simplest basis sets and Koopmans' approxi-

TABLE III

Calculated (Koopmans' approximation) and measured vertical ionization energies (eV) of the P_4 molecule

Valence-MO	$4a_1$	$5t_2$	$5a_1$	$6t_2$	$2e$
(2*s*,1*p*)	33.8	22.3	11.9	10.5	9.4
(3*s*,2*p*)	31.1	20.4	12.8	11.0	10.2
(3*s*,2*p*,1*d*)	28.7	19.0	12.6	10.3	8.9
STO-3G[15]	26.0	18.6	10.8	9.8	9.0
STO-3G + *d*[15]	26.1	17.9	11.4	9.8	9.1
STO-3G, *ab initio*[10]	30.3	19.9	11.6	10.4	9.7
(11*s*,7*p*), [4*s*,3*p*] *ab initio*[11]	31.5	21.0	12.5	11.2	10.5
Experiment[11,18]	—	(14–19)	11.9	10.4	9.7

mation, one can obtain good agreement with experimental data. This fact sometimes led to the questionable conclusion that the inclusion of *d* orbitals in the P_4 basis set is generally insignificant.[10,18] Note that in comparing the Koopmans' vertical ionization energies with the measured values, one should refer to the average values because of the Jahn–Teller splitting. These are given in the last row of Table III.

THE ELECTRON DENSITY OF THE P_4 MOLECULE

Since the PPP valence angle is 60°, the electron density, in particular the valence electron density, of the P_4 molecule becomes extremely interesting. Most authors have discussed the so-called bent bonds. Along with the canonical valence orbitals,[11] the localized P—P bonding orbital has been exhibited.[10] The maxima of the electron density were found by Hart *et al.*[19] to be located at the corners of a basic cube not occupied by the P atoms. However, this could have been an artefact resulting from the use of an unrealistic pure (3*p*) basis. Osman *et al.*[15] investigated the effect of 3*d* orbitals on the valence electron density and arrived at the same results with those of this work. In Figure 2 a one-dimensional representation along the molecular axes C_2 and C_3 was chosen in order to present a clearer picture of the electron density within the molecule. Independently of the choice of the basis set, bent bonds were obtained over the P—P edges of the tetrahedron. The electron density decreases along a C_3 axis outside a face of the P_4 tetrahedron. The inclusion of *d* orbitals in the basis set increases the density in the bent bonds that lie above the P—P edges, as well as inside the tetrahedron, while a density decrease is observed in the lone pairs of the P atoms. In brief, the *d* functions exercise a fairly strong influence on the valence electron density.

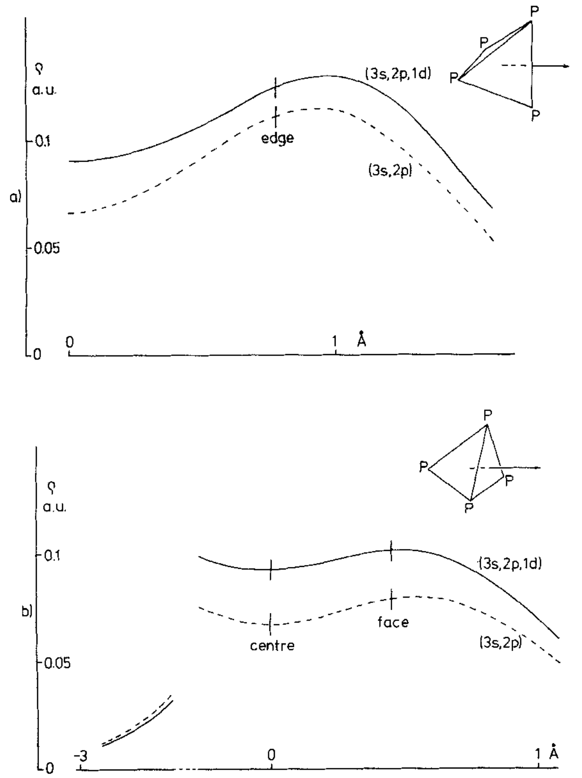

FIGURE 2 Valence electron density in the P_4 tetrahedron with and without *d* orbitals along a (a) C_2 axis and (b) C_3 axis.

THE NUCLEOPHILICITY OF THE P_4 MOLECULE

In order to describe the very complex concept of the nucleophilicity of a molecule, Mulliken's population analysis has been often employed, although hardly any causal relationship between these two concepts exists. Moreover, Mulliken's population analysis fails completely when applied to homoatomic molecules such as P_4.

