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ESR of Radiation Damage in Inorganic Solids

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The way in which electron spin resonance can be applied to the problem of identification of species formed on exposure of inorganic materials to high energy radiation is outlined. Recent results for a wide range of inorganic radicals formed in this way are collated and discussed. Radicals are classified as σ *or* π *depending upon their electronic structure, and the problem of spin-polarization in* π*-radicals is discussed in some depth. Among the more recently discovered radicals mentioned are* SH, S_2^-, Se_2^-, PH_2, CS_2^-, FOO, $ClOO$, BH_3^-, CO_3^{3-}, $C_2H_2^-$, *and* $S_2N_2^+$. *The structure of a center originally described as* F^{2-} *formed in beryllium oxide is discussed in terms of the unit* Be_2F^{2+}. *Assignments are viewed critically, and in some instances alternative identifications are offered.*

The primary aim of this review is to supplement three earlier discussions of the magnetic properties of inorganic radicals (*9, 19, 83*).

Irradiation of diamagnetic solids commonly results in the formation of one or more paramagnetic "centers" because the initial act is electron ejection. If the ejected electron can be trapped in some manner at a distance from the parent molecule or ion and if the residual cation becomes sufficiently modified to prevent hole-migration, then these initially trapped products, which must necessarily be paramagnetic, can generally be detected by ESR.

Now that a large number of such centers have been identified, the study of new centers is often quite straightforward. Apart from electrons trapped at holes in the solid, such as anion vacancies (for brevity, these will be referred to simply as "trapped electrons"), the centers are usually molecular in nature, having properties that are largely those of a small molecule or ion, with relatively minor perturbations by the environment.

For systems with orbitally degenerate ground states, such as S_2^- (*see Some Diatomic Radicals*), there is often a large "crystal field" splitting of the levels. Sometimes there is a minor hyperfine coupling to adjacent ions; interesting recent examples being the H-center in alkali halides which consists of Hal_2^- units weakly coupled to two flanking halide ions lying along the molecular axis (*1*), and ^{23}Na hyperfine coupling in the spectra of CS_2^- (*13*) and N_2^- (*48*). The ENDOR technique should prove to be particularly powerful for studying such weak interactions.

However, if the magnetic center is part of a polymeric system such as the silicates or borates, then its properties may be considerably distorted compared with expectation for the corresponding small molecule. This field has been recently reviewed (*19, 83*) and will not be elaborated here.

The great power of the ESR technique is that the hyperfine- and, to a less extent, the *g*-tensors give quite intimate structural detail, leading to estimates of spin-density in *s*- and *p*-orbitals on one or more of the atoms in the center. It is convenient to classify radicals as σ or π (*82*), the major distinction being that in the former there is a real contribution from an atomic *s*-orbital of at least one of the atoms, this giving rise to an appreciable isotropic hyperfine coupling if the nucleus involved is magnetic. For π-radicals there is usually a small residual isotropic coupling which appears to stem largely from spin-polarization of the valence electrons, especially those involved in σ-bonding (*57*). This also gives useful structural information and the magnitude of this coupling can be an important aid in identification. One way of proceeding will be outlined later.

It has proved convenient to classify centers other than trapped electrons as monatomic, diatomic, triatomic, tetra-atomic and penta-atomic (*9*), these classes being expanded to include more complex species having similar basic structures. Thus, the radicals R_2NO and $(SO_3)_2NO^{2-}$ were classed with the corresponding simple AB_3 tetra-atomic radicals.

A selection of the basic radicals discussed at length in References 9, *19*, and *83* are given in Table I. In this review we examine a range of more recently studied radicals and conclude with a brief discussion of the mechanisms of damage in the solids under consideration.

Spin Polarization in π-Radicals

Despite the complexity of the theory underlying the appearance of contact hyperfine coupling in π-radicals, it seems that, for many radicals, the results are sufficiently simple as to provide a useful guide in identification and in structural analysis (*57*).

Our basic approach is to consider, as with σ-radicals, the apparent spin-density in the highest filled atomic *s*-orbital of the atom concerned. It has proved convenient to invoke the U^X-value which is related to the familiar Q^X-value (*65*) by dividing by the appropriate A^X-value for the atom (X) concerned and multiplying by 100 to give the value as a percentage.

