AN ESR STUDY OF RADICALS IN γ -IRRADIATED
~~~~~POLYCRYSTALLINE AsF_3 AND AsCl_3^*
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~~~~~Abstract  
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The free radicals produced in frozen, polycrystalline AsF_3 and AsCl_3 by γ -irradiation have been characterized by ESR and shown to be AsF_3^- and, most probably, AsCl_3^- . Hyperfine interactions with arsenic are observed in each case and in AsF_3^- ligand hyperfine splittings by three fluorine atoms, two of one kind and one of another, are also seen. The ESR parameters are consistent with trigonal bipyramidal structures for the radicals with the odd electron and lone pair occupying an apical and an equatorial position, respectively, and the arsenic 4d orbitals being involved in the bonding.

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INTRODUCTION

Irradiation of tetra-atomic oxyions of Groups V-VII usually produces a hole-type radical by removal of an electron from the highest filled molecular orbital.¹ In the AB_3 -type pyramidal molecules (e.g., PO_3^{3-} , SO_3^{2-} , ClO_3^-) the highest filled MO is an antibonding a_1 orbital built largely from an sp^n hybrid on the central atom.^{2,3} Removal of an electron leaves a radical of structure similar to the parent except for a slight flattening as a result of reduction in the valence electron pair repulsion¹ and the ESR properties of such radicals are well characterized.⁴⁻⁸ On the other hand, addition of an electron to give a species with 27 valence electrons requires the use of outer d orbitals, at least in writing covalent valence-bond structures. Since 28-electron molecules such as C_2F_3 and BrF_3 have structures which may be considered as based on a trigonal bipyramid with two corners occupied by lone-pair electrons,^{9,10} it seems likely that 27-electron AB_3 -type radicals will also have such structures and evidence for this behavior has been found in an ESR study of the IO_2F^- radical ion.¹¹ Similarly, penta-atomic molecules with 34 valence electrons, such as¹² $IO_2F_2^-$, appear to have roughly trigonal bipyramidal structures with the unshared pair in the fifth position and the 33-electron radical^{13,14} PF_4 may be described similarly with the odd electron in the fifth position. While it is not necessary that outer d orbitals be involved in bonding in these cases where the ligands are very electronegative,¹⁵ there is a temptation to describe the bonding as something approaching dsp³.

In this article we identify the radicals produced by γ -irradiation of AsF_3 and AsCl_3 as AsF_3^- and AsCl_3^- and show that the ESR results are consistent with structures based on the trigonal bipyramid and with some contribution of the arsenic 4d orbitals in bonding.

EXPERIMENTAL

Anhydrous AsF_3 and AsCl_3 were obtained from Research Inorganic Organic Chemicals Inc., and were used without further purification. Frozen beads of these compounds, formed by freezing droplets in liquid nitrogen, were then irradiated with γ -rays from a ^{60}Co source producing an effective dose of 20 mrad/hr. Irradiations were performed at 77°K ¹¹ for periods of 3 - 4 hours.

ESR measurements were carried out using a Varian V-4502 X-band spectrometer with 100 KHz field modulation. Magnetic field calibration and klystron frequency measurements were achieved by methods previously described.¹⁶ ESR measurements at 77°K were done by immersing the sample in a Dewar filled with liquid nitrogen, the quartz lip of which fitted inside the Varian V-4531 Multipurpose Cavity. Measurements were also done at temperatures above 77°K using a nitrogen-flow type quartz Dewar and the Varian V-4540 variable temperature unit.

Results

Arsenic Trifluoride

Frozen polycrystalline AsF_3 , γ -irradiated at 77°K and observed without warmup, showed ESR spectra spread over a field range of about 1000 G with well-resolved hyperfine components. The spectra were sensitive to

the microwave power level, showing a tendency to saturate at power levels above 15 mw. The best spectra were obtained at a microwave power level of about 11 - 12 mw. and for a modulation amplitude of about 8 G. The lines were broad with an average linewidth of about 15 G. A typical spectrum of AsF_3 , irradiated and observed without warmup at 77°K, is shown at the top of Fig. 1 for optimum spectrometer settings. The spectrum from irradiated AsF_3 , when measured at temperatures above 77°K, showed little change until 180°K. Above this temperature the lines were broadened and, finally, irreversibly lost at temperatures above 225°K.

