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Ionization Potentials of the Tetraphosphorus Molecule

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The He(I) and He(II) photoelectron spectra of the P_4 molecule have been recorded and compared with the results of an *ab initio* calculation of the electronic structure using s- and p-type Gaussian orbital basis functions. The agreement for the first three ionization potentials is excellent and is taken to show that in a sufficiently good s,p basis, there is no need for 3d AO's, contrary to the claims of others. The "σ" bonds are unavoidably bent in a description which does not use (or need) 3d AO's. The first, second, and fourth ionizations show appreciable Jahn–Teller splitting, but vibrational structure is observed only in the third ionization ($^2A_1$, ν_1' excited). The optical spectrum of P_4 can be explained using configuration interaction among the valence-shell $^1T_2$ configurations, and the low oscillator strengths of certain bands are shown to result from strong mixing among allowed transitions, rather than from symmetry restrictions. Electron density plots of the valence-shell MO's are also presented.

Because of its tetrahedral geometry, the white allotrope of elemental phosphorus, P_4, has an extremely perplexing and contentious electronic structure. In the ground state of the phosphorus atom there are three electrons in the 3p AO's which can be used in the construction of trivalent compounds of the sort PX_3, having X–P–X angles only slightly larger than 90°. On the other hand, the P–P–P angles in tetrahedral P_4 are 60°, implying that the bonding orbitals are bent, *i.e.*, do not lie maximally along the lines connecting the nuclei. Hart, *et al.*,[2] also showed within this framework of bent bonds that there is a considerable deviation from perfect pairing in the valence-bond sense, with structures having double and triple bonds between phosphorus atoms also contributing to the ground state. The unorthodoxy of the bent bonds in P_4 necessitated by the 90° angles between 3p AO's on each atom can be exorcised in theory by hybridizing with large amounts of 3s and 3d AO's,[3] but Pauling and Simonetta[4] convincingly pointed out that the large atomic promotion energies will allow only a miniscule mixing of 3s and 3d with 3p. In line with this, Hart, *et al.*, were able to give a reasonable account of the optical spectrum of P_4 using a semiempirical calculation which completely neglected 3s and 3d orbitals in both the ground and excited states.

In the most recent round of this dispute, Van Wazer and Letcher[5] still argued for valence hybrids containing no 3s but having 4 times as much 3d as 3p in them(!), in order to explain the very large chemical shift of +450 ppm observed for P_4, and Archibald and Perkins[6] calculated that significant admixtures of 3d AO's stabilize the ground state of the P_4 molecule with respect to $2P_2$ but cannot so stabilize N_4 with respect to $2N_2$. In reply to the contentions of the semiempirical calculations of Archibald and Perkins, Hillier and Saunders[7] presented the results of *ab initio* calculations *sans* 3d AO's, which nonetheless predict that P_4 is stable, but N_4 is not.

In the present work, we report the results of an all-electron, *ab initio* calculation on P_4 which far eclipses the previous calculations as regards the quality of the basis set, accuracy of integral evaluation, and total energy. Most importantly, we have also determined the He(I) and He(II) high-resolution photoelectron spectra of P_4; *via* Koopmans' theorem, these experimental results are related to the calculated orbital energies in a most intimate way and offer an excellent test of the validity of the proposed ground-state wave function.

Experimental Section

The He(I) and He(II) photoelectron spectra of P_4 were obtained using an instrument employing a single-focusing 127° electrostatic analyzer.[8-10] The P_4 was bulb-to-bulb distilled under vacuum and was obtained as colorless crystals which slowly yellowed in room light. As mentioned previously,[9] the fraction of α-He(II) radiation (40.83 eV) present in our discharge lamp is only about 2–3% that of the α-He(I) (21.22 eV), and, therefore, the worth of the α-He(II) spectrum is limited by its weakness and interference from background ionization of helium which reaches the target chamber and is ionized by α-He(II), by small amounts of higher He(II) lines, and by overlapping with the strong He(I) spectrum at high ionization potential. Also, the low electron flux generated in the He(II) spectrum forces us to use wider analyzer slit widths, so that the resolution in the He(II) spectrum is far poorer than the normal value of 0.030 eV experienced using He(I) excitation. The He(I) and He(II) spectra are shown in Figures 1 and 2a, and vibronic details of the first three bands are shown in Figures 3 and 4. In this particular case, the apparently low ionization cross section of P_4 results in a very weak He(II) spectrum, and

TABLE I

IONIZATION POTENTIALS OF P_4

	IP, eV		
Orbital	Adiabatic	Vertical	Calcd
2e	9.2 (0)	9.5 (6)	9.627
	. . .	9.9 (2)	
$6t_2$	10.2 (0)	10.4 (2)	10.261
	. . .	10.6 (1)	
$5a_1$	11.80 (7)[a]	11.87 (4)	11.458
$5t_2$	*Ca.* 14.2	15.2 (5)	19.323
	. . .	16.3 (5)	
	. . .	*Ca.* 17.5	

[a] The adiabatic ionization potential is taken at the center of the 0–0 transition.

