# **90.** *Unstable Intermediates. Part XVII.*[1] *Electron-spin Resonance Spectra of Some Simple Inorganic Radicals.*

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Hyperfine coupling and *g*-tensors for a variety of radicals including $F_2^-$, $F_3^{2-}$, $N_2^-$, $N_4^-$, $NH_2$, and OH are discussed in terms of simple theory.

Recent calculations by Whiffen and his co-workers[2] have shown that electron-spin resonance data for simple inorganic radicals can be used in deriving details of the wave-function of the unpaired electron, and we have used their approach to interpret results for a variety of oxy-radicals of non-metals.[1,3]

Data in the literature for a number of simple inorganic radicals are discussed from this viewpoint. Pertinent results are summarised in Table 1. Because of ambiguities in relative signs, there are often alternative sets of results for the isotropic and the anisotropic parts of the hyperfine coupling tensor. In general, however, when the *s*-character in the contributing atomic orbitals is negligible, only one combination of results fulfils the requirement that $\sum a^2_{p_i} = 1$, where $a^2_{p_i}$ is the *p*-character of the wave-function on the i'th nucleus. Values for this and corresponding *s*-orbital data are given in Table 2, for each alternative except for the radical $F_3^{2-}$. For $F_3^{2-}$, since four sets of data are obtained for the central atom and four for the outer atoms, there are sixteen possible combinations. However, only sets (i) of Table 1 fulfil the above criterion. Sets (ii) are also given in Table 2, but they gave an answer corresponding to two unpaired electrons. Other

Table 1.

*Electron-spin resonance data.* (i), (ii), etc., give alternative values for the isotropic and anisotropic parts of the hyperfine tensors which arise because of ambiguities in sign.

| | | *g*-Tensor | | | Hyperfine coupling (gauss) | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Radical | | $g_x$ | $g_y$ | $g_z$ | $A_x$ | $A_y$ | $A_z$ | $A_{iso}$ | Ref. |
| $F_2^-$ | (i) | 2·0227 | 2·0234 | 2·0031 | −276 | −276 | 552 | 335 | *a* |
| | (ii) ‡ | | | | −315·3 | −315·3 | 630·6 | 256·3 | |
| $Cl_2^-$ | (i) | 2·043 | 2·045 | 2·001 | −25·8 | −25·8 | 51·7 | 43·6 | *b* |
| | (ii) | | | | −37·6 | −37·6 | 75·3 | 20 | |
| $F_3^{2-}$ (central atom) | (i) | Not given | | | −322 | −266 | 588 | 534 | *c* |
| | (ii) | | | | −143 | −623 | 767 | 355 | |
| | (iii) | | | | −605 | −125 | 729 | 393 | |
| | (iv) | | | | −426 | −482 | 908 | 214 | |
| $F_3^{2-}$ (outer atoms) | (i) | | | | −58 | −120 | 178 | 200 | |
| | (ii) | | | | −5 | −227 | 231 | 147 | |
| | (iii) | | | | −247 | −25 | 273 | 105 | |
| | (iv) | | | | −194 | −132 | 326 | 52 | |
| $N_2^-$ | (i) | 2·0027 | 2·0008 | 1·9832 | 10·6 | −5·2 | −5·4 | 1·4 | *d* |
| | (ii) | | | | 5·3 | −2·6 | −2·7 | 6·7 | |
| $N_4^-$ | (i) | 2·0016 | 2·0051 | 1·9876 | 8 | −4 | −4 | 1·2 | *d* |
| | (ii) | | | | 4·3 | −2·15 | −2·15 | 4·9 | |
| OH * | | 2·0077 | 2·0077 | 2·0127 | −6 | −6 | 12 | 41·3 | *e* |
| — *† | | 2·002 | 2·002 | 2·040 | ±7·3 | ±2·3 | ∓9·6 | ∓13·6 | *f* |

* Hyperfine coupling data refer to the proton. † Unidentified radical in γ-irradiated $Li_2SO_4,2H_2O$. ‡ This alternative is probably excluded on experimental grounds by the work of Hayes and Twidell, *Proc. Phys. Soc.*, 1962, **79**, 1296.