It can be seen from Fig. 1 that the spectrum from irradiated polycrystalline AsF_3 is characteristic of a radical with an axially symmetric g-tensor, the weaker features appearing at the low-field and the high-field wings being attributable to the outer "parallel" components and the stronger quartet feature in the middle to the "perpendicular" components. Upon closer examination the parallel components can be readily analyzed in terms of a major quartet of lines resulting from interaction between the odd electron and an arsenic nucleus (^{75}As , $I = 3/2$, abundance 100%). These four main resonances are further split into a triplet with intensity ratios 1:2:1 by interaction with two equivalent fluorine nuclei (^{19}F , $I = 1/2$, 100%) and the component lines of these triplets themselves are split into doublets from interaction with a third, non-equivalent fluorine ligand. The parallel hyperfine pattern is indicated in Figure 1. Based on this unambiguous interpretation we found $g_{||}$, $A_{||} (^{75}\text{As})$ and values of $A_{||} (^{19}\text{F})$ for both the two major fluorines and the third, non-equivalent minor fluorine.

In the so-called "perpendicular" region we see only a quartet of broad-lines. The apparent splitting of these perpendicular features and the appearance of shoulders on these can be completely attributed to

the superposition of the parallel features. Therefore, in the perpendicular region we see only ^{75}As hyperfine interaction, the ligand fluorine "perpendicular" hyperfine coupling constants being very small and of the order of the linewidths. The ESR parameters derived from this spectrum are given in Table I.

We have confirmed the above interpretation of the spectrum of Fig. 1 by computer simulation using the parameters derived from the powder pattern with variable line-widths and ligand fluorine perpendicular hyperfine coupling constants. The parameters based on the axially-symmetric model were varied until good agreement between the calculated and experimental spectrum was obtained. The parameters derived in this manner are also included in Table I and the computer simulated spectrum is shown at the bottom of Fig. 1. The spin Hamiltonian for the radical in irradiated AsF_3 can be written as:

$$\begin{aligned} \mathcal{H} = & \beta[g_{\parallel}H_zS_z + g_{\perp}(H_xS_x + H_yS_y)] + A_{\parallel}|I_zS_z + A_{\perp}(I_xS_x + I_yS_y) \\ & + A'_{\parallel}|I'_zS_z + A'_{\perp}(I'_xS_x + I'_yS_y) + A''_{\parallel}|I''_zS_z + A''_{\perp}(I''_xS_x + I''_yS_y) \\ & - g_N\beta_N I - g'_N\beta_N I' - g''_N\beta_N I'', \end{aligned}$$

assuming that the ligand fluorine and the arsenic hyperfine tensor axes are coincident (an assumption necessary to interpret the powder spectra). The non-primed hyperfine and nuclear Zeeman components refer to the ^{75}As interaction, singly primed ones to the two equivalent major fluorines ($I'=1$), and doubly primed ones to the single, non-equivalent fluorine ligand ($I''=1/2$). The quadrupolar interaction term in the Hamiltonian is omitted.

Arsenic Trichloride

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The spectrum of irradiated polycrystalline AsCl_3 (Fig. 2) is characteristic of a radical with a single unpaired electron interacting with one magnetic nucleus of spin $3/2$, and possessing a rhombic g tensor.¹⁷ Since the component linewidths are much smaller than both the separation between the g -tensor components and the arsenic hyperfine components, the spectrum can be unambiguously analyzed based on the theoretical lineshapes of ESR powder patterns.¹⁸⁻²⁰ Such an analysis yields the principal values of the g tensor and of the $A(^{75}\text{As})$ tensor reported in Table I. The quartet hyperfine interaction could arise from either $\text{Cl}(^{35}\text{Cl}, I = 3/2, 75\% \text{ abundance}; ^{37}\text{Cl}, I = 3/2, 25\%;$ $(^{35}\text{Cl}):(^{37}\text{Cl}) = 1:0.83)$ or $^{75}\text{As}(I = 3/2, 100\%)$ but the magnitude of the interaction and the absence of isotopic splittings from the two isotopes of chlorine indicates that the hyperfine interaction arises from arsenic. Chlorine hyperfine interactions must therefore be very small, of the order of the linewidths (~ 25 G). The temperature dependence of the spectrum is similar to that observed in the case of irradiated AsF_3 .