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[1] (a) Bell Telephone Laboratories. (b) Ford Motor Co.

[2] R. R. Hart, M. B. Robin, and N. A. Kuebler, *J. Chem. Phys.*, **42**, 3631 (1965).

[3] (a) J. R. Arnold, *ibid.*, **14**, 351 (1946); (b) M. Mashima, *ibid.*, **20**, 801 (1952).

[4] L. Pauling and M. Simonetta, *ibid.*, **20**, 29 (1952).

[5] M. M. Crutchfield, C. H. Dungan, J. H. Letcher, V. Mark, and J. R. Van Wazer, "P^{31} Nuclear Magnetic Resonance," Interscience, New York, N. Y., 1967, p 183.

[6] R. M. Archibald and P. G. Perkins, *Chem. Commun.*, 569 (1970).

[7] I. H. Hillier and V. R. Saunders, *ibid.*, 1233 (1970).

[8] D. W. Turner, *Proc. Roy. Soc. Ser. A*, **307**, 15 (1968).

[9] C. R. Brundle, M. B. Robin, and G. R. Jones, *J. Chem. Phys.*, **52**, 3383 (1970).

[10] C. R. Brundle and M. B. Robin in "Determinations of Organic Structures by Physical Methods," F. Nachod and G. Zuckerman, Ed., Academic Press, New York, N. Y., 1971.

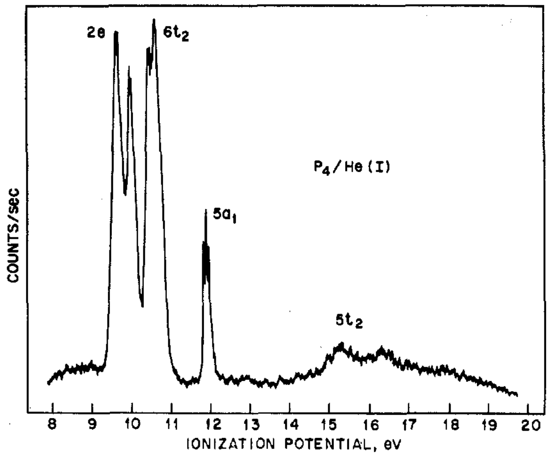

Figure 1.—The photoelectron spectrum of P_4 vapor using He(I) excitation.

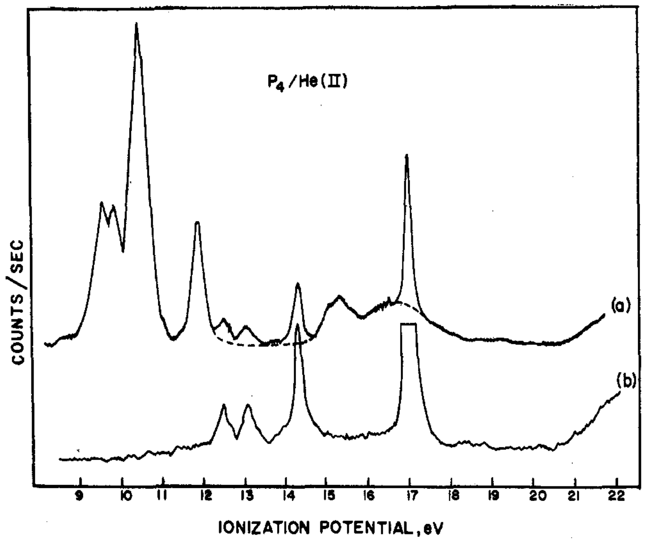

Figure 2.—(a) The He(II) spectrum of P_4 vapor. (b) Photoelectron signal using He(II) excitation but without sample in the target chamber.

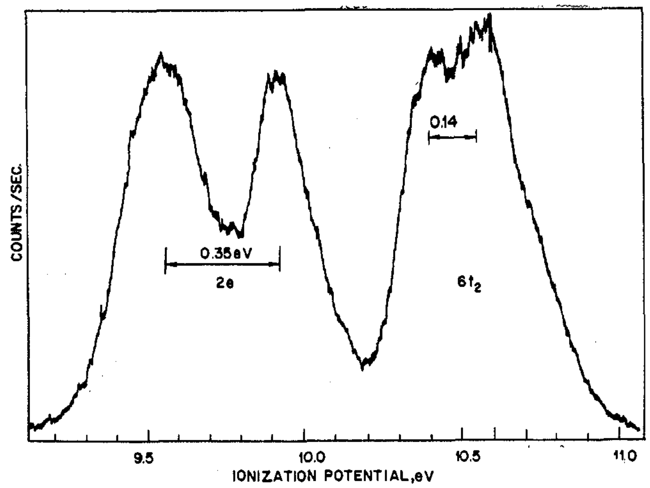

Figure 3.—Details of the 2e and $6t_2$ photoelectron bands of P_4 vapor.