References: (*a*) Castner and Kanzig, *Phys. and Chem. Solids*, 1957, **3**, 178. (*b*) Hayes and Nichols, *Phys. Rev.*, 1960, **117**, 993. (*c*) Cohen, Kanzig, and Woodruff, *Phys. and Chem. Solids*, 1959, **11**, 120. (*d*) Horst, Anderson, and Milligan, *ibid.*, 1962, **23**, 157. (*e*) McMillan, Matheson, and Smaller, *J. Chem. Phys.*, 1960, **33**, 609. (*f*) Wigen and Cowen, *Phys. and Chem. Solids*, 1960, **17**, 26.

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[1] Part XVI, *J.*, 1963, 250.

[2] Ovenall and Whiffen, *Mol. Phys.*, 1961, **4**, 135; Horsfield, Morton, and Whiffen, *ibid.*, p. 475.

[3] Atkins, Keen, and Symons, *J*, 1962, 2873; Atkins, Brivati, Keen, Symons, and Trevalion, *J.*, 1962, 4785.

combinations are even less satisfactory and have been omitted. The $p : s$ ratio is also given in Table 2. Only in set (ii) for $N_4^-$ is this ratio less than 15, which demonstrates that $s$–$p$ hybrisisation is unimportant for the orbital of the unpaired electron in these radicals.

It should be stressed, not only that the values used for $\psi^2(0)$ and $\langle r^{-3}\rangle_{av}$ are subject to error, but also that they are calculated for the corresponding neutral atoms. Also overlap has been neglected[2] throughout, and dipolar interactions from spin density on neighbouring atoms have not been included. Neglect of overlap is not thought to be important since the antibonding orbitals involved have nodes in the region of overlap. The dipolar effect of spin density on neighbouring nuclei has been calculated for the case of nitrogen dioxide and found to be negligibly small.[3] Since earlier applications of the procedure used herein have apparently been quite successful[2,3] it is felt that these and other deficiencies may not be too serious.

*Electron-deficient Centres.*—The " molecular " nature of so called V-centres in alkali halide crystals is now well established.[4,5] Loss of an electron from a halide ion leaves an anion which stabilises itself by moving towards a neighbouring atom until a symmetrical unit $Hal_2^-$ is formed. The unpaired electron must then be in an antibonding $\sigma^*$-orbital, and the electron-spin resonance results are in good accord with this.[4]

Since the $\sigma$-bond of the parent halogen molecule can be described as a combination of pure $p_z$-atomic orbitals or some hybridisation of appropriate $s$-, $p$-, and even $d$-atomic orbitals, it is of interest to calculate the relative $s$- and $p$(or $d$)-character from the hyperfine coupling tensor. This can be done by using the results of recent calculations of $\psi(0)^2$ and $\langle r^{-3}\rangle$ for the $2s$- and $2p$-levels of fluorine atoms and the $3s$- and $3p$-levels of chlorine atoms.[6] From these values one can calculate coupling constants for these levels, and hence obtain estimates of the spin populations on each atom in $F_2^-$ and $Cl_2^-$. These results are given in Table 2. It seems almost certain that in both these radicals the $\sigma^*$- and presumably also the $\sigma$-bonds are built up entirely from $p_z$-atomic orbitals. The isotropic coupling is far too small to be caused by appreciable $s$–$p$ hybridisation, and it probably represents the sum of small contributions from excited states.

TABLE 2.

Calculated spin populations.

| Radical | | $a^2{}_s$ | $a^2p_x$ | $a^2p_y$ | $a^2p_z$ | $a_p{}^2/a_s{}^2$ | Total $p$-character |
|---|---|---|---|---|---|---|---|
| $F_2^-$ | (i) | 0·02 | | | 0·51 | 25·5 | 1·02 |
| | (ii) | 0·015 | | | 0·58 | 38·6 | 1·16 |
| $Cl_2^-$ | (i) | 0·026 | | | 0·505 | 19·4 | 1·01 |
| | (ii) | 0·012 | | | 0·75 | 62·5 | 1·5 |
| $F_3^{2-}$ | (i) * | 0·031 | 0·035 | | 0·56 | 18 | 1·004 |
| | (i) † | 0·012 | | 0·039 | 0·184 | 15·3 | |
| | (ii) * | 0·021 | | 0·296 | 0·86 | 41 | 2·0 |
| | (ii) † | 0·008 | 0·137 | | 0·283 | 35 | |
| $N_2^-$ | (i) | 0·0024 | 0·37 ± 0·1 | 0·01 | | 18·5 | 0·75 ± 0·2 |
| | (ii) | 0·012 | 0·185 | | | 15·4 | 0·37 ± 0·2 |
| $N_4^-$ | (i) | 0·0087 | 0·27 | | | 31 | 1·08 |
| | (ii) | 0·0356 | 0·147 | | | 4·12 | 0·59 |

* Central F. † Outer F.

