for the rotational constant of water.[32] The rotational constants for methanol and dimethyl ether are calculated from the structures assuming that bond angles about carbon and oxygen are tetrahedral and using bond lengths (in Å) of 0.956 for O–H, 1.43 for C–O, and 1.10 for C–H.[33] The final set of parameters used for these species is summarized in Table II.

Protonated Species. Vibrational frequencies for $CH_3OH_2^+$ and $(CH_3)_2OH^+$ are taken to be those of the nonprotonated neutrals with three additional frequencies added to account for the proton (one stretch and two bends). Rotational constants are calculated from the structures assuming 120° bond angles (planar) about oxygen[34] and taking the O–H bond length to be 1.0 Å, and assuming that the rest of the structure is the same as that of CH_3 neutral. The final parameters used are summarized in Table III.

Proton-Bound Polymers. There are three polymers to consider: $(CH_3OH)_2H^+$, $(CH_3OH)_3H^+$, and $[CH_3OH][(CH_3)_2O]H^+$. In each case it is assumed that each of the neutral ligands retains its vibrational frequencies in the polymer. Each of the dimers has one internal rotation, and the trimer has three internal rotations for which the rotational constants can be calculated from the structures. This leaves nine vibrational modes in each dimer and twelve vibrational modes in the trimer for which the frequencies are not well known. Some of these can be estimated by comparison with other species, but for some modes it is difficult to obtain any reliable estimate of the frequencies. These are chosen so that the resulting value of ΔS calculated from statistical thermodynamics for the association reaction of interest agrees with the experimental value.[27b] Rotational constants for the polymers are calculated by assuming that the bond angles about oxygen are 120° and that the O–H$^+$–O bond angles are 180° in the dimers and 120° in the timer, and taking the O–H$^+$ bond lengths to be 1.2 Å. The parameters are summarized in Table IV.

Transition States. There are three orbiting transition states to consider: $CH_3OH_2^+ + CH_3OH$; $(CH_3OH)_2H^+ + CH_3OH$; and $(CH_3)_2OH^+ + CH_3OH$. In each case the parameters for the separated fragments are obtained as explained above for each species. The zero-point energy differences, E_0, as shown in Figures 1 to 3, are taken to be equal to the ΔH values, which are available in the literature.[27b]

The only tight transition state in this work is that for water loss from the proton-bound methanol dimer. The structure and properties of this transition state are essentially unknown, as discussed in the text. Regardless of the exact structure, a number of vibrational frequencies can be estimated from those of the methyl group and methanol molecule. The remaining frequencies, as well as the rotational constant and energy barrier, $E^{\ddagger}$, as shown in Figure 1, must be treated here as adjustable parameters. The final set of parameters used in the calculations is summarized in Table V.

Registry No. $CH_3OH_2^+$, 17836-08-7; $(CH_3)_2OH^+$, 17009-82-4; CH_3OH, 67-56-1.

---

(32) G. Herzberg, "Molecular Spectra and Molecular Structure", Vol. III, Van Nostrand, Princeton, N.J., 1967.

(33) R. C. Weast, (Ed., "Handbook of Chemistry and Physics", Chemical Rubber Co., Cleveland, Ohio, 1979.

(34) L. M. Tel, S. Wolfe, and I. G. Csizmadia, *J. Chem. Phys.*, **59**, 4047 (1973).

Nature of the Frontier Orbitals in Phosphine, Trimethylphosphine, and Trifluorophosphine

Shen-Xiu Xiao,[†] William C. Trogler,*[‡] D. E. Ellis,* and Ziva Berkovitch-Yellin[§]

Contribution from the Department of Chemistry, Northwestern University, Evanston, Illinois 60201. *Received March 14, 1983*

Abstract: The electronic structures of PH_3, $P(CH_3)_3$, and PF_3 have been examined with the aid of self-consistent multipolar $X\alpha$ calculations (SCM-$X\alpha$-DV). There is excellent agreement between the theoretical and experimental ionization energies. When the transition-state procedure is used, first ionization potentials of 10.39, 8.41, and 12.19 eV are calculated for PH_3, $P(CH_3)_3$, and PF_3, respectively. Experimental values are 10.58, 8.58, and 12.27 eV, respectively. Plots of the highest and lowest unoccupied orbitals provide insight into the role of phosphorus donor ligands in transition-metal systems. Especially interesting is the π-symmetry p–d hybrid that comprises the lowest empty orbital in the π-acceptor PF_3 ligand.