DISCUSSION

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Arsenic Trifluoride

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Since the hyperfine structure in the ESR spectrum of the radical produced in γ -irradiated AsF_3 indicates that the unpaired electron interacts with one arsenic atom and three fluorine atoms, the radiation damage must have resulted in either removing an electron from, or adding an electron to, AsF_3 to give the cation AsF_3^+ or anion AsF_3^- .

If both these are produced, either one of them is unstable and decomposes, or has a fast relaxation so its ESR lines are broadened beyond detection.

Removal of an electron from AsF_3 would produce a 25-valence electron radical AsF_3^+ , isoelectronic with PO_3^{2-} ¹⁰ and CF_3 ²¹. In the correlation diagrams given by Walsh² the odd electron in a 25-valence electron AB_3 system occupies an antibonding σ orbital built from the central atom n_s and np orbitals. Also, in such molecules the bonds to the three ligands make the same angles with the orbital of the unpaired electron so that the molecule retains its C_{3v} symmetry and in the "parallel" direction the three ligand hyperfine interactions should be identical. Again, in such 25-electron "hole" systems the g_{av} values of the radical are always above, or very near, but never less than the free spin¹ value (with the exception of PO_3^{2-}). The present results reveal non-equivalent ligands with g_{av} far below the free spin value (Table I). The magnetic parameters for 25-valence electron radicals are given in Table II for comparison and it is clear that the radical cannot be AsF_3^+ .

The alternative is that it is AsF_3^- , a 27-valence electron ("electron-excess") radical which would be produced by an electron capture process. It is well-known that gamma radiations interact with matter to produce a large number of secondary electrons and, indeed, in alkali halides one product of γ -irradiation is trapped electrons or F centers.²² It is probable then that the radical is the 27-electron species AsF_3^- .

formed by an electron-trapping process. Since the only excess-electron radicals studied by ESR appear to be $\text{PF}_4^{13,14}$ and $\text{IO}_2\text{F}^{-11}$ the experimental results for these radicals are listed in Table I for comparison.

Fluorine Hyperfine Interactions ~~~~~

Higuchi¹⁴ showed, in some calculations on the PF_4 molecule, that the isotropic fluorine hyperfine interaction $a(^{19}\text{F})$ should decrease from 360 G to nearly zero as the angle between the P-F bond and the phosphorus orbital carrying the unpaired electron increases from 90° to about 130° ; at the same time the maximum component of the anisotropic coupling tensor $2B(^{19}\text{F})$ decreases from ~ 28 G to an unobservably low value. The experimental values¹³ are in agreement with these calculations.

We have estimated the isotropic and anisotropic components of the tensors for both the two equivalent fluorines and for the unique fluorine of AsF_3^- by breaking down the experimental tensors in the usual way, assuming axial symmetry for the anisotropic portions (in MHz):

$$\begin{pmatrix} 240 & & \\ & 20 & \\ & & 20 \end{pmatrix} = \begin{pmatrix} 93 & & \\ & 93 & \\ & & 93 \end{pmatrix} + \begin{pmatrix} 147 & & \\ & -73.5 & \\ & & -73.5 \end{pmatrix}$$

$$\begin{pmatrix} 78.4 & & \\ & 10.0 & \\ & & 10.0 \end{pmatrix} = \begin{pmatrix} 32.8 & & \\ & 32.8 & \\ & & 32.8 \end{pmatrix} + \begin{pmatrix} 45.6 & & \\ & -22.8 & \\ & & -22.8 \end{pmatrix}$$

Using Hartree-Fock values for the isotropic and anisotropic fluorine $2s$ and $2p$ hyperfine interactions,²³ $a_{2s}(^{19}\text{F}) = 17, 110$ MHz and $2B_o(^{19}\text{F}_{2p}) = 3030$ MHz, the unpaired spin densities of Table IV have been calculated. The total spin density on the three fluorine atoms is then $2[0.002+0.048] + [0.001+0.015] = 0.132$.