These results were obtained from the data of Table 1 together with values of $\psi^2$ (0) and $\langle r^{-3}\rangle_{av}$ (obtained by both Mayers and Roothaan) for the neutral atoms kindly communicated by D. H. Whiffen.

The results (set i) for $F_2^-$ and $Cl_2^-$ are remarkably similar and, since $\sum p_i^2$ is so close to unity, it seems reasonable to postulate that the $\sigma^*$-bonds are the same for these radicals. Since participation of $3d$-orbitals in $F_2^-$ is most unlikely, this result strongly suggests

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[4] Castner and Kanzig, *Phys. and Chem. Solids*, 1957, **3**, 178; Hayes and Nichols, *Phys. Rev.*, 1960, **117**, 993.

[5] Symons and Doyle, *Quart. Rev.*, 1960, **14**, 62.

[6] Mayers and Roothaan, personal communication from D. H. Whiffen.

that it is equally unlikely for $Cl_2^-$. This conclusion is stressed since many authors assume that $3d$-levels play a very important role in bonding for such molecules.

Unfortunately, the very small $s$-character in the $\sigma^*$-level cannot be taken as evidence that the $\sigma$-bond in the corresponding neutral molecules comprises only $p_z$-atomic orbitals, since the presence of an electron in the $\sigma^*$-level may modify the bonding considerably. Thus, even if the neutral molecules had the extreme tetrahedral distribution of electrons demanded by $sp^3$-hybridisation on each atom, the addition of a further electron would repel the six sets of $\pi$-type lone-pairs in such a way that they would tend to avoid the $z$-axis and must thus tend towards an $sp^2$-hybridisation in the planes through the nuclei normal to the molecular axis. This would result in a decrease in the atomic $s$-character in the $\sigma$- and $\sigma^*$-bonds. Since addition of a further electron to $F_2^-$ would give two fluoride ions, whose electron distribution is well represented in terms of $sp^3$-hybridisation,[7] it seems reasonable that $F_2^-$ should have almost pure $2p_z$-character in its $\sigma$-bond. In a sense, this situation is similar to the transition state in a nucleophilic displacement ($S_N2$) on saturated carbon, $F_2^-$ approximating to the transition state, there being a net inversion on addition of two electrons.

*The Ion* $F_3^{2-}$.—Another V-centre discovered by Kanzig and his colleagues [8] in irradiated lithium fluoride has been identified as $F_3^{2-}$ without much ambiguity. However, if the interpretation given by these workers is correct, this ion has a curious structure in that the unpaired electron is thought to be in an in-plane, pseudo-$\pi^*$-orbital in the nearly linear molecule rather than in the $\sigma^*$-level analogous to that of $F_2^-$ discussed above. It has been suggested [8] that this inversion of levels is the result of a crystal field arising from a triple vacancy which, being effectively negative, tends to draw the " hole " inwards. These conclusions were based on the following arguments. (i) Symmetry considerations require that if the orbital is $\sigma^*$ in type there can be no $2s$-character in the contribution from the central fluorine, whereas admixture is permitted if the $\pi^*$-level is involved. (ii) Direct hybridisation will give a positive $2s$-character, but core polarisation will contribute a negative component; this conclusion was based on calculation rather than experiment. (iii) The isotropic splitting, especially for the central fluorine, which is very large numerically, indicates considerable $s$-character which can only arise through hybridisation.

We wish to reconsider these arguments.

First, although the isotropic coupling for each fluorine is large, the actual contribution from $2s$-levels is extremely small, whatever combination of values is taken (Table 2). Next, the conclusion that polarisation effects must give rise to a negative coupling is not compelling. We stress that the isotropic coupling for $F_2^-$ is also positive and of very similar magnitude. Experimental results for many comparable radicals confirm this. It thus seems that it is not necessary to postulate a " hole " in the $\pi^*$-level. Therefore, in accord with expectation, and by analogy with $F_2^-$, we postulate that the electron is in a $\sigma^*$-level, composed, primarily, of an antibonding combination of fluorine $2p_z$-orbitals.

