

839. *Unstable Intermediates. Part XXV.¹ The Radical PF₄.*

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The electron spin resonance spectrum of a radical in γ -irradiated ammonium and potassium hexafluorophosphate, identified by Morton ² as PF₄, has been studied between 77 and 300°K. The results are discussed in terms of an orbital-level scheme for the tetrahedral cation PF₄⁺ and it is concluded that the unpaired electron causes considerable distortion from T_d symmetry, but that at room temperature rapid inversions render all the fluorines equivalent.

Outer orbitals for the families MnO₄⁻; MnO₄²⁻; MnO₄³⁻ and PF₄⁺; PF₄⁻ are compared, and it is concluded that the 3*d* level plays a relatively minor role in the latter family.

THE radical PF₄, identified with little ambiguity by Morton ² as one of the paramagnetic products from γ -radiolysis of ammonium hexafluorophosphate, is of interest to us in that it has one electron more than the "closed-shell" ion PF₄⁺, which is structurally similar to the phosphate ion. Thus a situation is realised which may be compared with that achieved with the manganate ion (MnO₄²⁻) when the extra electron helped to probe the electronic structure of permanganate and related ions.³ Little is known about the electronic structure of the corresponding tetroxides of the non-metals, and our attempts to add an extra electron to such ions as perchlorate have met with failure.⁴ We have succeeded in preparing ions with a hole in the closed-shell system, such as SO₄⁻,⁵ PO₄²⁻,^{4,6} and SeO₄⁻,⁷ but the spin resonance spectra do not give much structural information since the level involved is a non-bonding orbital on oxygen.

Just as PF₄ can be compared with MnO₄²⁻, so also PF₄⁻, which is isoelectronic with SF₄, can be compared with MnO₄³⁻. The molecule sulphur tetrafluoride may be pictured as having a trigonal bipyramidal structure, with a lone-pair of electrons taking one of the equatorial positions. This configuration has been attributed to the presence of 3*d* electrons by Chantry and Ewing,⁸ but no detailed theoretical study of such molecules is known to us. Wolsberg and Helmholtz have, however, discussed the structure of the perchlorate ion in terms of the simple molecular-orbital treatment developed to explain the spectra of permanganate and related ions.⁹

One of the major unsolved problems concerning the structure of closed-shell tetroxides of the non-metals is that of the extent of π -bonding and the role *d*-atomic orbitals of the central atom in such bonding. This study was undertaken in the hope that a better understanding of the electronic structure of PF₄ might, for the reasons given above, shed light on these problems.

EXPERIMENTAL AND RESULTS

Materials.—Potassium hexafluorophosphate was kindly supplied by Dr. R. D. W. Kemmitt of these laboratories; the ammonium salt was obtained from the Ozark-Mahoning Co. Both were used without further purification.

¹ Part XXIV, Blandamer, Catterall, Shields, and Symons, preceding Paper.

² Morton, *Canad. J. Phys.*, 1963, **41**, 706.

³ Carrington and Symons, *Chem. Rev.*, 1963, **63**, 443.

⁴ Symons, *Advances in Chemistry Series, Amer. Chem. Soc.*, No. 36, 1962, 76.

⁵ Atkins, Brivati, Horsfield, Symons, and Trevalion, Sixth International Symposium on Free Radicals, Cambridge, 1963.

⁶ Atkins, Keen, Symons, Wardale, unpublished results.

⁷ Atkins, Symons, and Wardale, to be published.

⁸ Chantry and Ewing, *Mol. Phys.*, 1962, **5**, 210.

⁹ Wolsberg and Helmholtz, *J. Chem. Phys.*, 1952, **20**, 837.

Radiolysis.—Samples were exposed at room temperature to a 1900c ^{60}Co γ -ray source for at least 10 hr.

Electron Spin Resonance.—All spectra were obtained on a Varian 4502-03 EPR spectrometer with a variable temperature attachment.

The spectrum obtained from potassium fluorophosphate powder at room temperature is shown in Fig. 1 (A). It is identical with that obtained by Morton² except for the absence of lines which he attributed to trapped fluorine atoms. We shall not be concerned with the other radicals present which include a quartet attributed² to PF_2^\pm and an unidentified species giving the spectrum in the centre of the main spectrum. As the sample was cooled the spectrum went through the form shown in Fig. 1 (B) to the final state shown in Fig. 1 (C). Spectra from single crystals also give the envelope spectrum because the radicals take up random positions in the lattice.² The hyperfine splitting constants and g -values obtained by Morton are given in the Table, together with the present results.