The probable structure for PF_4 , and two possible arrangements for AsF_3 giving non-equivalent fluorines, are shown in Fig. 3. In the structure of Fig. 3(a) the two equivalent equatorial ligands ($\theta=120^\circ$) would be expected, following the treatment of Higuchi,¹⁴ to give rise to values of $a(^{19}F)$ smaller than that of the apical ligand ($\phi=90^\circ$), whereas the structure of Fig. 3(b) with $\theta = 90^\circ$, $\phi = 180^\circ$ would give rise to two major and one minor fluorine hyperfine splitting as observed and place the odd electron largely in an equatorial orbital. Both major and minor isotropic fluorine splittings are considerably smaller than observed for PF_4 , however, reflecting the smaller transfer of spin density from arsenic ($r_{AsF} = 1.72 \text{ \AA}$) to fluorine than from phosphorus ($r_{PF} = 1.52 \text{ \AA}$) to fluorine. It should also be noted that in PF_4 inversion leading to partial averaging of the apical and equatorial fluorines has been postulated to account for the decrease with temperature of $a(^{19}F)$ for the major fluorines (Table I); a similar effect may be operating here and it is planned to extend the measurements to 4°K.

Arsenic Hyperfine Interaction

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The experimental $A(^{75}As)$ tensor may be broken down into isotropic and axially-symmetrical anisotropic components as follows (in MHz):

$$\begin{pmatrix} 764.4 & & \\ & 442.4 & \\ & & 442.4 \end{pmatrix} = \begin{pmatrix} 549.7 & & \\ & 549.7 & \\ & & 549.7 \end{pmatrix} + \begin{pmatrix} 214.7 & & \\ & -107.3 & \\ & & -107.3 \end{pmatrix}$$

then

and the value $\rho_{4s} = 0.056$ computed from the Hartree-Fock value²³ $a_{4s}(^{75}As) = 9538 \text{ MHz}$ for ^{75}As ; this is considerably smaller than $\rho_{3s} = 0.13$ found¹³ for PF_4 (Table I).

The dipolar term $2B = 214.7$ MHz arises from both $4p$ and $4d$ contributions which should total about 0.76 since the spin density on the three fluorines, the lone pair and the $4s$ orbital of arsenic together are about 0.24 if the lone pair is assigned the same value as each equatorial fluorine. The fraction x in the $4p$ orbital of arsenic is then obtained from the expression $510x - 382.5(0.76 - x) = 214.7$ where $2B_O(^{75}\text{As}_{4p}) = 510 \text{ MHz}^{23}$ and $2B_O(^{75}\text{As}_{4d}) \approx 765 \text{ MHz}$. The latter value is estimated for the $4d_{z^2}$ orbital by extrapolation of $\langle r^{-3} \rangle$ values for the first-row transition elements.²⁴ In this way we obtain $\rho_{4p} = 0.57$ and $\rho_{4d} = 0.20$.

The low value of $a(^{75}\text{As})$ remains puzzling but since this value is a sum of positive and negative terms for the various s levels, it is possible that the lone-pair orbital has most of the arsenic $4s$ character (by analogy with Walsh's arguments²) and that spin polarization of the lone-pair orbital contributes appreciable negative terms to $a(^{75}\text{As})$. Nonetheless, the agreement with the behavior expected for the molecule of Fig. 3(b) is good and the deviation of the $s:p:d$ ratios found above (0.056:0.57:0.20) from the ideal sp^3d values is not unreasonable since ρ_{4s} can be expected to appear low as a result of spin polarization of the inner s orbitals; also, strict sp^3d hybridization is not expected.¹⁴

The g Tensor

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Both components of the g tensor are below free-spin value lending further support to the hypothesis that the unpaired electron is in an spd -hybrid orbital; a negative g shift was also noted in PF_4 (Table I). Since the arsenic $4d$ orbitals will be much higher than $4s$ or $4p$, and the antibonding orbitals of AsF_3 will be empty in the ground state, spin-orbit

coupling will result in mixing empty d orbitals with the odd-electron d orbital giving a negative g shift. It is similarly found²⁶ that g_{av} values for transition metal complexes with the d^1 configuration are below 2.0023. The similarity between the electronic structures of PF_4 and AsF_3^- is further emphasized by the fact that $[2.0023 - g_{av}(AsF_3^-)]/[2.0023 - g_{av}(PF_4)] = \lambda_{As}/\lambda_P \approx 4.5$, where the λ 's are the spin-orbit coupling constants of the central atoms. A qualitative MO scheme for AsF_3^- based on Walsh diagrams² and compatible with the ESR data is given in Fig. 4. In the absence of single-crystal data it has, of course, been necessary to neglect the quadrupolar terms and no information concerning the angular variation of the fluorine hyperfine coupling has been available.