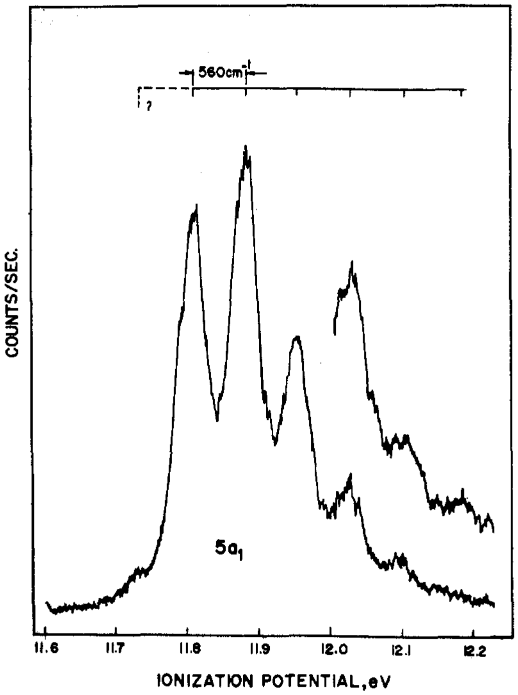

Figure 4.—Details of the $5a_1$ photoelectron band of P_4 vapor.

accordingly no additional data were obtained above 21 eV. Consequent photoelectron work with phosphorus-containing compounds has shown that phosphorus AO photoionizations have an extremely low cross section for He(II) radiation. From the He(II) background spectrum (Figure 2b) the helium ionization peaks caused by the well-known He(II) lines at 256, 243, 237, and 234 Å (giving apparent ionization potentials of 17.0, 14.35, 13.05, and 12.45 eV) can be observed.[11] The adiabatic and vertical ionization potentials of P_4 are listed in Table I.

Theoretical Techniques

The calculation was performed using a Gaussian-type orbital (GTO) basis set having s- and p-type components only, Table II. The fixed linear combinations of GTO's which comprise the basis set (called GTF's) were determined in an SCF calculation of the ^4S phosphorus atom by means of a procedure described previously,[12] which optimizes both the exponents and the contraction coefficients of the GTF's. The total atomic energy in this basis set is −340.5177 au, which is to be compared with the Hartree–Fock value of −340.6301 au.[13] Note that the basis set is constructed so as to provide a single-ζ representation of the core AO's but a double-ζ description of the 3s and 3p va-

TABLE II

GAUSSIAN ORBITAL COEFFICIENTS (AND EXPONENTS) USED FOR THE PHOSPHORUS AO's

	s Type
1s	0.006366(7130.0) + 0.047861(1078.0) + 0.210484(241.80) + 0.492967(68.820) + 0.386465(21.800)
2s	−0.097710(37.30) + 0.413918(5.0250) + 0.659632 (1.930)
3s	−0.289906(2.1050) + 1.132966(0.32290)
3s′	1.000000(0.12020)
	p Type
2p	0.040484(90.560) + 0.206499(21.30) + 0.447974 (6.9730) + 0.494893(2.3130)
3p	0.392414(0.65070) + 0.662306(0.26520)
3p′	1.000000(0.0990)

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[11] J. A. R. Samson, "Techniques of Vacuum Ultraviolet Spectroscopy," Wiley, New York, N. Y., 1967.

[12] H. Basch, C. J. Hornback, and J. W. Moskowitz, *J. Chem. Phys.*, **51**, 1311 (1969).

[13] E. Clementi, *IBM J. Res. Develop., Suppl.*, **9**, 2 (1965).

lence AO's. As usual, the known molecular dimensions were used in the calculation on P_4 (r_{P-P} = 2.21 Å),[14] and the orbitals are labeled according to the representations of the T_d point group. The self-consistent field solution yielded a total energy of −1362.0041 au, a figure considerably below that of Hillier and Saunders (−1348.0794 au) whose basis set was only of single-ζ quality but above that computed for four noninteracting phosphorus atoms, −1362.0709 au. This apparent lack of atomic binding in the P_4 molecule is in part due to the fact that the basis set is optimum for the atom but not necessarily so for the molecule. Also, as is known to be the case in the F_2 molecule, a considerable fraction of the binding energy in P_4 might be due to correlation effects which are not accounted for in a calculation of the type described here.

The occupied orbital energies are listed in Table III together with the same values empirically reduced by 8%. In several past studies of this sort,[15] the 8% reduction was found to be a near-universal correction necessary to bring the computed orbital energies and the vertical ionization potentials into agreement. Its use, of course, is purely aesthetic in general, for it does not change the predicted ordering or assignments of the MO's.