Trivalent phosphorus donor ligands, PZ_3 (Z = F, Cl, H, alkyl, aryl, *O*-alkyl, *O*-aryl), have played an important role in the development of coordination and organometallic chemistry. They form tractable complexes with nearly all the transition elements, and PZ_3 ligands are compatible with most metal oxidation states and ancillary ligands. The electron-pair donor properties of phosphine ligands appear to follow sensible patterns. For example, trialkylphosphines generally form stronger metal–ligand bonds than triarylphosphines, when ligand basicity effects predominate.[1] Of course, steric factors[2] may be important in congested complexes. Ligand basicity trends fail to explain[3] the unusual stability of complexes that contain phosphite and PX_3 (X = F, Cl) ligands. Because these latter compounds frequently contain metals in low formal oxidation states, it has been generally thought that π-acceptor behavior may be important; however, arguments[3-11] can be made either in favor or against the π acidity of the PZ_3 ligand. Our interest centers around the following question; if PZ_3 ligands exhibit π-acceptor properties, then what is the nature of the

---

[†] Permanent address: Department of Chemistry, Sichuan University, Chengdu, Sichuan, Peoples Republic of China.

[‡] Alfred P. Sloan Research Fellow (1983-1985). After September, 1983, address correspondence to this author at the Department of Chemistry D-006, University of California, San Diego, La Jolla, CA 92093.

[§] Permanent address: Department of Structural Chemistry, Weizmann Institute of Science, Rehovot, Israel.

(1) Tolman, C. A. *J. Am. Chem. Soc.* **1970**, *92*, 2953-2956.

(2) Tolman, C. A. *Chem. Rev.* **1977**, 77, 313-348.

(3) Huheey, J. E. "Inorganic Chemistry: Principles of Structure and Reactivity"; Harper & Row: New York, 1972; pp 350-358.

(4) Basolo, F.; Pearson, R. G. "Mechanisms of Inorganic Reactions"; John Wiley and Sons, Inc.: New York, 1967; pp 527-540.

(5) Mason, R.; Meek, D. W. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 183-194.

(6) Yarbrough, L. W.; Hall, M. B. *Inorg. Chem.* **1978**, *17*, 2269-2275.

(7) Corderman, R. R.; Beauchamp, J. L. *Inorg. Chem.* **1977**, *16*, 3135-3139.

(8) Graham, W. A. G. *Inorg. Chem.* **1968**, *7*, 315-321.

(9) Angelici, R. J.; Ingemanson, C. M. *Inorg. Chem.* **1969**, *8*, 83-86.

(10) Darensbourg, D. J.; Brown, T. L. *Inorg. Chem.* **1968**, *7*, 959-966.

(11) Parshall, G. W. *J. Am. Chem. Soc.* **1966**, *88*, 704-708.

0002-7863/83/1505-7033$01.50/0

Table I. Comparison of Experimental and Theoretical Ionization Potentials for PH_3, $P(CH_3)_3$, and PF_3

		ionization potentials, eV			
molecule	orbital	expt[24]	SCM-Xα-DV	SCF-MO[21]	SCF-Xα-SW[20]
PH_3	$5a_1$	10.58	10.39	10.02[a]	10.61
	2e	13.50	13.09	13.70	13.42
	$4a_1$	21.2	20.43		20.55
$P(CH_3)_3$	$8a_1$	8.58	8.41	8.49	
	6e	11.31	10.67	12.04	
	$1a_2$		12.01	13.87	
	5e	12.7	12.11	14.63	
	$7a_1$		13.13	15.88	
	4e	15.8	13.07	15.89	
	$6a_1$		15.75	na	
	3e	19.6	19.53	na	
PF_3	$8a_1$	12.27	12.19	12.68	
	6e	15.88	15.00	18.32	
	$1a_2$	16.30	14.68	17.93	
	5e	17.46	16.00	19.67	
	$7a_1$	18.60	17.17	21.11	
	4e	19.50	17.83	21.45	

[a] Other values calculated for the first IP of PH_3 are 10.9 eV (SCF-LCAO-MO calculations reported in ref 22) and 10.80 eV (Cl calculation reported in ref 19).

π-acceptor orbital? The conventional rationale suggests that low-lying phosphorus 3d orbitals can participate in back bonding as, for example, do the π^* orbitals in the carbon monoxide ligand. It can be argued that the 3d orbitals in phosphorus compounds are too diffuse to engage in directional bonding;[12] yet, the π-acceptor properties of certain PZ_3 ligands appear undeniably real.