If the molecule were linear, as one would expect for the free ion, it would have a structure similar to that for $F_2^-$. The slight deviation from linearity in the crystal is probably the result of environmental constraints, which will be more effective than usual in view of the very weak overall bonding in this ion. A possible indication of this weak bonding comes from the marked lack of axial symmetry in the anisotropic tensors given in Table 1. These tensors can be represented as the sum of two other axial by symmetric tensors; thus for set (i) of Table 1, for the central fluorine atom, we have:

$$\begin{bmatrix} -322 & & \\ & -266 & \\ & & 588 \end{bmatrix} = \begin{bmatrix} -303 & & \\ & -303 & \\ & & 606 \end{bmatrix} + \begin{bmatrix} -19 & & \\ & +38 & \\ & & -19 \end{bmatrix}$$

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[7] Linnett and Poe, *Trans. Faraday Soc.*, 1951, **47**, 1035.

[8] Cohen, Kanzig, and Woodruff, *Phys. and Chem. Solids*, 1959, **11**, 120.

and for the outer pair:

$$\begin{bmatrix} -58 & & \\ & -120 & \\ & & 178 \end{bmatrix} = \begin{bmatrix} -99 & & \\ & -99 & \\ & & 198 \end{bmatrix} + \begin{bmatrix} +42 & & \\ & -21 & \\ & & -21 \end{bmatrix} \text{ gauss.}$$

The major tensors give the $p_z$-contribution for the atom concerned, the $z$-axis for the outer atoms being tilted 17° to that of the central atom.[8] The minor tensors then correspond to unpaired electron density in $p_y$ on the central atom and $p_x$ on the outer atoms (Table 2). (It is not certain which direction is perpendicular to the molecular plane.) These are relatively small contributions when sets (i) + (i) are used, but for several alternative sets they would be extremely large, which is physically an improbable result. This lends weight to the conclusion that only sets (i) + (i) are reasonable for $F_3^{2-}$. The minor contributions presumably arise because the corresponding excited states are relatively low-lying, which is reasonable, especially for the two outer fluorine atoms, which cannot differ much from being fluoride ions. These results give a measure of the degree to which contributions from $p_x$- and $p_y$-levels differ, since if they happened to be equal, as one would expect for $F_2^-$ or for *linear* $F_3^{2-}$, they would simply reduce the magnitude of the $p_z$-tensor.

It would be interesting to compare these minor tensors with corresponding $g$-values, but, unfortunately, these were not measured sufficiently accurately.[8] It may be significant that the $p_x$- or $p_y$-character estimated from the minor tensors are of the same order of magnitude as the 2$s$-character on the corresponding atom, which has been shown to be positive.[8] It was suggested above that the $\pi$-levels might well have considerable $s$-character through appropriate hybridisation. This would account for the positive sign of the isotropic coupling, but the results are certainly not sufficiently good to warrant quantitative comparison.

Finally, attention is called to the fact that, whatever may be the correct set of values derivable from the coupling tensors, the unpaired electron spends somewhat more time on the central fluorine than on either of the others. Using the results of set (i), we find that the spin density on the central fluorine is 0·56. This result is qualitatively in accord with our results for certain oxy-radicals.[1,3]

*The Radical* $N_2^-$.—Exposure of single crystals of potassium azide to ultraviolet light gives rise to two paramagnetic species, one containing two, and the other four, equivalent nitrogen atoms.[9] The identity of the former has not been considered in detail, and it is now postulated that the spin-resonance results (Table 1) are in good accord with the formulation $N_2^-$.* The only reasonable alternative seems to be the molecule $N_3$, but, for reasons given below, this is thought to be somewhat less acceptable.

The radical $N_2^-$ is isoelectronic with NO, and must therefore have a single electron in the $\pi^*$-level. In order that spin-resonance absorption be detected close to $g = 2$ there must be considerable quenching of the spin–orbit coupling by the crystal field of the surrounding ions. This is not unexpected in view of results for the very similar anion $O_2^-$ in a comparable environment.[10] However, the $g$-tensor does not exhibit the axial symmetry one might expect for such an ion. If, therefore, the present identification is correct, we must postulate that the crystal field is asymmetric and splits the $\pi^*$-levels to such an extent that the electron is largely confined to one of these. The direction associated with $g = 2{\cdot}0027$ is then taken as the density axis of the occupied $p$-$\pi$ level ($x$), and the low $g$-value of 1·983 is identified as $g_z$, when $z$ is the molecular axis. This leaves $g_y = 2{\cdot}0008$.

