The Radicals PF_4 and PF_5^-

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Summary It is shown by e.s.r. spectroscopy that a radical in γ-irradiated NH_4PF_6 and KPF_6, previously identified as PF_4, is in fact PF_5^-.

SOME years ago, Morton detected the isotropic e.s.r. spectrum of a radical containing one phosphorus and four equivalent fluorine atoms in irradiated NH_4PF_6.[1] He identified this as PF_4 and suggested that the extra electron was accommodated largely in the outer, 4*s*-atomic orbital on phosphorus. Subsequently, we reported the same species in γ-irradiated KPF_6,[2] and, accepting Morton's identification, we suggested that the radical should be distorted towards the trigonal bipyramidal structure for PF_5, the unpaired electron being accommodated in an orbital having 3*s*- and 3*p*-character on phosphorus, together with some σ^*-character. The detection of four equivalent

fluorine atoms was then explained in terms of a rapid pairwise interconversion of two sets of inequivalent fluorine atoms.[2]

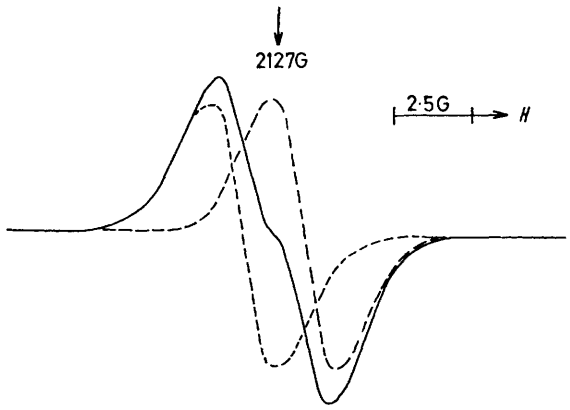

FIGURE. The first low-field component of the first derivative e.s.r. spectrum from γ-irradiated KPF_6 at room temperature assigned to PF_5^- radicals. The dashed curves represent the deconvoluted doublet with $A_F = 2{\cdot}3$ G.

This received support from Fessenden and Schuler's discovery[3] of a radical formed from PF_3 in liquid SF_6, having two sets of two equivalent fluorine atoms, which they assigned to distorted PF_4 radicals undergoing slow inversion. A radical containing one strongly interacting sulphur and four equivalent fluorine atoms was, by analogy, described as SF_4^+, although it was surprising that two such similar radicals should be inverting at very different rates.

This picture was destroyed by the recent work of Morton and Preston,[4] who showed that the species thought to be SF_4^+ is really SF_5, having four, chemically equivalent, strongly interacting fluorine atoms, together with one unique fluorine atom which fortuitously has a zero hyperfine coupling constant. Realising that this could explain the difference between results for 'PF_4' in irradiated hexafluorophosphates and in liquid SF_6, we have re-examined the e.s.r. spectra of the former systems, and conclude that the species with four equivalent fluorine atoms is not PF_4, but is almost certainly PF_5^-.

The most compelling datum is that at room temperature, when the lines are isotropic and relatively narrow, each component appears, under high resolution, as a doublet, as is shown for the first low-field line in the Figure. Since this splitting is repeated equally for all components, it must be the result of hyperfine interaction, and, by analogy with the results for SF_5, we assign this to the lone axial fluorine atom in PF_5^-. Two other results support this assignment. One is that the species now identified as PF_5^- was formed on exposure to γ-rays at 77 K as well as at room temperature. The dissociative electron capture process (1) is expected to

$$PF_6^- + e^- \rightarrow PF_5^- + F^- \quad (1)$$

take place readily even at low temperature, but the subsequent loss of a second fluoride ion is no more to be expected in an ionic crystal than is the dissociation (2).

$$PF_6^- \rightarrow PF_5 + F^- \quad (2)$$

Furthermore, we have re-examined the spectrum for 'PF_5^-' as a function of temperature between 77 K and room temperature, and find that the four equivalent fluorine atoms remain equivalent throughout. The broadening effect previously reported[2] arises only from a restriction of the overall rotation of the radical, and the non-rotating radical exhibits a spectrum in which the four strongly coupled fluorine atoms remain chemically equivalent.

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[3] R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, 1966, **45**, 1845.
[4] J. R. Morton and K. F. Preston, *Chem. Phys. Letters*, 1973, **18**, 98.