Chemical was well as photoelectron spectroscopic[6] evidence places the π-acceptor abilities of PF_3 in the same class as CO. At the other extreme, $P(CH_3)_3$ exhibits no such tendencies.[3,6,12] Complete UV photoelectron spectroscopic studies[6] of $M(CO)_5PZ_3$ (M = Cr, Mo, W) systems place $P(CH_3)_3$ and PF_3 at the extreme ends of the phosphorus ligand σ-donor and π-acceptor series. In this paper we have analyzed the electronic structure of PF_3, PH_3, and $P(CH_3)_3$ within the framework of SCF-Xα theory. Special attention is devoted to the nature of the frontier orbitals within this series. The results reveal empty phosphorus 3p orbital character in the potential π-acceptor orbital.

Computational Details. Theoretical calculations employed the SCC-Xα-DV[14] and SCM-Xα-DV[15] methods described previously. The SCC results were in qualitative agreement with SCM-type calculations; however, the quantitative accuracy of SCC ionization potentials (IP's) was poor. Errors in the long-range part of the SCC Coulomb potential, which is determined from Mulliken atomic orbital populations, led to systematically overestimated IP's. A least squares self-consistent multipolar (SCM) expansion of the charge density led to quantitatively accurate IP's; however, the computational effort increased significantly. Therefore, SCC calculations were primarily used to explore the influence of basis sets and geometry. All Xα calculations were performed with the aid of a PRIME-750 minicomputer.

Experimental gas-phase geometries[16] were used in most calculations. The ultimate numerical valence atomic orbital basis sets included 3d and 4s functions on P, 3s, and 3p orbitals on F and C, and 1s, 2s, and 2p orbitals on H. Basis functions were also optimized for the partial atomic charges found in initial Xα calculations. The "ionic" basis sets gave better values for calculated IP's than neutral atomic basis orbitals. SCM calculations included spherical and dipolar angular terms on each nuclear site in the least-squares expansion of the Coulomb potential. Quadrupolar terms were found to be unimportant. Several radial degrees of freedom were allowed for the least-squares expansion, in addition to the radial atomic densities. Five additional fit functions[15] were included for PH_3 and PF_3 while twelve such functions were chosen for PMe_3. In all calculations the 1s core orbitals on P, F, and C were "frozen"[15] and the variational valence orbitals were constrained to be orthogonal to the core. The exchange parameter was set equal to 0.70 in all calculations. Ionization potentials were calculated by the transition-state procedure[17] in order to include final state relaxation effects. A separate calculation was performed for each orbital ionization.

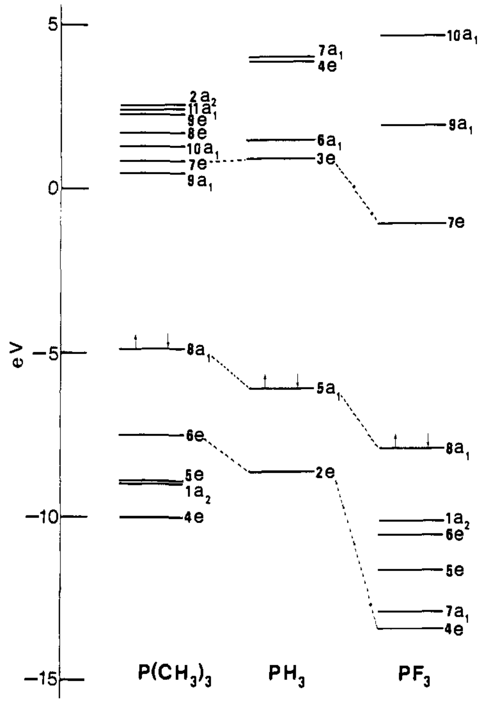

Figure 1. Valence orbital energy diagrams for $P(CH_3)_3$, PH_3, and PF_3.

Table II. Ground-State Valence Orbitals in PH_3 (SCM-Xα-DV $l \leqslant 1$)

		atomic compositions					
		P			H		
orbital[a]	energy, eV	3s	3p	3d	1s	2s	2p
$4a_1$	−15.47	0.64	0.01		0.33		
2e	−8.63		0.47	0.01	0.52		
$5a_1$*	−6.08	0.14	0.67		0.16		
3e	0.88		0.36	0.23	0.30		0.11
$6a_1$	1.61	0.08	0.12	0.01	0.19	0.09	0.43
4e	3.98		0.07	0.29			0.62
$7a_1$	4.02	0.10	0.08	0.35			0.45

[a] An asterisk denotes highest occupied orbital.