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* [Note added in proof.] This conclusion has also been drawn by Wylie, Shuskus, Young, Gilliam, and Levy (*Phys. Rev.*, 1962, **125**, 451).

[9] Horst, Anderson, and Milligan, *Phys. and Chem. Solids*, 1962, **23**, 157.

[10] Bennett, Ingram, Symons, George, and Griffith, *Phil. Mag.*, 1955, **46**, 443.

The hyperfine tensor is in accord with this provided the isotropic coupling is taken to be positive. Of the alternative sets given in Table 1, we favour that which gives +10·7 gauss for the anisotropic coupling along $x$. This corresponds to about 0·4 for the spin density in $2p_x$ on either nitrogen when $\langle r^{-3}\rangle_{2p}$ is taken as $22{\cdot}5 \times 10^{24}$ cm.$^{-3}$.[11] Comparison with results for other radicals having their unpaired electrons largely in a $p$-$\pi$ level on nitrogen shows that these results accord with expectation,[12] although the discrepancy of 20% in the total coupling is large for such a small radical. However, there was a large error in the estimate of the maximum hyperfine splitting [9] (Table 1) and, if the largest of the extreme values is used, then the total $p$-character is very close to unity.

The alternative, that this radical is $N_3$, should be considered since the unpaired electron will be largely confined to the outer atoms in this molecule, and hence hyperfine coupling to the central nitrogen could well be lost in the line width. The 15-electron molecule, $N_3$, should be linear, with a " hole " in the degenerate $\pi_g$-level on the outer nitrogens. Hence, to accord with the results, there must be a large, asymmetric crystal field which quenches orbital motion and raises the degeneracy of the $\pi_g$-level to such an extent that the " hole " is confined to the upper level. However, although the hyperfine interaction is then reasonable for $N_3$, the $g$-tensor is not since, in contrast to $N_2^-$, this molecule should have a $g$-value greater than 2·0023 along the molecular axis. It thus seems that the radical under consideration is $N_2^-$ rather than $N_3$.

*The Radical* $N_4^-$.—That a radical in irradiated azide should have four equivalent nitrogen atoms [9] is surprising at first sight, and if one accepts the formulation $N_4^-$ it is of interest to speculate about the geometry and electronic structure of this ion. Addition of a nitrogen atom to an azide ion could give four reasonable structures. One having a central nitrogen atom attached to three others can be dismissed, since the central atom would interact very weakly with the unpaired electron relative to the other three. The same applies to a linear arrangement of four nitrogen atoms. However, a planar, square arrangement appears to be in accord with the results, as also is an arrangement in which each atom occupies one corner of a tetrahedron.

Of these, we favour the planar configuration and recall that the hypothetical ion $N_4^{2-}$ is isoelectronic with the dimer of nitric oxide, which is known to have a square-planar configuration. Loss of an electron then leaves a " hole " in a doubly degenerate $\pi$-level similar to that for the planar form of the unknown compound, cyclobutadiene. Once again, in order to conform with the results, we must postulate distortion, although in this instance, even in the absence of interionic forces, there would probably be a considerable Jahn–Teller distortion, lifting the degeneracy of the levels.

The spin-resonance results are remarkably similar to those assigned to $N_2^-$, which can be understood in terms of a valence-bond description of $N_4^-$ as a resonance hybrid of equivalent structures comprising $N_2^-$ and $N_2$. The $g$-tensor is understandable in terms of such a structure having alternate strong and weak N–N bonds. Then taking $z$ and $y$ parallel to the strongly and the weakly bonded atoms, respectively, we expect to find $g_z \ll 2{\cdot}0023$, and $g_x \doteqdot g_y \doteqdot 2{\cdot}0023$. The tensor given in Table 1 is not far from these requirements except that either $g_x$ or $g_y$ is slightly greater than expected. This assignment requires that the largest hyperfine coupling occurs when the magnetic field is parallel to $x$; in fact, the largest coupling is associated with $g = 2{\cdot}0016$, so that this is taken as $g_x$.

As with $N_2^-$, there is ambiguity regarding the relative signs of the principal values of the hyperfine tensor. Taking each principal value as positive gives an isotropic coupling of +4·93 gauss for each nitrogen and +4·3 for $A_x$ (set ii). The total $p$-character of 0·59 is smaller than expected, and the total $s$-character of 0·143 very much larger than expected, giving a $p : s$ ratio of 4·12. This alternative is therefore rejected in favour of set (i), which

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[11] Dousmanis, *Phys. Rev.*, 1955, **97**, 967.