TABLE III

CALCULATED GROUND-STATE ORBITAL ENERGIES IN P_4

Orbital	Energy, au	Calcd IP,[a] eV
$1a_1$	−79.9810	2002.18
$1t_2$	−79.9810	2002.18
$2a_1$	−7.5571	189.17
$2t_2$	−7.5568	189.17
$3a_1$	−5.4473	136.36
$3t_2$	−5.4470	136.36
1e	−5.4435	136.26
$1t_1$	−5.4435	136.26
$4t_2$	−5.4434	136.26
$4a_1$	−1.1575	28.976
$5t_2$	−0.7719	19.323
$5a_1$	−0.4577	11.458
$6t_2$	−0.4099	10.261
2e	−0.3846	9.627
$2t_1$	+0.0612	
$7t_2$	+0.0657	

[a] 92% of Koopmans' theorem.

Results

According to the ground-state calculation, Table III, removal of an electron from the uppermost filled orbital of P_4 leaves the ion in a degenerate ^2E state which is Jahn–Teller unstable; this is evidenced by the quite large (0.35 eV) splitting of the ground state of the ion observed in the first band in the spectrum (Figure 3). No vibrational structure is observed on either component of this band. The mean vertical ionization potential of the two Jahn–Teller components (9.74 eV) is given quite accurately by 92% of the calculated orbital energy (9.627 eV). An adiabatic ionization potential of 9.2 (0) eV can be estimated from our spectrum. In an earlier photoionization study, Watanabe found an ionization threshold of 9.08 ± 0.05 eV,[16] and the optical spectrum of P_4 vapor shows the onset of continuous absorption at about 8.9 eV.[2] Group theoretically, the Jahn–Teller distorted configurations in the ^2E state are achieved *via* motion along the e normal coordinates, and spin–orbit coupling is not a factor here, since the electronic angular momentum is zero in a ^2E state.

Removal of an electron from the second highest orbital, $6t_2$, leaves the ion in a degenerate $^2T_2$ state, which is also susceptible to Jahn–Teller effects (compare with the $^2T_2$ ground state of CH_4^+).[17] The splitting of the $^2T_2$ state is much less than for the ground ionic state, but the two Jahn–Teller components (A and E) are nonetheless still observable. There is no evidence for further splitting of the E state, as there was for methane, unless the third component appears as the barely noticeable feature at 10.60 eV. In any event, the relative intensities within the $6t_2$ band suggest that the peak at 10.36 eV is the ^2A component, and that at 10.52 eV is the ^2E component. Koopmans' theorem again does a good job of predicting the $6t_2$ ionization potential (10.261 eV, predicted; 10.44 eV, observed), as it does for the next orbital, $5a_1$.

The photoelectron band corresponding to the removal of the $5a_1$ electron at 11.87 (4) eV (Figure 4) exhibits a short, well-resolved vibrational series. The spacing of *ca.* 560 cm^{-1} may be compared with the ground-state frequencies of 606 (a_1), 465 (t_2), and 363 cm^{-1} (e).[18] Clearly, the totally symmetric stretch is being excited here, as expected if the ionization proceeds from a nondegenerate orbital and leaves the resulting ion with T_d symmetry. The small change in vibrational frequency, the brevity of the vibrational progression, and the intense origin all argue that the $5a_1$ MO is a relatively nonbonding one. In qualitative support of this, the overlap populations in the 2e and $6t_2$ MO's are calculated to be 0.0398 and 0.0576, respectively, whereas that for the $5a_1$ MO is only 0.0029. Though the origin for the $5a_1$ ionization is taken as 11.80 (7) eV, a weak shoulder is observed at about 11.73 eV. In spite of the fact that it has the proper frequency to be a member of the vibrational progression in the excited state, on the basis of its very low intensity relative to its neighbors in the spectrum it is more likely assigned as a hot band. Most importantly, the $5a_1$ ionization potential predicted by the application of Koopmans' theorem (11.458 eV) is in good agreement with the experimental value of 11.87 (4) eV.

Perhaps the easiest band in the photoelectron spectrum to identify should be the ionization from the $5t_2$ MO, for the nearest band on either side is predicted to be at least 8 eV removed, Table III. Thus the two or possibly three broad bands in the region 14–19 eV, split by approximately 2 eV, are taken to represent a very strong Jahn–Teller interaction in the $^2T_2$ state resulting from removal of an electron from the $5t_2$ orbital. In keeping with such a large Jahn–Teller distortion, a large (antibonding) overlap population of −0.3093 is calculated for the $5t_2$ MO's. The atomic populations show $5t_2$ to be composed overwhelmingly of 3s AO's, whereas the six higher MO's are composed largely of 3p AO's. Curiously, the excellent agreement between theoretical and experimental ionization energies which character-

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(14) L. R. Maxwell, J. B. Hendricks, and V. M. Mosely, *J. Chem. Phys.*, **3**, 699 (1935).

(15) See, for example, H. Basch, M. B. Robin, N. A. Kuebler, C. Baker, and D. W. Turner, *ibid.*, **51**, 52 (1969).

(16) K. Watanabe, quoted in ref 2.

(17) C. R. Brundle, M. B. Robin, and H. Basch, *J. Chem. Phys.*, **53**, 2196 (1970).