Results and Discussion

Calculated Ionization Potentials. Previous theoretical studies of trisubstituted phosphorus compounds include Hartree–Fock (HF),[18] HF-CI,[19] and SCF-Xα-SW[20] calculations of PH_3, SCF-MO studies of PH_3,[21,22] PF_3,[21] and $P(CH_3)_3$,[21] and Xα studies of PCl_3.[23] Although the nature of the frontier orbitals was not

---

(12) Ball, E. E.; Ratner, M. A.; Sabin, J. R. *Chem. Scr.* **1977**, *12*, 128–141.

(13) Holladay, A.; Churchill, M. R.; Wong, A.; Atwood, J. D. *Inorg. Chem.* **1980**, *19*, 2195–2198.

(14) Rosen, A.; Ellis, D. E.; Adachi, H.; Averill, F. W. *J. Chem. Phys.* **1976**, *65*, 3629–3634.

(15) Delley, B.; Ellis, D. E. *J. Chem. Phys.* **1982**, *76*, 1949–1960.

(16) Callomon, J. H; Hirota, E.; Kuchitsu, K.; Lafferty, W. J.; Maki, A. G.; Pote, C. S. "Landolt-Bornstein, Structure Data of Free Polyatomic Molecules"; Springer-Verlag: Berlin, 1976; pp 73, 90, and 258.

(17) Slater, J. C. "The Self-Consistent Field for Molecules and Solids"; McGraw-Hill: New York, 1974.

(18) Rothenberg, S.; Young, R. H.; Schaefer, H. F. *J. Am. Chem. Soc.* **1970**, *92*, 3243–3250.

(19) Petke, J. D.; Whitten, J. L. *J. Chem. Phys.* **1973**, *59*, 4855–4866.

(20) Norman, J. G. *J. Chem. Phys.* **1974**, *61*, 4630–4637.

(21) Hillier, I. H.; Saunders, V. R. *Trans.* Faraday Soc. **1970**, *66*, 2401–2407. Guest, M. F.; Hillier, I. H.; Saunders, V. R. *J. Chem. Soc.*, Faraday *Trans. 2* **1972**, 867–873.

(22) Moccia, R. *J. Chem. Phys.* **1964**, *40*, 2176–2183; Boyd. D. B; Lipscomb, W. N. *Ibid.* **1967**, *46*, 910–919. Cook, D. B.; Palmieri, P. *Chem. Phys. Lett.* **1969**, *3*, 219–222. Lehn, J. M.; Munsch, B. *J. Chem. Soc., Chem. Commun.* **1969**, 1327–1329.

(23) Topol', I. A.; Kondratenko, A. V.; Mazalov, L. N.; Dolenko, G. N.; Chesnyi, S. A. *J. Struc. Chem.* (*Engl. Transl.*) **1981**, *22*, 161–167.

Table III. Ground-State Valence Orbitals in PMe_3 (SCM-Xα-DV $l \leq 1$)

		atomic compositions										
		P				C				H		
orbital[a]	energy, eV	3s	4s	3p	3d	2s	3s	2p	3p	1s	2s	2p
3e	−16.40			0.03		0.56	0.02			0.37	0.01	0.00
$6a_1$	−12.56	0.41				0.03	0.02	0.17		0.33	0.01	0.01
$7a_1$	−10.10	0.02		0.05	0.01			0.37		0.55		0.00
4e	−10.03			0.05				0.43	0.02	0.49		0.01
$1a_2$	−9.00							0.40		0.52	0.02	0.06
5e	−8.96			0.02				0.44	0.02	0.50	0.00	0.00
6e	−7.52			0.26	0.01	0.07	0.01	0.50	0.02	0.12	0.00	0.01
$8a_1$*	−4.90	0.11	0.01	0.60		0.01	−0.01	0.12		0.11	0.01	0.02
$9a_1$	0.43			0.01			0.13	0.05	0.03	0.19	0.42	0.17
7e	0.85			0.14	0.10	0.06	0.02	0.05		0.10	0.25	0.28
$10a_1$	1.30	0.07	0.01		0.01		0.05	0.13	0.02	0.04	0.02	0.64
8e	1.72			0.02	0.05	0.03	0.01	0.01	0.10	0.17	0.27	0.34
9e	2.30			0.03	0.11	0.05	0.06	0.03	−0.03	0.10	0.04	0.60
$11a_1$	2.44	0.25	0.01	0.02			0.02	0.02	0.09	0.03	0.00	0.55
$2a_2$	2.54							0.02	0.17	0.29	0.11	0.41

[a] An asterisk denotes highest occupied orbital.

considered in the early studies, ionization spectra were predicted. In Table I we compare the experimental ionization potentials[24] with those calculated by the various theoretical methods. The SCM-Xα-DV orbital energy schemes are also summarized in Figure 1.