[12] Symons, " Inorganic Free Radicals," ed. R. F. Gould, A.C.S. Monograph, 1962 (Advances in Chemistry Series).

is in fair accord with the model except that the total *p*-character is considerably greater than for $N_2^-$.

Although the hyperfine coupling constants of set (ii) are incompatible with the distorted square-planar model, it is conceivable that they would be in accord with a distorted tetrahedral arrangement. Lipscomb [13] has discussed such a structure for the molecule $C_4H_4$ in terms of approximate tetrahedral hybridisation on each carbon atom. The extra electron would then be in an orbitally degenerate *e* antibonding level. This might account for the low average *g*-value and the considerable *s*-character. However, a consideration of crystal structure shows that the tetrahedral is sterically less reasonable than the planar arrangement, so no further elaboration will be given.

*Amino- and Hydroxyl Radicals.*—Despite the unusual pattern of intensities amongst hyperfine components, there seems little doubt that the spectrum recorded by Foner *et al.*[14] for radicals trapped in an argon matrix at 4·2°K is correctly assigned to $NH_2$. This was established [14] by comparing spectra for $^{14}NH_2$, $^{15}NH_2$, and $^{14}ND_2$. One factor which probably contributes to the curious pattern of intensities is that the radicals may be undergoing a form of restricted rotation similar to that observed [15] for $NH_3^+$.

At elevated temperatures, the spectrum assigned to $NH_3^+$ consists of a well-resolved triplet of quartets having the expected intensities and splittings. As the temperature is lowered, the outer pair of quartets broaden and are ultimately lost whereas the central quartet remains well resolved. At very low temperatures this central pattern becomes asymmetric in a manner comparable with that noted for the spectrum of methyl radicals [16] and silyl radicals [17] at low temperatures. These changes can be understood in terms of a rotation which is rapid only in the molecular plane, in which interconversion requires relatively slight movement.

Such motion will normally result in a marked change in the spectrum since an axially symmetric anisotropic component will be added. If the *g*-anisotropy is small, then all we need to consider is that from the $^{14}N$ and proton hyperfine coupling. The latter will remain small for rotation within the plane of the molecule since, when the field is normal to the plane, the anisotropic coupling is close to zero, and when the field is parallel it will average almost to zero. Coupling to $^{14}N$, however, will be large but to a first approximation, will affect only the outer components of the $^{14}N$ triplet, since the central component is derived from $I_s = 0$.

Similar reasoning goes some way to explain the apparently anomalous intensities of the lines in the spectrum assigned [14] to $NH_2$, if it so happens that rotation in the molecular plane is sufficiently restricted to broaden the $I_s = \pm 1$ components of the $^{14}N$ triplet. However, the distribution within these triplets should normally be 1 : 2 : 1 from two equivalent protons, whereas the intensities are close to 1 : 1 : 1. It is not obvious why this should occur, though the effect could be understood in terms of a slight inequivalence of the protons giving rise to a small broadening of the central line.

Isotropic coupling constants for amino-radicals are close to those for $NH_3^+$, and show that the unpaired electron is still largely in the *p*-orbital normal to the molecular plane. This is not the case, however, for hydroxyl radicals.

Before discussing results for hydroxyl radicals, some justification for the assignment must be given. McMillan, Matheson, and Smaller [18] have given principal values for the *g*-tensor and proton hyperfine coupling tensor for a radical containing only one hydrogen atom and formed in single crystals of ice on exposure to $\gamma$-radiation. Siegel *et al.*,[19] have similarly treated polycrystalline $H_2O$ and $D_2O$ and it is possible to extract, from the

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[13] Lipscomb, *Tetrahedron Letters*, 1959, No. 4, 20.

[14] Foner, Cochran, Bowers, and Jen, *Phys. Rev. Letters*, 1958, **1**, 91.

[15] Hyde and Freeman, *J. Phys. Chem.*, 1961, **65**, 1636.

[16] Jen, " Formation and Trapping of Free Radicals," Academic Press, Inc., New York, 1960, p. 243.

[17] Cochran, 4th Internat. Symposium on Free Radicals, 1959, D11.

[18] McMillan, Matheson, and Smaller, *J. Chem. Phys.*, 1960, **33**, 609.