Arsenic Trichloride ~~~~~

The ESR spectrum of γ -irradiated polycrystalline $AsCl_3$ shows no resolvable chlorine hyperfine interactions and the arsenic hyperfine interaction is similar to that found for AsF_3^- ; the g values have increased, with $g_{av} = 2.0053$ somewhat greater than the free-spin value, and the g tensor is rhombic.

It is difficult to give any detailed interpretation of these limited data but they may be reasonably well accounted for by ascribing them to a radical $AsCl_3^-$ with structure similar to that proposed for AsF_3^- (Fig. 3(b)). Since the molecule would then have only a reflection plane the rhombic g and $A(^{75}As)$ tensors would be accounted for. Breaking the experimental tensor into three parts in the usual manner we may write for $A(^{75}As)$ (in MHz):

$$\begin{pmatrix} 674.8 & & \\ & 366.8 & \\ & & 266.8 \end{pmatrix} = \begin{pmatrix} 436.8 & & \\ & 436.8 & \\ & & 436.8 \end{pmatrix} + \begin{pmatrix} -33 & & \\ & +66 & \\ & & -33 \end{pmatrix}$$

The isotropic term $a(^{75}\text{As}) = 436.8$ leads to a value $\rho_{4s} = 0.045$ lower than in AsF_3^- but the principal dipolar term $2B(^{75}\text{As}) = 271$ MHz is larger, indicating somewhat greater spin density in the arsenic $4p$ and $4d$ orbitals ($\rho_{4s,4d} > 0.77$). The second dipolar term could arise from appreciable spin density in the As-Cl bonds.

The absence of observable chlorine hyperfine splittings is not surprising. Even if ρ_{3s} and ρ_{3p} for the chlorine ligands were double the values 0.002 and 0.048 found for the major fluorine ligands of AsF_3^- , the values of $a(^{35,37}\text{Cl})$ and $2B(^{35,37}\text{Cl})$ would only be of the order of 20 MHz and 14 MHz, respectively, well below the observed linewidths.

The large value of g_{33} , 2.0215, is not inconsistent with the proposed structure since ligand spin-orbit coupling contributions in the case of chlorine may be appreciable. It was suggested²⁷ that the large increases in $g_{||}$ in the series MoOF_5^{2-} , MoOCl_5^{2-} and MoOBr_5^{2-} ($g_{||} = 1.874$, 1.963 and 2.090) resulted from increasing spin-orbit interaction of the ligand. The value of $g_{||}$ for AsCl_3^- remains below 2.0023 as expected for some arsenic d orbital participation.

The fact that the g and A tensors for AsF_3^- are axially symmetrical rather than rhombic may be a result of a rotation about the axis of the lone-pair orbital (Fig. 3(b)) which is not frozen out at 77°K in AsF_3^- but is in AsCl_3^- . There is evidence of broadening of the lines of AsCl_3^- as the temperature is raised above 77°K but the radical decays soon after

the onset of broadening so it is not possible to determine whether the spectrum eventually shows axial g symmetry.

While it is not unreasonable, then, to identify the radical in γ -irradiated AsCl_3 as AsCl_3^- further details of the structure cannot be given in the absence of single crystal ESR data.

References

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1. P. W. Atkins and M. C. R. Symons, The Structure of Inorganic Radicals (Elsevier, Amsterdam, 1967).