From the data in Table I we observe that the SCM-Xα-DV transition-state IP's agree within 0.8 eV for PH_3, within 0.6 eV for $P(CH_3)_3$, and within 1.6 eV for PF_3. In each instance the SCM-Xα-DV error results from an underestimation of the IP. However, there is much evidence to suggest that valence level binding energies are systematically underestimated by the simple Xα exchange potential. More sophisticated treatments of exchange and correlation interactions, using for example the Hedin–Lundqvist potential,[25] typically give a binding energy increase of ~1 eV. Perhaps there remains a small systematic error in the SCM Coulomb potential. Overall the quantitative accuracy is excellent considering the range of ionic and covalent bonding spanned for PH_3, $P(CH_3)_3$, and PF_3. There has been but one previous theoretical study[21] of all three molecules (SCF-MO, Table I). Numerically the SCM-Xα-DV results are superior to the SCF-MO[21] calculated IP's. Several studies[18-22] of PH_3 have been reported including Hartree–Fock, HF-CI, and SCF-Xα-SW. Only the SCF-Xα-SW results[20] lead to more accurate IP's; however, it should be recalled that this procedure relies on the muffin-tin potential approximation with adjustable sphere-overlap parameters. In this context, we note the $5a_1$–2e and 2e–$4a_1$ splittings are reproduced equally well by the SCM-Xα-DV and SCF-Xa-SW methods.

The only major discrepancy between the present assignments and photoelectron spectroscopic data is found for the 6e and $1a_2$ IP's in PF_3. Both levels are predominantly fluorine lone pairs, and our calculations as well as SCF-MO results[21] predict an opposite relative ordering when compared to experiment.[24]

Nature of the Frontier Orbitals. Having established the quantitative merits of the SCM ionization energy calculations, we turn toward the qualitative aspects of the frontier orbitals. A summary of valence orbitals and their atomic compositions (as determined from Mulliken population analyses of the constituent orbitals) is provided in Tables II–IV for PH_3, $P(CH_3)_3$, and PF_3. The highest occupied molecular orbital (HOMO) consists primarily of a lone pair s–p hybrid on phosphorus. In PF_3 this orbital is slightly more compact than in PH_3 or $P(CH_3)_3$ (Figure 2). The IP and orbital energy ordering (Figure 1) $P(CH_3) < PH_3 < PF_3$ also parallels the percent phosphorus s character of the HOMO: $P(CH_3)_3$ (11% s and 60% p), PH_3 (14% s, 67% p), PF_3 (29% s, 32% p). All of these trends follow the expected electron withdrawing ability of the substituents $CH_3 < H < F$ and conform to Bent's rule.[26] In each case the back lobe of the s–p hybrid interacts with the substituent attached to phosphorus in a σ-bonding fashion. This appears most clearly in the contour map for PF_3 (Figure 2).

Table IV. Ground-State Valence Orbitals in PF_3 (SCM-Xα-DV $l \leq 1$)

		atomic compositions							
		P				F			
orbital[a]	energy, eV	3s	4s	3p	3d	2s	3s	2p	3p
$6a_1$	−16.37	0.35				0.23	0.01	0.40	0.01
4e	−13.42			0.16	0.01	0.06	0.01	0.76	
$7a_1$	−12.92	0.06		0.14	0.02	0.01		0.77	
5e	−11.61				0.02			0.97	
6e	−10.55				0.01			0.99	
$1a_2$	−10.14							0.99	
$8a_1$*	−7.90	0.29		0.32	0.01		0.01	0.36	
7e	−1.05			0.44	0.23	0.04	0.03	0.26	
$9a_1$	1.94		0.12	0.24		0.08	0.33	0.21	0.01
$10a_1$	4.74	0.04	0.13	0.09	0.01	0.02	0.52	0.10	0.02

[a] An asterisk denotes highest occupied orbital.