(18) H. S. Gutowsky and C. J. Hoffman, *J. Amer. Chem. Soc.*, **72**, 5751 (1950).

izes the first three transitions is no longer present in the case of the $5t_2$ ionization, for it is predicted to come at 19.32 eV. Of the various explanations one can advance, the most likely seems to be that in the case of $5t_2$, the reorganization energy correction is much larger than usual and swamps the opposing correlation energy correction, though it cannot be said why this should be so. A similar discrepancy has been noted for the deepest valence-shell MO's in XeF_2, XeF_4, and XeF_6,[19] and it has been tentatively suggested[20] that the situation in these molecules is complicated by bands due to simultaneous ionization and electronic excitation of the ion.[21] As applied to P_4, one would argue that the bands at 15.2, 16.3, and *ca.* 17.5 eV are due to simultaneous ionization and excitation within the 2e, $2t_1$ set of MO's, while the $5t_2$ ionization is present as a weak feature in the vicinity of 19 eV. Since the spectra are rather poor in the 19-eV region, it is possible that such a transition could go undetected, but it seems unlikely that this is the source of our problem with the $5t_2$ ionization. As regards the true position of the $5t_2$ ionization potential, it is interesting to note that Issleib and Gründler[22] performed a far less sophisticated calculation on P_4 and found that the $5t_2$ MO came at 16.76 eV, in good agreement with the center of gravity of our experimental values.

The intensities of the bands in the P_4 spectrum merit some comment. From the He(I) spectrum it is quite apparent that there is little correlation between intensities and orbital degeneracies. The 2e and $6t_2$ bands are of approximately equal intensities, and the $5t_2$ band, even after a correction for discrimination of the analyzer against low-energy electrons,[9] is less intense than either of these. The $5a_1$ band is the weakest in the spectrum, however, as might be expected for ionization from a nondegenerate orbital. On going to the He(II) spectrum, the intensity ratios change somewhat and are more in accord with the orbital degeneracies, with the 2e, $5a_1$, and $5t_2$ bands being approximately in the ratio 2:1:3 but with $6t_2$ now being too intense. Such marked changes in intensity ratios have been noticed previously.[10,17]

Having better wave functions at hand, we have briefly reinvestigated the predicted optical spectrum of P_4, with results substantially in agreement with those of ref 2. Since the only allowed transition from the ground state of P_4 is ${}^1A_1 \rightarrow {}^1T_2$, the ${}^1T_2$ excited state manifold has been mixed using interaction among the five lowest energy configurations generated by all possible one-electron promotions among the MO's made primarily of 3p AO's. By Brillouin's theorem, the SCF ground state has mixed into it all one-electron excitations of the proper symmetry. Therefore it was hoped that the ground and lowest ${}^1T_2$ excited states could be placed on an equivalent footing by doing single-excitation configuration interaction on the ${}^1T_2$ excited-state manifold. The configuration mixing proved to be very strong, and as a result the original configurations are thoroughly mixed in the final states. Under such conditions, the calculated oscillator strengths will be very dependent upon the mixing coefficients, while the energy is less so. Thus it is felt that the calculated dipole-length oscillator strengths are of qualitative value at best and should not be taken too seriously. The predicted spectral quantities are compared in Table IV with the experimental quantities taken from Figures 2–4 of ref 2.

TABLE IV

CALCULATED AND OBSERVED OPTICAL TRANSITIONS IN P_4

	Calcd		Obsd	
Excited-state symmetry	Energy, eV	Oscillator strength	Energy, eV	Oscillator strength
${}^1T_2$	5.72	0.505	5.6	0.13
${}^1T_2$	6.53	0.0096	6.3	0.13
${}^1T_2$	7.00	1.297	7.1	1.30
${}^1T_2$	8.53	0.518	8.40	0.40
$2e \rightarrow 3d$ (${}^1T_2$)	. . .	. . .	7.8–8.1	*Ca.* 1.7

The two lowest allowed transitions in P_4 are predicted to come at 5.72 and 6.53 eV. Experimentally, two vertical excitations are observed at 5.6 and 6.3 eV, each with an oscillator strength of 0.13. It seems clear that the 5.6-eV band is the first of the ${}^1A_1 \rightarrow {}^1T_2$ excitations, but the 6.3-eV band could equally well be assigned as the weakly allowed ${}^1A_1 \rightarrow {}^1T_2$ or perhaps a low-lying forbidden ${}^1A_1 \rightarrow {}^1T_1$ excitation having an intensity enhanced by vibronic effects. The strong configurational mixing in the ${}^1T_2$ block shifts intensity out of the first two transitions and into the third ${}^1A_1 \rightarrow {}^1T_2$ transition, predicted to come at 7.00 eV with an oscillator strength of 1.297. There can be no doubt that this is associated with the strong feature ($f = 1.3$) observed at 7.1 eV. The fourth ${}^1A_1 \rightarrow {}^1T_2$ band (8.53 eV) would seem to match up with the band of moderate intensity situated at 8.40 eV. This assignment scheme offers no explanation for the very strong complex of bands ($f =$ *ca.* 1.7) between 7.6 and 8.2 eV. Our tentative explanation here is that these bands correspond to the allowed parts of the $2e \rightarrow 3d$ Rydberg system. Comparison of the spectra of several phosphine compounds and that of the phosphorus atom reveals that the term value of the $3p \rightarrow 3d$ excitation is rather constant at 1.5–1.9 eV in these materials, while combination of the photoelectron and optical spectra yields a term value of 1.7 eV for the absorption band at 7.8 eV in P_4. Though we make no claims for these assignments as irrefutable, it does seem that the optical spectrum of P_4 can be explained by just considering excitations to ${}^1T_2$ upper states.