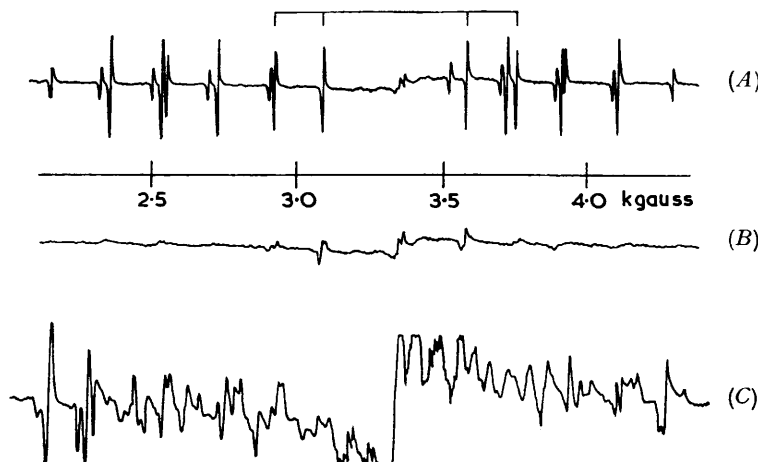


FIG. 1. Electron spin resonance spectrum from γ -irradiated potassium hexafluorophosphate at various temperatures.

A, 300°K. B, 210°K. C, 200°K.

Electron spin resonance and molecular parameters for PF_4 .

Hyperfine splitting constants (Mc./sec.)				Orbital population		
$A_{\text{iso}}^{\text{P}}$	$A_{\text{iso}}^{\text{F}}$	β	g_{av}	P(3s)	F(2s)	F(2p)
3769 *	549 *	110	1.9985 *	0.37	0.011	0.07

* Morton, *Canad. J. Phys.*, 1963, **41**, 706.

DISCUSSION

Morton² has interpreted the isotropic spectrum as arising from four equivalent fluorine nuclei which he supposed to be tetrahedrally distributed about a central phosphorus atom to form the species PF_4 . The breakdown of the binomial intensity distribution law is successfully accommodated by this model since the degeneracy of the transitions is removed by off-diagonal matrix elements which are not negligible when the hyperfine splitting is as large as that observed for PF_4 .^{2,10,11} It was further suggested² that the unpaired electron occupied what is approximately a 4s orbital on phosphorus. However, although it is very difficult to assess the coupling to be expected for an electron entirely in this orbital, since its numerical form is unknown and the effect of the fluorine ligands would

¹⁰ Mackor and de Boer, *Mol. Phys.*, 1962, **5**, 493.

¹¹ Fessenden, *J. Chem. Phys.*, 1962, **37**, 747.

be pronounced, it is reasonably safe to estimate that the coupling would be about one tenth of that for an electron in the $3s$ orbital. Since this latter is approximately $10,178 \text{ Mc./sec.}$ ¹² it would seem that the experimental result is far too large to be accommodated by this hypothesis. If the only phosphorus orbital involved was the $3s$ orbital, the splitting could be accommodated if its population was 0.37 . The isotropic fluorine splitting indicates that there is 0.011 electron in the $2s$ orbital of each fluorine; thus 0.41 of an electron has been accounted for. It is unlikely that no phosphorus $4s$ orbital is involved since configuration interaction would be important. It is unnecessary, however, to discuss the structure of the radical as involving this level to a significant extent.

In tetrahedral symmetry the only molecular orbital which can be constructed from an s orbital on the central atom is of a_1 symmetry. The particular a_1 orbital occupied by the electron in PF_4 must be antibonding, the fluorine components of the orbital being essentially σ with respect to a P-F axis and built from $2p$ and $2s$ atomic orbitals. Wolfsberg and Helmholtz⁹ have discussed the orbital levels for tetrahedral oxy-ions and would place the odd electron in the antibonding t_2 level. The actual sequence of levels in this region is obscure, however, and it is quite probable that the a_1 orbital could be below the t_2 level in a scheme involving just the $3s$ and $3p$ orbitals of phosphorus, or that the a_1 level is depressed below the t_2 level by configuration interaction with the $4s$ orbital. A