Below the energy of the $5a_1$ nonbonding lone-pair orbital in PH_3 lie the occupied 2e and $4a_1$ levels. In agreement with a preious SCF-Xα-SW description,[20] we find the 2e orbital to be P–H σ bonding; however, the SCM-Xα-DV wave function (Table II) incorporates significantly less d-orbital character (1%) than the SCF-Xα-SW description (15% d). The $4a_1$ orbital reflects bonding between the phosphorus 3s orbital and the totally symmetric linear combination of the hydrogen 1s orbitals. It is interesting that only the 1s atomic orbital of hydrogen contributes to the bonding levels. For the $6a_1$ orbital significant amounts of 2s and 2p functions on hydrogen are necessary to describe this Rydberg state. The SCM-Xα-DV results differ significantly from the SCF-Xα-SW calculations in the nature of the lowest lying unoccupied molecular orbital (LUMO), presumably due to the volume averaging of the potential in the latter method. Previous work[20] indicated a $6a_1$ LUMO whereas we find 3e to lie lower in energy than $6a_1$. This e orbital possesses π symmetry with respect to the principal axis of symmetry (Figure 3).[27] Also worthy of note is the tilting off phosphorus of the "horizontal" nodal plane. In C_{3v} symmetry there is no restriction on the location of this plane, and the partial contribution from hydrogen makes it appear as if there is a pseudo d orbital centered away from phosphorus.

---

[24] Maier, J. P.; Turner, D. W. *J. Chem. Soc., Faraday Trans. 2* **1972**, 711–719.

[25] von Barth, U.; Hedin, L. *J. Phys. C* **1972**, *5*, 1629–1636. Gunnarsson, O.; Lundqvist, B. I. *Phys. Rev.* B: Solid State **1976**, *13*, 4273–4280.

[26] Bent, H. A. *Chem. Rev.* **1961**, *61*, 275–311.

[27] A reviewer suggested the stabilization of the π orbital may influence the calculation of inversion barriers. See: Cherry, W.; Epiotis, N.; Borden, W. T. *Acc. Chem. Res.* **1977**, *10*, 167–173. Levin, C. C. *J. Am. Chem. Soc.* **1975**, *97*, 5649–5655.

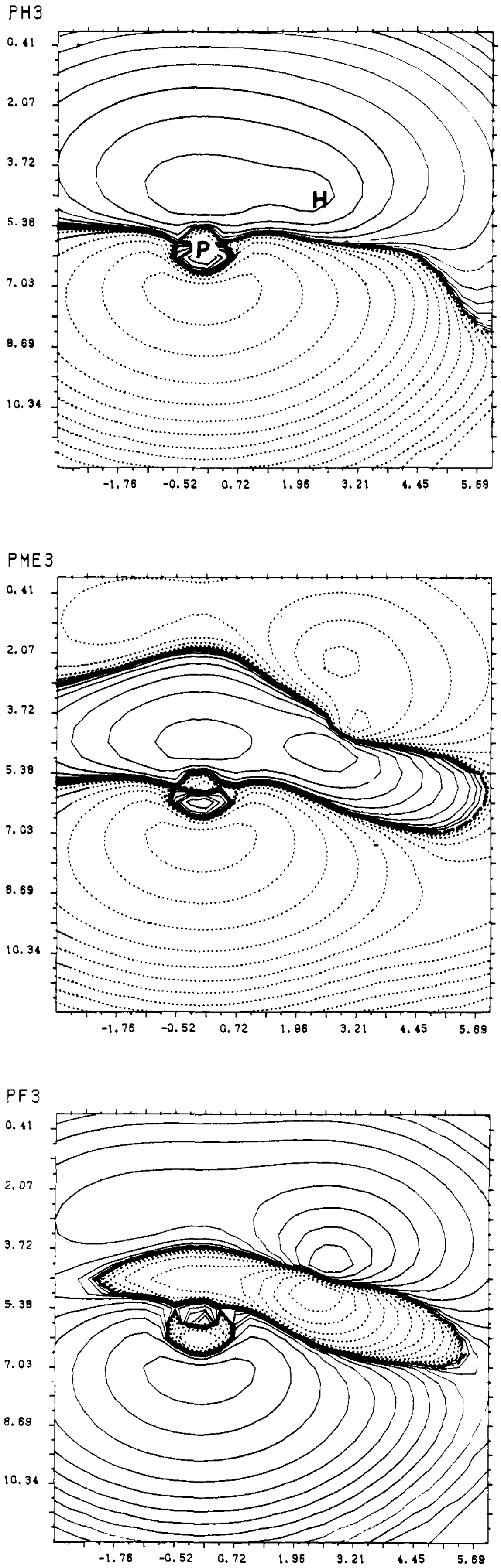

Figure 2. Contour plots of the highest occupied "lone pair" orbitals in PH_3 (top), $P(CH_3)_3$ (middle), and PF_3 (bottom). All plots use a contour interval of $(2 \times 10^{-5})^n$ e/au.[3] The plot section lies in the plane of a P–H, P–C, or P–F bond.