Discussion

The SCF calculations and Koopmans' theorem satisfactorily reproduce the first three valence-shell ionization potentials but give too high a value for the fourth ionization potential. This is a great improvement over the earlier calculation done using a pure 3p AO basis set,[2] which gave a first ionization potential of 17.05 eV. However, it should be noted that the earlier calculation placed the first three ionization potentials in their proper order and within 2 eV of one another, as observed. From the generally good agreement between the photoelectron spectra and the GTO calculation, we conclude that 3d orbitals do not play any significant role in the ground-state wave function of P_4. Our earlier work based solely on the optical spectrum

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(19) C. R. Brundle, G. R. Jones, and H. Basch, *J. Chem. Phys.*, **55**, 1098 (1971).

(20) H. Basch, J. W. Moskowitz, C. Hollister, and D. Hankin, *ibid.*, **55**, 1922 (1971).

(21) J. C. Lorquet and C. Cadet, *Chem. Phys. Lett.*, **6**, 198 (1970).

(22) K. Issleib and W. Gründler, *Theoret. Chim. Acta*, **11**, 107 (1968).

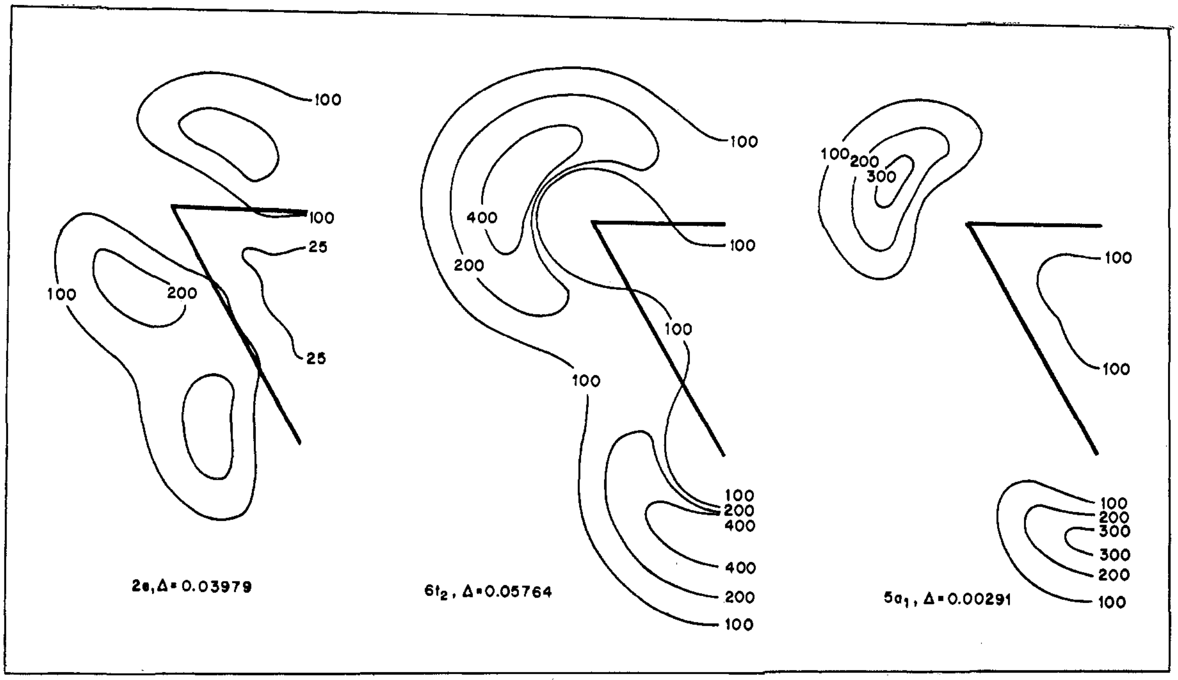

Figure 5.—Electron density contours ($e/a_0^3 \times 10^4$) and overlap populations (Δ) for the 2e, $6t_2$, and $5a_1$ MO's of P_4. The high electron density close to each nucleus has been omitted.