[19] Siegel, Baum, Skolnik, and Flournoy, *J. Chem. Phys.*, 1960, **32**, 1249.

overall spectrum, values for $g_{\perp}$, $g_{//}$, and $A_{\perp}$ which are close to those derived from single crystals.*

The only other reasonable postulate is that this species is $HO_2$. This alternative is rejected on the following grounds. (i) The results are not in accord with expectation for $HO_2$, and, in particular, the anisotropic hyperfine coupling is too large. (ii) A radical thought to be $HO_2$ can be formed from hydrogen peroxide under a variety of conditions,[20] and the constants derived from the spin-resonance spectrum assigned to this species are very different from those under consideration. (iii) A spectrum similar to that assigned to $HO_2$ remained after irradiated ice had been annealed until the primary spectrum was completely lost.[19] The relative intensity of this secondary spectrum increased as the overall damage was increased. This result is in good accord with the postulate [19] that the primary radicals are hydroxyl and the secondary $HO_2$, and it is hard to formulate any alternative.

If the postulate of McMillan *et al.*[18] is accepted, then the results reproduced in Table 1 must be characteristic of hydroxyl radicals. Two alternative models can be adopted for linear radicals: one in which the orbital contribution is quenched but axial symmetry retained, and the other in which asymmetric forces from the environment lift the degeneracy of the $\pi$-orbitals to such an extent that only one is occupied (cf. $N_2^-$). The present results are incompatible with the latter model, since the anisotropic proton hyperfine coupling has axial symmetry. For an electron in a *p*-orbital on carbon in radicals of type $R_2{\cdot}CH{\cdot}$, dipolar coupling to the $\alpha$-proton has typical principal values $+15{\cdot}4$ gauss for the field along C–H ($z$), $-1{\cdot}6$ for the field perpendicular to the model plane ($x$), and $-13{\cdot}8$ for the field along $y$. For an electron in a degenerate $\pi$-orbital $A_z$ is unchanged, but $A_x$ and $A_y$ must both equal the average value, which is $-A_z/2$. For an electron in a $\pi$-orbital composed of $p_x$ and $p_y$ on oxygen, $A_z$ should be somewhat greater than 15·4 gauss since $\langle r\rangle_{2p}$ for oxygen and carbon atoms are 0·6519 and 0·9096 Å, respectively.

The measured value for $A_z$ is only 12 gauss. This result suggests that the electron spin is either " delocalised " in some manner by interaction with the environment, or that the orbitals involved are not pure $2p$ in character. The latter suggestion is supported by the surprising result that the isotropic proton coupling is relatively large, and *positive*. This is in marked contrast with results for $CH_3$, $NH_3^+$, and $NH_2$, all of which have an isotropic coupling constant close to $-23$ gauss. The negative sign has been confirmed for methyl,[21] and is theoretically predicted for coupling between $\alpha$-protons and unpaired electron in *p*-orbitals.

The positive sign and relatively large magnitude for the isotropic proton coupling for trapped hydroxyl radicals would be understandable if, possibly as a result of strong hydrogen-bonding to neighbouring water molecules, there was a slight admixture of $2s$-character into the $\pi$-orbitals. If this can occur it would result in a movement out of the $xy$-plane through the oxygen nucleus, so that the average spin density would be further from the proton. This would cause a reduction in the dipolar coupling without altering its form. At the same time, as discussed in the preceding paper,[1] the isotropic coupling should pass through zero and increase to a large positive value. Qualitatively, a value of $+40$ gauss is in accord with this trend.

This suggestion is tentative, and it is concluded that both theoretical and experimental studies are required to resolve the problem. Our main intention is to draw attention to a very curious apparent paradox.

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* Comparison of the text of the paper by McMillan *et al.* with their quoted data suggests that there may be a misprint, and that the correct *g*-values should be $g_{//} = 2{\cdot}0077$ and $g_{\perp} = 2{\cdot}0127$. If so, then some explanation must be found for the unexpectedly large *g*-value perpendicular to the molecular axis.

[20] Smith and Wyard, *Nature*, 1960, **186**, 226; Livingston, Ghormley, and Zeldes, *J. Chem. Phys.*, 1956, **24**, 483; Gibson, Symons, and Townsend, *J.*, 1959, 269.

[21] Cole, Pritchard, Davidson, and McConnell, *Mol. Phys.*, 1958, **1**, 406.