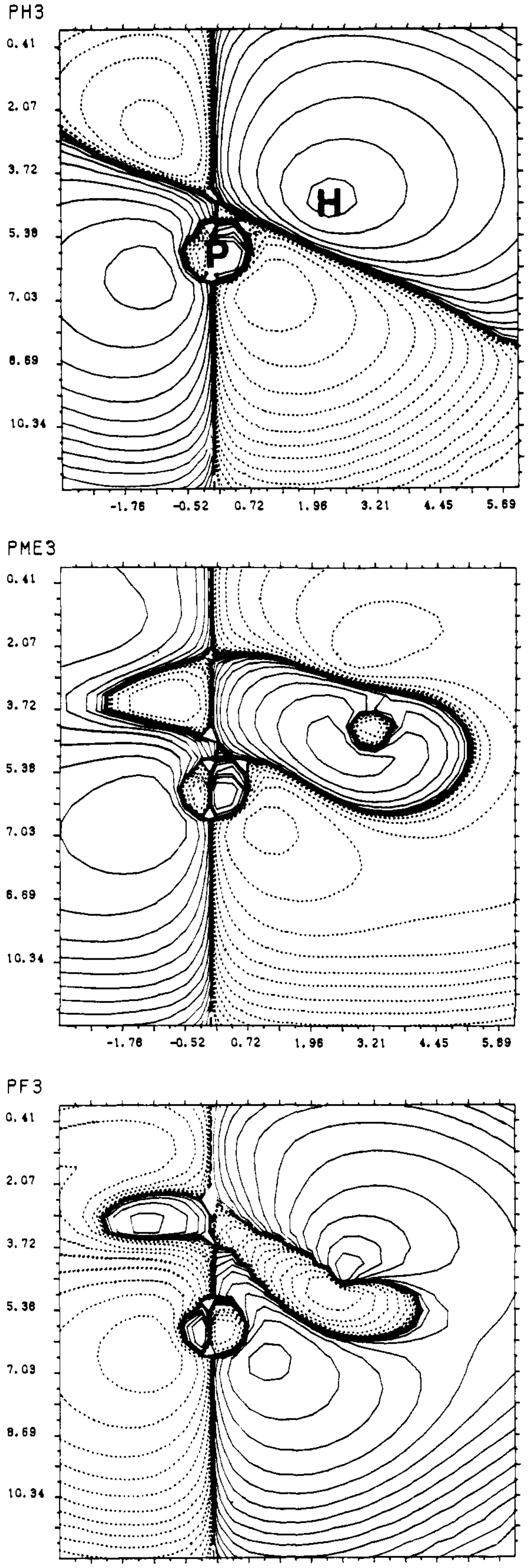

Figure 3. Contour plots of the lowest unoccupied π-acceptor (e) orbitals in PH_3 (top), $P(CH_3)_3$ (middle), and PF_3 (bottom). Plot parameters are identical with those in Figure 2.

Although previous theoretical studies of trisubstituted phosphines have not examined this orbital, we believe it pertains to the π-acceptor properties of phosphorus ligands. A similar type of acceptor orbital may be found in $P(CH_3)_3$ and PF_3 (Figure 3), but there are several important quantitative differences. First, the energy of 7e in PF_3 is lower than that in PH_3 or $P(CH_3)_3$ (Figure 1). This will enhance back-bonding to PF_3, when complexed to a metal, relative to PH_3 and $P(CH_3)_3$. Second, the nature of the lowest unoccupied e orbital changes. In PH_3, 3e is a hybrid of 36% 3p and 23% 3d on phosphorus, while the respective percentages are 14% and 10% for $P(CH_3)_3$ (7e) and 44% and 23% for PF_3 (7e). Contrary to conventional wisdom,[28] which ascribes the π-acceptor properties of PF_3 to empty phosphorus 3d orbitals, the π-acceptor orbital on phosphorus mostly consists of phosphorus 3p character. Mixing in 3p orbital character has the effect (Figure 3) of directing the empty π orbital in the direction of the lone pair (i.e., where a metal would bind). In PF_3 the acceptor orbital contains the maximum amount of phosphorus 3p character and is directed most effectively toward the region where a metal would bind.

This behavior can be viewed in the context of a crystal field[29] bonding model. The more highly electronegative the substituent attached to P to the more ionic the bond will be. Consequently, the substituent valence orbitals will dominate the occupied bonding orbitals and the antibonding levels will acquire more character of phosphorus valence 3p orbitals. Note the antibonding P–F character in the 7e orbital for PF_3 (Figure 3).