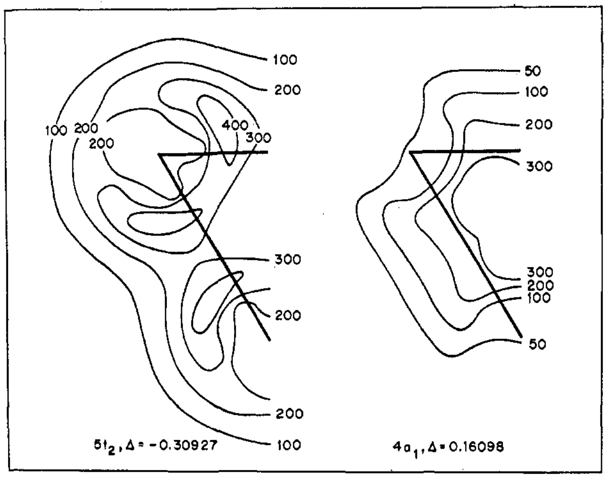

Figure 6.—Electron density contours ($e/a_0^3 \times 10^4$) and overlap populations (Δ) for the $5t_2$ and $4a_1$ MO's of P_4. The high electron density close to each nucleus has been omitted.

led to the same conclusion, though the evidence there was not as convincing. Perhaps it is worth emphasizing that though the agreement between experiment and theory was forced by the empirical reduction of the calculated values, this factor of 8% is universally appropriate for GTO calculations on molecules such as ethylene, formamide, butadiene, etc., the ground state MO's of which contain no significant amounts of 3d AO's. In its way, the calculation of the optical spectrum and its unusually good agreement with experiment also can be taken as reinforcing our primary conclusion that an adequate ground-state wave function for P_4 can be constructed without the explicit inclusion of 3d AO's. Though the apparent disagreement with the $5t_2$ ionization potential casts a shadow on our work, it must be remembered that the $5t_2$ MO is essentially made up of 3s AO's and that the 3s–3d interval in the phosphorus atom is about 18 eV. Therefore, it is highly unlikely that the discrepancy can be linked to the lack of 3d AO's in our basis set.

Another fact of consequence to the discussion of the role of d orbitals in phosphorus-containing molecules was uncovered in Lipscomb and coworkers' theoretical study of PH_3. In that molecule, 3d AO's were prominent in the ground-state wave function when calculated in a single-ζ basis, but when the quality of the 3p functions was improved as in a double-ζ basis, the need for 3d AO's to achieve a comparable accuracy and total energy was diminished. This point should be kept in mind whenever low-quality calculations are discussed.

It is interesting to note that the 3s and 3p AO's are not mixed very strongly in P_4, as anticipated from the 3s–3p energy difference. However, that is not to say that the 3s AO's are not involved in the bonding, for the overlap populations in the essentially 3s MO's, $4a_1$ and $5t_2$, are strongly bonding (+0.1610) and antibonding (−0.3093), respectively, rather than nonbonding as usually assumed for phosphorus lone pairs. Since we cannot assess either the net effect on the molecular binding energy of the $4a_1$ bonding and the $5t_2$ antibonding orbitals or of the correlation energy errors, it would be premature to attribute the bonding in P_4 to the weakly bonding interactions in the 2e, $6t_2$, and $5a_1$ MO's. One interesting possibility is that the oriented 3p AO's do not form bonds of any significant strength in the disadvantageous geometry of P_4 but that the omnidirectional 3s AO's can do so and are responsible (in part) for the stability of P_4.

Plots of the valence shell MO electron densities are of interest in regard to the question of bent bonds in the P_4 molecule. In Figures 5 and 6, the electron densities ($e/a_0^3 \times 10^4$) are plotted in a plane containing a triangular face of the tetrahedron; the high and rapidly varying electron density closely surrounding each nucleus has been omitted in these drawings. One sees immediately that $5a_1$ is truly a nonbonding MO, whereas the $6t_2$ and 2e MO's have a moderate electron density between the atoms. This density, however, along a P–P line is far from symmetric side to side, as expected for bent bonds. The $4a_1$ MO is the electron density complement of $5a_1$, being bonding along the P–P line, with a low density behind the vertices and a high density *within* the triangular face. Thus, as with cyclopropane, the various MO's are bent both outward and inward. The strong antibonding character of the $5t_2$ MO is evident as a trough at midpoint. It is hoped that these contours might be of future value in understanding the chemistry of the P_4 molecule, for example, in elucidating the recently discovered bonding of molecular P_4 in various rhodium complexes.[23]

Acknowledgment.—It is a pleasure to acknowledge the contribution of Miss Mary Dolan, who calculated the electron densities.

[23] A. P. Ginsberg and W. E. Lindsell, *J. Amer. Chem. Soc.*, **93**, 2082 (1971).