If under the term nucleophilicity is understood the reactivity of a molecule, represented by a nucleophilic centre B, and a protonic acid HA, then, provided an early transition state exists (see the following sketch), one can assume that the height of the transition state is controlled, to a large degree, by the properties of B. It follows that, in order to discuss the relative reactivities of various molecules among themselves, as well as the regioselectivity of a

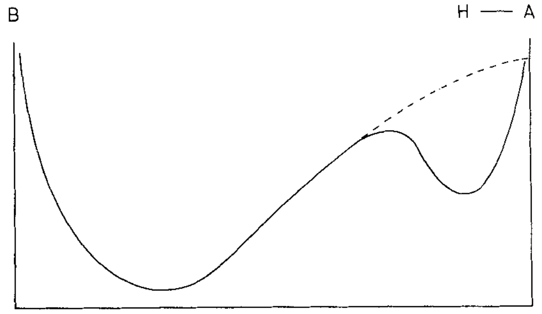

FIGURE 3 Interaction energy of a proton donor–acceptor complex (B · · · · H–A) as a function of the proton position. The dashed line refers to the complex B · · · · H^+.

molecule, the knowledge of the heights of the transition states is not absolutely necessary, and that even just the interaction energies of the systems $B \cdots H^+$ can be considered as a measure of the reactivity (dashed line in Figure 3).

The computational effort for a perturbational calculation of the interaction energies between B and H^+ as a function of position (regioselectivity) is not substantially larger than that needed for a population analysis. The first order perturbation energy represents the electrostatic interaction, which has already been studied for numerous molecules in the form of the molecular potential.[20,21] The most important term in the second order perturbation energy is the polarization energy. The most comfortable way to calculate it is Dalgarno's uncoupled Hartree–Fock formalism.

In the following, four topics are going to be discussed:

1) The regioselectivity of P_4 against H^+.

2) The energy partitioning into electrostatic and polarization contributions.

3) The influence of the *d* orbitals on the nucleophilicity.

4) The multiple protonation of the P_4 molecule.

Investigating the regioselectivity of P_4, three different ways for the proton attack can be distinguished. A proton moving along a C_3 axis can either approach a P atom or, if it moves in the opposite direction, a PPP face. Moving along a C_2 axis, it can attack the centre of a P–P bond. Independent from the inclusion of *d* orbitals the electrostatic potential yields a weakly bound proton, with *ca.* 12 kcal/mole, at an apex of the tetrahedron. According to this finding, one can consider P_4 as relatively inactive with respect to protonation, and therefore comparable to the N_2 molecule. The most important contribution in the interaction energy arises from the polarization of P_4 in the field of the proton. Thus the binding energy (Figure 4, without *d* orbitals) of a proton above the apex of the tetrahedron increases to 80 kcal/mole, above an edge the binding energy lies at 25 kcal/mole (not illustrated) and above a PPP face no bonding exists. The use of *d* orbitals changes substantially the results of the regioselectivity: the protonation of a face, with 80 kcal/mole, becomes now realizable, whereas the bond energies of a proton above an apex or an edge of the tetrahedron increase to 100 and 60 kcal/mole, respectively. It is therefore reasonable to suppose that a proton could penetrate the face and come inside the tetrahedron. This hypothesis is also supported by the fact that in the perturbational calculations a rigid P_4 molecule was involved which does not favour energetically the configuration of "proton in the centre". For this reason a relaxation of the P–P distance is advisable. Taking this possibility into account the P–P bond length increases by 0.13 Å and the valence electron energy decreases by 21 kcal/mole. Without taking these numbers as too serious, one can infer that, because of an external protonation at a P atom, an internal protonation through a face cannot be excluded energetically, especially due to the fact that the proton in the centre of the tetrahedron is stabilized by an energy barrier height of 5 kcal/mole. Attempts are in progress to isolate P_4H^+ in the form of salts.

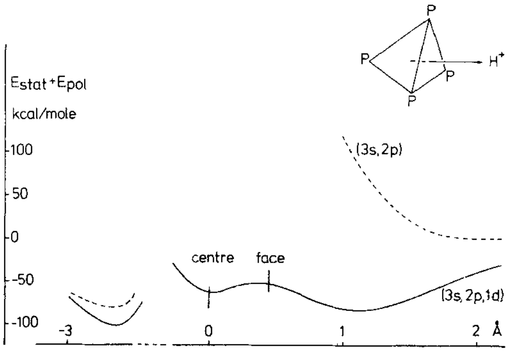

FIGURE 4 Perturbative interaction of the $P_4 \cdots H^+$ complex in the C_{3v} symmetry with and without *d* orbitals.

Comparing the electron density with the interaction energy above an apex of the tetrahedron, it can be seen that the *d* orbitals reduce the density of the lone pairs and increase the interaction energy. Consequently it can be concluded that in P_4 the lone pair of a P atom does not constitute a nucleophilic centre, but that the total electron density inside the tetrahedron forms a unique nucleophilic centre. This idea can find additional support by investigating eventual multiprotonation of the P_4 molecule.

In the multiprotonation study of the P_4 molecule the $P–H^+$ distance was taken from Figure 4 to be 1.29 Å. Moreover, the simplifying assumption was made that all protonations can take place above a tetrahedral apex and that the tetrahedron retains its form. The P_4 molecule can be protonated essentially only once. The corresponding calculated proton affinity, 155 kcal/mole, is comparably low. The $P_4H_2^{++}$ system is still stable by 20 kcal/mole, while all other higher protonated systems are unstable.

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