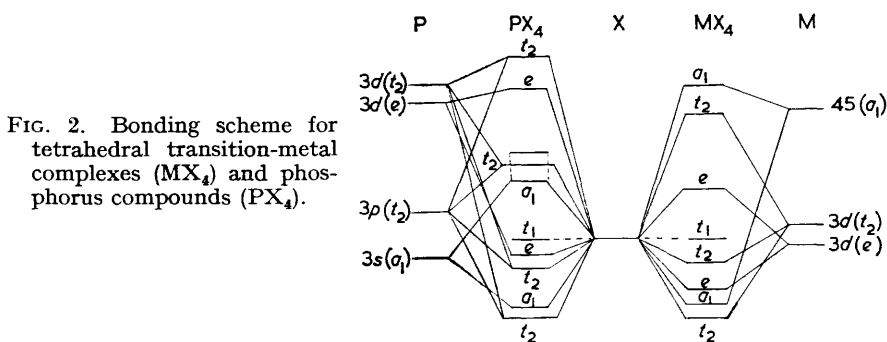


FIG. 2. Bonding scheme for tetrahedral transition-metal complexes (MX_4) and phosphorus compounds (PX_4).

possible bonding scheme is shown in Fig. 2 which also includes the effect of d -orbitals. This diagram will be discussed more fully below. It must be stressed that in T_d symmetry the occupied orbital cannot be t_2 because this orbital does not contain any phosphorus s -character.

The situation can be probed further by attempting to estimate the $2p$ -character of the fluorine orbitals by measuring the anisotropic spectrum obtained at low temperatures. The major difficulty here is that in the crystal PF_4 units take up random orientations at low temperatures so that only an envelope spectrum can be obtained; the lack of strongly directional forces in crystals containing PF_6^- ions has recently been demonstrated by the NMR studies of Miller and Gutowsky.¹³ We have investigated the powder spectrum of PF_4 at temperatures from 300 down to 77°K , and although much information is concealed by the complexity of the spectra we have been able to glean some structural data.

It is useful to discuss a synthesis of the spectrum to be expected from a tetrahedral PF_4 radical. The greatest difficulty in this programme is the fact that the principal axes of the phosphorus and fluorine hyperfine coupling tensors are not coincident, nor, except for a few special orientations, are those of the fluorine atoms with each other. Impressed upon this is the fact that the off-diagonal components of the term **S.A.I.** in the spin-Hamiltonian are important when the fluorines come into positions such that two, three,

¹² Rowlands and Whiffen, National Physical Laboratory Report, No. B.P.R.13.

¹³ Miller and Gutowsky, *J. Chem. Phys.*, 1963, **39**, 1983.

or four nuclei are magnetically equivalent.^{10,11} The isotropic spectrum shows the consequence of one such equivalent set, as mentioned previously. A further implication is that the entire spectrum is displaced to low field, to the extent of about 10 gauss.

Neglecting these second-order corrections for the moment, we can calculate the positions of the lines for any given orientation of the radical by considering the effects of rotations about three orthogonal axes. As an example, Fig. 3 shows one half of the

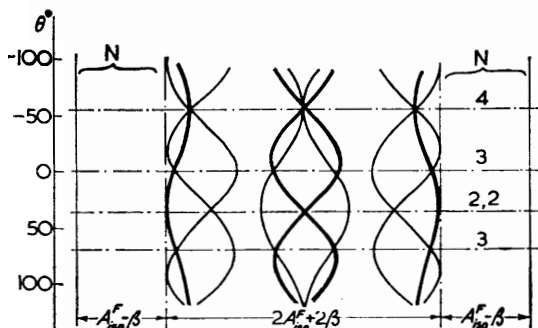


FIG. 3. One half of the calculated electron spin resonance spectrum of tetrahedral PF_4 during the rotation illustrated in Fig. 4.

spectrum to be expected as the molecule is rotated about an axis perpendicular to a C_3 axis and such that two fluorines are always equivalent. This rotation is illustrated in Fig. 4. During this rotation, positions are reached such that two, two pairs, three, and four fluorine nuclei become equivalent; these positions are indicated by the peripheral numbers in Fig. 4 and are manifest as cross-over points in Fig. 3. To calculate this spectrum each fluorine anisotropic coupling tensor was taken to have the form $(-\beta, -\beta, 2\beta)$ with the positive coupling along the particular C_3 axis of the tetrahedron. Arbitrarily it was assumed that the ratio of the isotropic to the anisotropic splitting (β) was 5:1. In a tetrahedral environment the spin density is distributed symmetrically