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A Nuclear Magnetic Resonance Investigation of the Bonding in Fourth-Group Phenylphosphines[1]

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The compounds $(CH_3)_3MPHC_6H_5$ where M = C, Si, and Sn have been synthesized, and $J(^{31}P-^{1}H)$ values recorded. Infrared assignments in the region 4000–400 cm^{-1} are also presented. Controlled oxidation of the tin compound yields $(CH_3)_3SnOPHC_6H_5$ as established by ^{31}P couplings which also give information concerning the exchange of groups at phosphorus in mixtures of the two tin compounds. The one-bond $^{31}P-^{1}H$ couplings have been interpreted in terms of a pyramidal arrangement of bonds at phosphorus.

We have been engaged for some time in investigations designed to test the hypothesis of $(p \rightarrow d)\pi$ contributions to the bonds formed between nitrogen and the fourth-group elements silicon, germanium, and tin. We have reported the results of nmr studies on derivatives of aniline-^{15}N containing these elements where $J(^{15}N-^{1}H)$ values were measured and interpreted in terms of the stereochemistry and bonding at nitrogen.[2,3] In this paper we extend the treatment to phosphorus.

Experimental Section

Apparatus.—The nmr data were obtained on a Varian HA-100D spectrometer using a benzene lock in the frequency sweep mode. Infrared spectra were recorded as liquid films on a Beckman IR-12 instrument and calibrated with polystyrene.

Syntheses.—All manipulations were carried out under an inert atmosphere of nitrogen or argon in a Vacuum Atmospheres Corp. glove box equipped with a Model HE-193-1 Dri-Train. Boiling points are uncorrected.

***tert*-Butylphenylphosphine (I).**—Phenyldichlorophosphine (0.05 mol) in methylene chloride (4 ml) was added with stirring during 45 min to freshly sublimed aluminum chloride (6.7 g, 0.05 mol) in methylene chloride (10 ml). After a further 45 min the solution was cooled to 10° and *tert*-butyl chloride (5.8 g, 0.062 mol) was added during 1 hr. The solution was then added to chloroform (25 ml) and poured into concentrated hydrochloric acid (16 ml) and crushed ice (50 g). The aqueous layer was separated and extracted with chloroform (two 5-ml portions) and the solvent was removed under reduced pressure from the combined organic layer. The crude *tert*-butylphenylphosphinic chloride was not purified further but was reduced using lithium aluminum hydride in ether to *tert*-butylphenylphosphine (bp 110–113° (16 mm); 5.95 g, 72% yield). *Anal.* Calcd for $C_{10}H_{15}P$: C, 72.27; H, 9.05. Found: C, 71.41; H, 8.77.

Trimethylsilylphenylphosphine (II).—*n*-Butyllithium (31.3 ml, 1.6 *M* in hexane, 0.05 mol) was added dropwise with stirring to phenylphosphine (5.5 g, 0.05 mol) in ether (50 ml) to form the pale yellow monolithiophosphine. Trimethylchlorosilane (5.5 g, 0.05 mol) in ether (20 ml) was added dropwise. The yellow color was discharged, and lithium chloride precipitated and was filtered. Solvents were then removed under reduced pressure, and the residue was distilled trap to trap (room temperature to 77°K at 0.1 mm) to yield trimethylsilylphenylphosphine as a mobile, colorless liquid (4.1 g, 45%). *Anal.* Calcd for $C_9H_{15}PSi$: Si, 15.8. Found: Si, 15.2. The product is very sensitive to atmospheric moisture and oxygen.

Trimethylgermylphenylphosphine (III) was prepared according to the published method.[4]

Trimethylstannylphenylphosphine (IV).—*n*-Butyllithium (31.3 ml, 1.6 *M* in hexane, 0.05 mol) was added dropwise with stirring to phenylphosphine (5.5 g, 0.05 mol) in dry ether (50 ml) to form the monolithiophosphine. Trimethyltin chloride (10 g, 0.05 mol) in tetrahydrofuran (30 ml) was added over 0.5 hr with stirring. The yellow color of the lithiophosphine was discharged, and lithium chloride precipitated and was filtered. The solvent was removed under reduced pressure and the residue was carefully distilled to yield trimethylstannylphenylphosphine as a very moisture- and oxygen-sensitive, mobile, colorless liquid (bp 38° (0.1 mm); 3.1 g, 22.7%). *Anal.* Calcd for $C_9H_{15}PSn$: C, 39.6; H, 5.5; Sn, 43.5. Found: C, 38.9; H, 5.1; Sn, 43.0.

Trimethylstannoxyphenylphosphine (V) was made by controlled oxidation of IV in the drybox.

Results and Discussion

The carbon, silicon, and tin derivatives of phenylphosphine are new compounds. The *tert*-butyl group was attached to phosphorus by the method of Crofts and Parker[5] as shown in eq 1. The reaction of *tert*-butyl chloride with the monolithium derivative of phenylphosphine yields mainly *sec*-butane,

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[1] A preliminary account of this work has appeared: P. G. Harrison, S. E. Ulrich, and J. J. Zuckerman, *J. Amer. Chem. Soc.*, **93**, 2307 (1971).

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