2. A. D. Walsh, J. Chem. Soc. 2296 (1953).
3. R. S. Mulliken, Rev. Mod. Phys. 14, 204 (1942).
4. A. Horsfield, J. R. Morton and D. H. Whiffen, Mol. Phys. 4, 475 (1961).
5. T. Cole, J. Chem. Phys. 35, 1169 (1961).
6. G. W. Chantry, A. Horsfield, J. R. Morton and D. H. Whiffen, Mol. Phys. 5, 233 (1962).
7. C. Jaccard, Phys. Rev. 124, 60 (1961).
8. W. C. Lin and C. A. McDowell, Mol. Phys. 7, 233 (1964).
9. R. D. Burbank and F. N. Bensey, J. Chem. Phys. 21, 602 (1953).
10. D. F. Smith, J. Chem. Phys. 21, 609 (1953).
11. S. Subramanian and M. T. Rogers, unpublished results.
12. L. Helmholz and M. T. Rogers, J. Am. Chem. Soc. 62, 1537 (1940).
13. W. Nelson, G. Jackel and W. Gordy, J. Chem. Phys. 52, 4572 (1970);
R. W. Fessenden and R. H. Schuler, J. Chem. Phys. 45, 1845 (1966).
14. J. Higuchi, J. Chem. Phys. 50, 1001 (1969).
15. E. A. C. Lucken, Nuclear Quadrupole Coupling Constants (Academic Press, New York, 1969).
16. H. A. Kuska and M. T. Rogers, J. Chem. Phys. 40, 910 (1964).
17. C. P. Poole, Jr., Electron Spin Resonance (Interscience Publishers, New York, 1967).

18. R. P. Kohin and C. P. Poole, Jr., Bull. Am. Phys. Soc. II, 3, 8 (1958).
19. F. K. Kneubühl, J. Chem. Phys. 33, 1074 (1960).
20. J. A. Weil and H. G. Hecht, J. Chem. Phys. 38, 281 (1963).
21. R. W. Fessenden and R. H. Schuler, J. Chem. Phys. 43, 2704 (1965).
22. A. R. Reinberg and L. I. Grossweiner, Phys. Rev. 122, 1734 (1961).
23. J. R. Morton, J. R. Rowlands and D. H. Whiffen, Nat. Phys. Lab. G. Brit. Rept. BPR13.
24. E. Clementi, J. Chem. Phys. 41, 295 (1964).
25. A. Abragam and B. Bleaney, Electron Spin Resonance of Transition Ions (Oxford U.P., Oxford, England, 1970).
26. H. A. Kuska and M. T. Rogers, in Radical Ions, edited by E. T. Kaiser and L. Kevan (Wiley, New York, 1968), Chap. 13.
27. P. T. Manoharan and M. T. Rogers, J. Chem. Phys. 49, 5510 (1968).

Table I. ESR parameters for AsF_3^- , AsCl_3^- and some other excess-electron radicals.

Radical	g Tensor	Hyperfine Interactions (MHz)				
		Central atom	^{19}F (major)	^{19}F (minor)	θ^{e}	ϕ^{e}
AsF_3^-	$g_{ } = 1.9648$	$A_{ } (^{75}\text{As}) = 764.4$	$A_{ } (^{19}\text{F}) = 240.8$	$A_{ } (^{19}\text{F}) = 78.4$	90°	120°
(in AsF_3 at 77°K) ^a	$g_{\perp} = 1.9986$	$A_{\perp} (^{75}\text{As}) = 442.4$	$A_{\perp} (^{19}\text{F}) = 20(\text{est})$	$A_{\perp} (^{19}\text{F}) = 10(\text{est})$		
		$a(^{75}\text{As}) = 549.7$	$a(^{19}\text{F}) = 93$	$a(^{19}\text{F}) = 32.8$		
		$2B(^{75}\text{As}) = 214.7$	$2B(^{19}\text{F}) = 147$	$2B(^{19}\text{F}) = 45.6$		
AsCl_3^-	$g_{11} = 1.9902$	$A_{11} (^{75}\text{As}) = 674.8$				
(in AsCl_3 at 77°K) ^a	$g_{22} = 2.0044$	$A_{22} (^{75}\text{As}) = 366.8$				
	$g_{33} = 2.0215$	$A_{33} (^{75}\text{As}) = 268.8$				
	$g_{\text{av}} = 2.0053$	$a(^{75}\text{As}) = 436.8$				
		$2B(^{75}\text{As}) = 271 \text{ and } 66$				
PF_4^b		$A_{ } (^{31}\text{P}) = 4222$	$A_{ } (^{19}\text{F}) = 1142$	$a(^{19}\text{F}) = 126$	90°	120°
(in PF_3 at 4.2°K)		$A_{\perp} (^{31}\text{P}) = 3718$	$A_{\perp} (^{19}\text{F}) = 1025$			