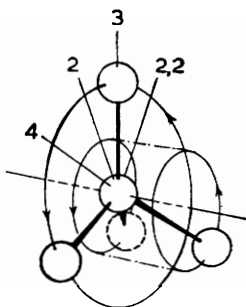


FIG. 4. The rotation of the PF_4 tetrahedron discussed in the text and used to construct Fig. 3.

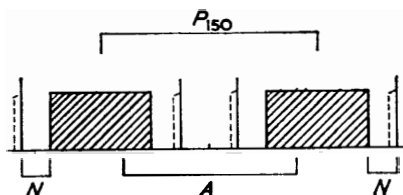


FIG. 5. The idealised powder spectrum calculated for PF_4 . The region marked A would be obscured by the other radicals present.

about the central atom and so neither phosphorus hyperfine or g -tensor anisotropy is expected. Similar diagrams to that in Fig. 3 may be constructed for other rotations. By increasing the magnitude of the anisotropic tensor it is possible to demonstrate that the anisotropic spectrum does not extend outside the isotropic spectrum as long as $\beta \leq \frac{3}{2}A_{iso}^F$. This condition cannot be exceeded for the present system as it would entail an impossibly large 2β contribution. The tetrahedral symmetry of the system has led to two effects. One is that no phosphorus anisotropy can be observed and the other that the fluorine anisotropy cannot extend the spectrum beyond the limits of the isotropic

spectrum. It is also found that there is always a region between the outermost lines and the furthest extent of the inner lines which remains free from spectral lines. This region is marked N in Fig. 3 and extends over $A_{\text{iso}}^{\text{F}} - \beta$ gauss.

On this basis the envelope spectrum should consist of four sharp lines and two very complex regions. An idealised spectrum is shown in Fig. 5. When the aforementioned second-order effects are allowed for, shoulders will appear on the low-field side of the lines, the maximum shift of the spectrum occurring when there are two pairs of equivalent fluorine nuclei. The positions of these shoulders are indicated by broken vertical lines in Fig. 5.

Comparison of Figs. 1 and 5 shows that there are points of resemblance inasmuch as there are empty regions from which one may calculate that $\beta \sim 40$ gauss, which is equivalent to 0.07 fluorine $2p\sigma$ character. There are, however, features which are not accommodated. These are that the shoulders on the wing lines cannot be accounted for by second-order shifts because they are too far removed from the main lines and there is a shoulder on the high-field side of the high-field wing line. Also the spectrum is not quite contained within the isotropic spectrum.

To explain these discrepancies it is necessary to assume that the radical is *not* tetrahedral, but because of the near correspondence to the spectrum from a tetrahedral species,

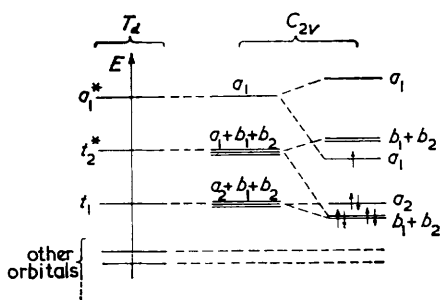


FIG. 6. Effect of the descent in symmetry $T_d \rightarrow C_{2v}$ on the orbital levels of PF_4 .

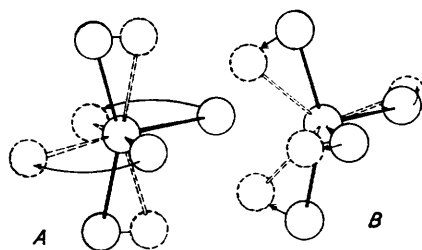


FIG. 7. The inversions of the PF_4 molecule.

the distortion must be small. The effect of distorting the molecule so that its symmetry is reduced to C_{2v} is to split the t_2 level into orbitals which transform as a_1 , b_1 , and b_2 . Because of the other closely lying a_1 orbital this a_1 level will be depressed beneath the b_1 and b_2 orbitals in the manner suggested by Fig. 6. Thus we have arrived at the correct lowest-lying antibonding orbital. The a_1 orbital now possesses both phosphorus $3s$ and $3p$ character, with possible contributions from $4s$ and $3d$ orbitals, and the resulting anisotropic spectrum will exhibit phosphorus hyperfine anisotropy and will, thereby, be considerably complicated.