Acknowledgment. This work was supported in part by the National Science Foundation (CHE-8210514 and DMR-8214966). The work Z.B.-Y. was supported in part by a Chaim Weizmann Fellowship. We thank Professor Mark Ratner for helpful discussions.

Registry No. PH_3, 7803-51-2; $P(CH_3)_3$, 594-09-2; PF_3, 7783-55-3.

---

[28] Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry"; John Wiley & Sons: New York, 1980; pp 87–89.

[29] Schnulle, G. W.; Parr, R. G *J. Am. Chem. Soc.* **1972**, *94*, 8974–8993.

Combination of Theoretical ab Initio and Experimental Information To Obtain Reliable Harmonic Force Constants. Scaled Quantum Mechanical (SQM) Force Fields for Glyoxal, Acrolein, Butadiene, Formaldehyde, and Ethylene

Pêter Pulay,[1a] Gêza Fogarasi,*[1b] Gâbor Pongor,[1c] James E. Boggs,[1d] and Anna Vargha[1e]

Contribution from the Institute for General and Inorganic Chemistry, Eötvös L. University, Budapest 8, Pf. 323, Hungary 1445, and the Department of Chemistry, The University of Texas at Austin, Austin, Texas 78712. *Received January 13, 1983*

Abstract: Fully optimized geometries, complete in- and out-of-plane force fields, and dipole moment derivatives have been calculated for the title compounds at the ab initio Hartree–Fock level using the 4-21 Gaussian basis set. The theoretical information is combined with experimental data by fitting the calculated force constants through a few parameters to the observed frequencies to obtain the final, scaled quantum mechanical (SQM) force fields. Recommendations for a standard procedure of this type are given. The SQM force fields give excellent reproduction of the fundamental frequencies and are considered as approaching the best accuracy which can be achieved in a harmonic treatment. The infrared intensities obtained at this level of theory are only qualitative estimates, but they are still useful for making assignments more reliable.

Introduction

Harmonic force fields of polyatomic molecules play an important role in several branches of molecular spectroscopy. Apart from their most straightforward application, the prediction and interpretation of vibrational frequencies, they are important in dealing with quantities which depend on the form of vibrations, like infrared and Raman intensities, or the vibrational structure in ultraviolet and photoelectron spectra, as well as vibrational averaging effects on molecular geometries and dipole moments. Also, a satisfactory harmonic analysis must obviously precede an anharmonic study. With the mounting interest in excited vibrational states, the importance of the latter is rapidly increasing.

The purely empirical deduction of force fields from spectral data for molecules of medium complexity has been rather unsuccessful. Highly simplified models, e.g., the Urey–Bradley force field,[2] usually give a correct qualitative picture but their accuracy is insufficient. If the number of parameters is increased, the fitting procedure often converges to an unphysical solution. This can only be counteracted by increasing the number of independent experimental observables, e.g., by recording the spectra of isotopomers, but the possibilities here are limited. Moreover, unless a completely general harmonic force field can be used, which is possible only for the smallest molecules, there is always an arbitrariness in the choice of the terms retained. As a case in point, a recent empirical force field for glyoxal,[3] which reproduces the fundamental frequencies of the parent molecule and its deutero derivatives quite precisely, is extremely improbable in the light of the present study. Another difficulty in empirical force field determination is the fact that the correct choice and assignment of the fundamentals is by no means evident in larger molecules and requires some prior knowledge of the force field.

As to the theoretical approach, with the development of gradient techniques[4,5] and rapid progress in computer facilities, the a priori

---

[1] (a) Eötvös L. University, Budapest; present address: Department of Chemistry, University of Arkansas, Fayetteville, AR 72701. (b) Eötvös L. University, Budapest; during part of this work on leave at the University of Texas at Austin. (c) Eötvös L. University, Budapest; (d) The University of Texas at Austin. (e) Eötvös L. University, Budapest; present address: Research Laboratory for Inorganic Chemistry, Hungarian Academy of Sciences, Budaörsi ut 45, 1112 Budapest, Hungary.

[2] Urey, H. C.; Bradley, C. A. *Phys. Rev.* **1931**, *38*, 1969–1978. Shimanouchi, T. *Pure Appl. Chem.* **1963**, *7*, 131–145.

[3] Cossart-Magos, C. *Spectrochim. Acta, Part A* **1978**, *34*, 415–421.

[4] Pulay, P. *Mol. Phys.* **1969**, *17*, 197–204.

0002-7863/83/1505-7037$01.50/0