These Q- or U-values can be broken down into terms for the polarization of σ-bonding, lone-pair and core electrons, but we find that the equation

$$100a^X/A^X = \rho_X U^X + \Sigma \rho_Y U^X_{YX} \quad (1)$$

adequately accommodates a wide range of results for organic and inorganic radicals (*57*). Here a^X is the experimental isotropic hyperfine coupling in gauss, A^X is the atomic value for the highest filled *s*-orbital, ρ_X and ρ_Y are spin-densities on X, the nucleus concerned, and on Y, any adjacent nucleus having significant spin-density.

Table I. Some of the Simple Radicals Recently Detected and Studied by ESR Spectroscopy

Atoms and Monatomic Ions	H, N, Cl, Ag
Diatomic Radicals	OH, N_2^-, F_2^-, Cl_2^-, FCl^-, XeF, KrF
Triatomic Radicals	CO_2^-, CS_2^-, NO_2, NO_2^{2-}, O_3^-, SO_2^-, SeO_2^-, NF_2, PF_2, FOO, ClOO
Tetra-atomic Radicals	BH_3^-, CH_3, NH_3^+, SiH_3, CO_3^-, NO_3, NO_3^{2-}, CF_3, PO_3^{2-}, SO_3^-, ClO_3, SeO_3^-, AsO_3^{2-}, HPO_2^-
Penta-atomic Radicals	PF_4, SF_4^+, $As(OH)_4$, PO_4^{2-}, SO_4^-

We find that in cases where ρ_X is known unambigously, U^X is remarkably constant, being about 3.9% for all radicals. There is a real trend to smaller values as the number of σ-bonds to X decreases and values as low as 2.2% have been obtained (*see* Table II). However, on going from molecules to atoms there is a dramatic fall to about 0.2%, and this has been taken to mean that the major contribution comes from polarization of bonding or lone-pair electrons, thus justifying the use of Equation 1.

The "adjacent atom" terms, U^X_{YX}, can also be obtained directly for a few radicals such as NO_3, where the unpaired electron is confined entirely to an orbital on the oxygen atoms. This term is found to depend markedly upon the hybridization of the σ-orbitals involved, but otherwise seems to be relatively insensitive to changes in the structure of the radicals studied.

Table II. Values of U^A and U_{BA}^{A} for Selected Atoms and Radicals

	Species	*Nucleus A*, (ρ^A)	U_{BA}^{A} [a]		U^A
Atoms	N	^{14}N (1)			0.22
	O	^{17}O (1)			0.20
	F	^{19}F			0.21
	P	^{31}P (1)			0.18
Average					0.20 ± 0.02
Diatomic Radicals	NO	^{14}N (0.8)	−2.0	(0.5)	2.2
	N_2^-	^{14}N (0.5)	−2.0	(0.5)	2.5
Average					2.35
Triatomic Radicals	NH_2	^{14}N (1)			2.3
		^{1}H (0)	−4.7	(1)	
	$NH(SO_3)^-$	^{14}N (1)			2.4
	$N(SO_3)_2^{2-}$	^{14}N (1)			2.4
	NF_2	^{14}N (0.8)	−1.0	(0.33)	3.7
		^{19}F (0.1)	−0.4	(0.1)	4.9
Average (central atom)					2.9
Tetra-atomic Radicals	CH_3	^{13}C (1)			3.4
		^{1}H (0)	−4.5	(1)	
	NH_3^+	^{14}N (1)			3.6
		^{1}H (0)	−4.9	(1)	
	$(SO_3)_2NO$	^{14}N (0.6)	−1.0	(0.33)	4.8
		^{17}O (0.4)	−0.7	(0.2)	4.1
	CO_3^-	^{13}C (0)	−1.0	(0.33)	
	NO_3	^{14}N (0)	−1.0	(0.33)	
Average (central atom)					3.9
Penta-atomic Radicals	PO_4^{2-}	^{31}P (0)	−0.7	(0.25)	

For atoms the hyperfine splitting has been divided by the number of unpaired electrons.

[a] The number in parenthesis gives the fractional *s*-character used for obtaining U^A_{BA}.

We feel that a sufficient number of results have now been accommodated to permit the application of Equation 1 to the calculation of spin-densities or to help the task of identifying unknown centers. Some results are gathered together in Table II.

Some Diatomic Radicals

·OH and ·SH. The hydroxyl radical, though well established through studies of electric-dipole transitions in the gas-phase, has proven most elusive in the liquid and solid states.

This is because of the strong coupling between the electron spin and its orbital angular momentum about the molecular axis. For an ESR signal to be readily detected in condensed phases an interaction with the medium is required to quench the angular momentum. Hence, rare-gas matrices are unsatisfactory, but strongly polar media such as ice or salt hydrates ought to be suitable, and strong resonance signals are indeed obtained from these materials after exposure to high energy radiation.