A further implication of the distortion is that the g -value will no longer be isotropic. Also, were the molecule purely tetrahedral, deviation from the free-spin g -value would depend upon the mixing of some t_1 orbital character into the a_1 ground-state by spin-orbit interaction. Since the only t_1 orbitals available are the non-bonding ligand orbitals which lie below the a_1 orbital, the g -shift by this mechanism would be positive, contrary to observation (Table). In C_{2v} symmetry, the spin-orbit coupling has non-vanishing matrix elements to orbitals of symmetry a_2 , b_1 , and b_2 . As discussed above, the b_1 and b_2 orbitals lie a little above the a_1 orbital and so g anisotropy is expected with g_{av} less than the free-spin value. Although the g -tensor could not be determined from the low-temperature spectrum the average value obtained from the room-temperature spectrum is less than the free-spin, as required.

Returning to the room-temperature spectrum, we can account for all the above

features if we assume that the molecule is undergoing a rapid inversion of the type discussed by Chantry and Ewing⁸ for sulphur tetrafluoride. There are two possible modes of inversion, as shown in Fig. 7. The actual inversion is a coupled form of modes *A* and *B* (Fig. 7) but it is mode *B* which makes the fluorines equivalent. The root-mean-square amplitude of the "equatorial" fluorine-fluorine distance in SF₄ is 0.130 Å (the value would probably be larger in PF₄ which, because there is one less electron constraining its stereochemistry, would have a much lower barrier to inversion). If the inversion is sufficiently rapid the fluorine atoms appear equivalent and the room-temperature spectrum is explicable and the low *g*-value accounted for. At low temperatures, when the inversion is sufficiently slow, the equivalence of the fluorines is removed and the anisotropic spectrum is obtained. On this argument, there should be an intermediate temperature at which the inversion rate is equivalent to the hyperfine splitting frequency; at this temperature only a broad line should be observed. Such a spectrum was indeed obtained at about 210°K [Fig. 1 (*B*)]. The residual structure is due to the other radicals present.

The electron populations of the orbitals are collected in the Table. It is interesting to compare the *p/s* ratio for the fluorine orbitals with that obtained for the same quantity in NiF₃ in the n.m.r. experiments of Schulman and Sugano.¹⁴ These authors obtained $\lambda^2 = 7.03$, the present analysis gives $\lambda^2 \doteq 7$.

Comparison with Transition-metal Complexes.—Here we compare the structure of ions such as MnO₄⁻, MnO₄²⁻, and MnO₄³⁻ with that of PF₄⁺, PF₄, and PF₄⁻ or isostructural species. The outer electrons in the former series do not seem to induce any major distortion of the original molecular framework, and have been found, by spin-resonance studies,³ to be in an *e*-level which is predominately atomic *d* on the central metal. The contrast with the PF₄⁺ series is most marked, and clearly demonstrates that the *d(e)* level does not play a major role in binding the outer electrons in PF₄ and SF₄. A qualitative illustration of the two classes of compound is given in Fig. 2, which relates to the hypothetical tetrahedral species.

As has been discussed for simpler molecules,¹⁵ PF₄ and SF₄ probably distort in order to reduce the antibonding character of the outer electrons. This is not necessary for the transition-metal complexes since the *e* level is already well distributed in favourable regions of space.

*Phosphorus-doped Silicon.*¹⁶—The extra electron associated with P⁺ in silicon may be compared with that in PF₄. Here, however, distortion is far more difficult, so that the electron is forced into a σ -antibonding level. In fact, this level is of such high energy that the electron is repelled from the vicinity of the phosphorus atom into a dispersed level having very small density at the central phosphorus.

We thank the D.S.I.R. for a maintenance grant (to P. W. A.).

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[Received, December 23rd, 1963.]

¹⁴ Schulman and Sugano, *Phys. Rev.*, 1963, **130**, 506.

¹⁵ Walsh, *J.*, 1953, 2266.

¹⁶ Feher, *Phys. Rev.*, 1959, **114**, 1219.