		$a(^{31}\text{P}) = 3886$	$a(^{19}\text{F}) = 1064$			
PF_4^b (in SF_6 , 138°K)	$g_{\text{av}} = 1.9985^c$	$a(^{31}\text{P}) = 3720$	$a(^{19}\text{F}) = 789$	$a(^{19}\text{F}) = 165$		
IO_2F^-	$g_{11} = 2.0989$	$A_{11} (^{127}\text{I}) = 759.1$		$A_{ } (^{19}\text{F}) = 117.6$	90°	130°
(in KIO_2F_2 , 295°K) ^d	$g_{22} = 2.0164$	$A_{22} (^{127}\text{I}) = 917.8$		$A_{\perp} (^{19}\text{F}) = 107.8$		
	$g_{33} = 1.9432$	$A_{33} (^{127}\text{I}) = 1433.3$		$a(^{19}\text{F}) = 111.1$		
		$a(^{127}\text{I}) = 1036.7$				

Footnotes to Table I

^a This work

^b Ref. 13

^c P. W. Atkins and M. C. R. Symons, J. Chem. Soc. 4363 (1964).

^d Ref. 11

^e See Fig. 3

Table II. ESR parameters for some 25-electron tetra-atomic radicals.

Radical	$g_{ }$	$g_{\perp}$	Central Atom (in MHz)		Ref.
			$A_{ }$	$A_{\perp}$	
ClO_3^-	2.007	2.008	401.7	323.2	5
SO_3^-	2.0036	2.0036	401.0	325.3	6
CF_3	2.0031	2.0031	$a_{\text{iso}}(^{19}\text{F})=399.2$ $a_{\text{iso}}(^{13}\text{C})=761.4$		21
SeO_3^-	2.0025	2.0148	1726.5	1204.1	a

^a P. W. Atkins, M. C. R. Symons and H. W. Wardale, J. Chem. Soc. 5215 (1964).

Captions for Figures

- Fig. 1. (A) First-derivative, X-band ESR spectrum of γ -irradiated AsF_3 at 77°K (observed without warmup). The g factors and hyperfine interactions are indicated for parallel and perpendicular orientations, (B) Computer-simulated spectrum of AsF_3^- using the parameters of Table I.
- Fig. 2. First-derivative, X-band ESR spectrum of γ -irradiated AsCl_3 at 77°K (observed without warmup). The g factors and arsenic hyperfine interactions are indicated.
- Fig. 3. (a) Structure of PF_4 , (b) Proposed structure for AsF_3^- . The angles between the axis of the unpaired orbital and the apical and equatorial bonds are ϕ and θ , respectively.
- Fig. 4. Qualitative MO scheme proposed for AsF_3^- based on Walsh diagrams. In C_3 symmetry the relative energies of the $2a' - 5a'$ and $1a''$, $2a''$ levels are not known. The $5,6a''$ non-bonding d levels are placed directly above the odd-electron orbital based on the low observed g values.

Fig.1. (A) First-derivative, X-band ESR spectrum of γ -irradiated AsF_3 at 77°K (observed without warmup). The g factors and hyperfine splittings are indicated for parallel and perpendicular orientations, (B) Computer-simulated spectrum of AsF_3 using the parameters of Table I.

Fig.2. First-derivative, X-band ESR spectrum of AsCl_3 , γ -irradiated at 77°K and observed without warmup. The g factors and hyperfine arsenic interactions are indicated.

Fig.3. (a) Structure of PF_4 , (b) Proposed structure for AsF_3^- . θ is the angle between the equatorial bonds and the axis of the unpaired electron orbital, ϕ is the angle between the apical bond and the axis of the unpaired electron orbital.

Fig.4. Qualitative MO scheme proposed for AsF_3 based on Walsh diagrams. In C_s symmetry the relative energies of the $2a' - 5a'$ and $1a'', 2a''$ levels are not known. The $5,6a''$ non-bonding d levels are placed directly above the odd-electron orbital based on the observed low g values.