Interpretation of the resulting spectra has not been an easy task. For ice this is probably because the spectra of single crystals for most orientations arise from radicals in many magnetically non-equivalent sites. These spectra are dominated by an apparently almost isotropic doublet close to the free-spin *g*-value and separated by about 40 gauss (*12*). However, the earlier discussion of U-values shows that the isotropic hyperfine coupling to the OH radical proton ought to be about −25 gauss rather than the +40 gauss suggested. Also, it was hard to understand why the result should differ so greatly from the value of −27 gauss obtained for gas-phase radicals (*76*), and why the purely dipolar coupling was apparently too small for unit spin-density (*81*).

Further study (*21*) has shown that a broad, low-field feature, previously assigned to other radical species, is really an integral part of the spectrum. Two full analyses of the single crystal data (*22, 36*) together with a re-interpretation of the spectra of various irradiated salt hydrates along the same lines (*53*) have revealed many details of the way in which the hydroxyl radical interacts with the environment, although there remain several obscurities (*22*).

Basically, it seems that one of the four hydrogens surrounding a given oxygen atom in ice is displaced, with a consequent relaxation of the oxygen probably towards the remaining three protons. It is the two hydrogen-bonded protons that are responsible for quenching the orbital angular momentum and their presence is confirmed by the appearance of a small triplet splitting on the main lines for certain orientations.

The hyperfine tensor (Table III) is now far closer to that expected, but the anisotropy is still less than that for gas-phase radicals or that calculated using simple theory (*22*). This may be because of a residual movement or libration and it is hoped that studies at 4.2°K. will shed further light on this.

It would be interesting to compare these results with those for the HS radical, and recently spectra have been described which are said to relate to this radical (*52, 55*). Hadley et al. (*55*) irradiated frozen aqueous hydrogen sulfide with ultraviolet light and obtained a powder spectrum which was reasonably well fitted by the parameters of Table III. This analysis was supported by the results from deuterated samples. Gunning *et al.* (*52*) obtained spectra from both H_2S and D_2S after irradiation of the solids, which are quite similar in appearance (Table III).

Table III. Magnetic Parameters

Lattice		g-values		
		g_x	g_y	g_z
OH	ice	2.005 ± 0.002	2.009 ± 0.001	2.06 ± 0.01
	ice	2.005 ± 0.001	2.009 ± 0.005	2.0585 ± 0.002
	$CaSO_4 \cdot 2H_2O$	2.0028	2.0028	2.1108
	$LiSO_4 \cdot H_2O$	2.0065	2.0065	2.0667
SH	H_2S	2.003	2.024	2.061
	aqueous H_2S	(2.000	2.025	2.039)

[a] Calculated (*21*) from Radford's gas phase data (*76*).

Table IV. Magnetic Parameters

Radical	*Medium*	*Nucleus*	g-tensor		
			g_{xx}	g_{yy}	g_{zz}
O_2^-	NaCl	^{17}O	1.9483	1.9436	2.4529
	KCl		1.9512	1.9551	2.4360
	KBr		1.9268	1.9314	2.5203
	KI		1.9370	1.9420	2.4859
	RbCl		1.9836	1.9846	2.2947
	RbI		1.9674	1.9695	2.3774
S_2^-	NaI	^{33}S	1.9942	2.0178	2.2303
	KCl		0.9484	0.9500	3.4303
	KBr		0.8388	0.8434	3.5037
	KI		1.6254	1.6369	3.0629
	RbI		1.2895	1.2968	3.3595
Se_2^-	NaI	^{77}Se	1.8148	1.9042	2.8015
	KI		0.7698	0.7824	3.7079
SSe^-	NaI	^{77}Se ^{33}S	1.9004	1.9575	2.6064
	KI	^{77}Se ^{33}S	0.9532	0.9681	3.6290

[a] The data in References 70, 71 and 60 were given in Mc/s. They have not been converted into gauss because of insufficient information.

The presence of a radical having an isotropic hyperfine coupling to a single proton in the 7 to 10 gauss region and an anisotropic g-tensor seems to be indicated, but several features of the results, especially on annealing, are puzzling.

Given that these spectra have been correctly analyzed, it is difficult to see how they could relate to the SH radical. The g-tensor is close to that for ·OH radicals, but for ·SH in H_2S one would expect a far larger

for OH and (possibly) SH

Hyperfine coupling constants (gauss)			
A_x	A_y	A_z	*Ref.*
−26 ± 4	−44 ± 2	0 ± 6	*22*
−26 ± 3	−43.7 ± 0.05	±5 ± 5	*36*
−32.5	−43	±3.3	*53, 54*
−24	−46	±4	*53*
−42.6 ± 0.3	−42.6 ± 0.3	+5.0 ± 0.3	[a]
−35.6	−49.6	+5.2	[b]
7	7	7	*52*
9.5	9.5	9.5	*55*

[b] Calculated (*21*) from Radford's gas phase value (*76*) of $A_{iso} = -26.7 \pm 0.2$ and using the method of McConnell and Strathdee (*66*).

for O_2^-, S_2^-, Se_2^-, and SSe^-

Hyperfine tensor (Mc/s)[a]			
a_{xx}	a_{yy}	a_{zz}	*Ref.*
189.3	0 ± 10	55.1	
181.3	0 ± 10	71.1	
184.3	0 ± 10	64.2	*60*
201.6			
193.7			
[b]	[b]	[b]	
[b]	[b]	137 ± 2	
[b]	[b]	145 ± 2	
64 ± 5	[b]	93 ± 3	
[b]	[b]	105 ± 5	
320 ± 10	<30	265 ± 10	*70, 71*
70 ± 10	45 ± 15	740 ± 5	
450 ± 10	30	145 ± 25	
[b]	[b]	[b]	
120 ± 5	<20	750 ± 5	
<20	<60	140 ± 5	

[b] Results not obtainable from the spectra.

variation in *g*. Also, it is hard to see why the proton coupling should be so small. Firstly, it should be strongly anisotropic, since any rotation capable of averaging the hyperfine anisotropy ought also to average the *g*-tensor, but, in fact, three different *g*-values are rather strongly indicated. Also, the U-value analysis of a range of radicals (*8*) strongly supports the contention that a_{iso} (H) ought to be in the region of −25 gauss. [Compare CH_3 (−24 gauss), NH_3^+ (−24 gauss), NH_2 (−25 gauss) and OH

(−27 gauss)]. The value assigned to PH_2 of (−)18 gauss is less (*26*), but the spectra were poorly resolved so this is only approximate. The coupling of ±8 gauss for SiH_3 is indeed very small, but this almost certainly arises because the radical is pyramidal (*see Some Tetra-atomic Radicals*).

It seems far more likely that radicals such as HS_2 or HS_x are responsible for these spectra. Some support for this stems from the fact that "polymeric" sulfur radicals were identified by their ESR spectra after annealing under various conditions (*52, 55, 77*).

Some confusion has arisen because of the result for HS radicals in the gas-phase. The proton hyperfine coupling of about 5 gauss (*67*) has been taken by both groups to be the Fermi contact value, whereas, in fact, it does not relate directly to the contact term.

O_2^-, S_2^-, Se_2^- and Related Species. Results for these radicals are given in Table IV. Although S_2^- and Se_2^- could well be important products of radiation damage of many materials, they were, in fact, formed by direct doping of alkali halide melts with the vapor of the elements. Their ESR spectra (*70, 71*) are of great interest, since the *g*-values are quite similar to the values of 4 and 0 which would be expected had there been no quenching of the orbital angular momentum.

If one uses the standard, highly simplified, procedure for deducing the total spin-density (*9*), the values which are obtained are so close to unity that they lend very strong support not only to the calculated value of $<r^{-3}>$ but also to the basic approach of neglecting overlap effects (which can be supported on other grounds although many authors contend that overlap ought to be taken into account) and neglecting orbital expansion or contraction. That the calculated $<r^{-3}>$ values are reasonable can also be gauged by the good agreement with the values obtained from atomic beam experiments (*58*).

Some AB σ-Radicals. In a previous review (*19*) we showed how the fluorine hyperfine parameters (*17, 23, 43, 44, 47*) for various XF^- σ-radicals (V_K centers) depend upon the electronegativity of the other halogen atoms (X). Revised values for the parameters (*79*) have led us to present the data again (*see* Figure 1 and Table V). Also included are results assigned to KrF and XeF, although direct comparison is difficult because it is not clear what measure of electron-attracting power one needs to use.

It is clear that there is a drift of spin-density away from fluorine as the electron-attracting power of X falls. This is because of the antibonding nature of the unpaired electron. Also, there is an increase in the *s*-character of the X-orbital as the electron-attracting power of X falls. This probably arises partly because of a greater direct admixture of the atomic *s*-orbital into the σ*-level and partly from a greater spin

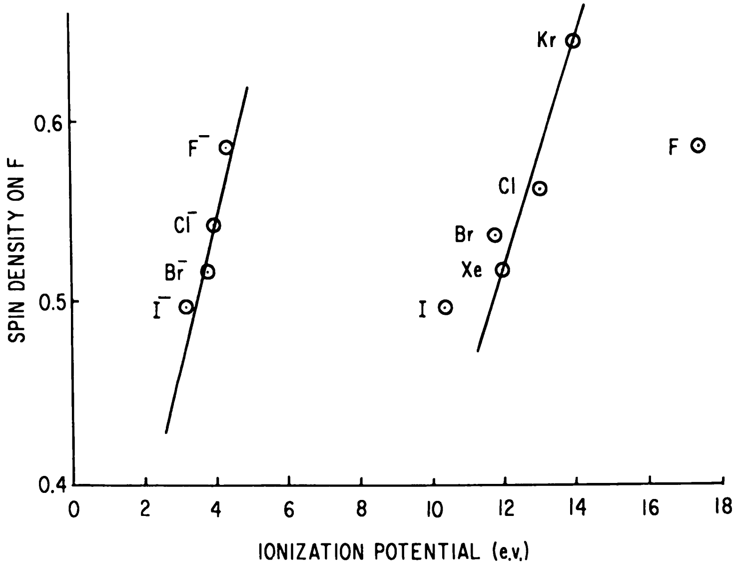

Figure 1. Dependence of the spin-density on fluorine in XF σ-radicals as a function of the ionization potential of X

polarization of the nearest filled σ-level which will have a relatively large contribution from the *s*-orbital of the least electronegative atom.

It is interesting to consider the parameters for a radical (*16*) thought to be FO^{2-} in the light of these trends. The data, which are included in Table V certainly accord, qualitatively, with expectation for this radical. However, the total spin-density on fluorine is very low indeed, being less than that in FOO. Because the sign of $A_\perp$ is unknown, there are two possible sets for the ^{17}O parameters (Table V). If set (i) is taken, then about 84% of the electron is accounted for, but the *p/s* ratio of about 60 is far larger than one would predict by comparison with the V_K centers. Set (ii) gives an acceptable *p/s* ratio, but the net spin-density is only 58%. It is not possible to predict a value for the spin-density on fluorine from the curves of Figure 1, but in view of the very small spread of values recorded there, the very different value for the radical described as FO^{2-} is hard to understand. Possibly, the unit is better pictured as an O^- ion strongly perturbed by an adjacent F^-. The ^{17}O parameters remain curious, however, and it may well be that the FO^{2-} formulation is oversimplified.

Some Triatomic Radicals

NH_2, PH_2 and SH_2^-. The radical NH_2 has been studied in a variety of matrices and pertinent results are summarized in Table VI. The

Table V. Magnetic Parameters for

Radical	*Nucleus*	*Medium*	*g-tensor*		
			g_1	g_2	g_3
F_2^-	^{19}F	KF	2.0020	2.0218	2.0218
Cl_2^-	^{35}Cl	KCl	2.0012	2.0426	2.0426
Br_2^-	^{81}Br	KBr	1.9833	2.169	2.169
I_2^-	^{127}I	KI	1.913	2.34	2.34
FCl^-	^{19}F	KCl	2.0018	2.030	2.030
	^{35}Cl				
FBr^-	^{19}F	KCl	1.9891	2.125	2.125
	^{81}Br				
FI^-	^{19}F	KCl	1.9363	2.26	2.26
	^{127}I				
XeF	^{19}F	XeF_4	1.9740	2.126	2.126
KrF	^{19}F	KrF_4	2.000	2.068	2.068
ICl^-	^{127}I	KCl	1.86	2.39	2.39
	^{35}Cl				
FO^{2-}	^{17}O	CaF_2	2.0016	2.0458	2.0458
	^{19}F				

[a] $a_{\parallel}$ and $a_{\perp}$ for ^{17}O and ^{19}F positive and [b] $a_{\parallel}$ positive and $a_{\perp}$ negative.

results for γ-irradiated aqueous ammonia are clearly anomalous, and relate in our view to the parallel features of the rigidly held radical, whereas the remainder relate to rotating NH_2 or have been analyzed to give the true isotropic data. Unfortunately, the spectra in ice are not well enough resolved to warrant detailed analysis. Even so, there seems to be a definite upward trend in the isotropic hyperfine coupling to ^{14}N as the hydrogen-bonding power of the medium is increased.

Changes in a_{iso} with medium are commonly detected, but arise generally because of changes in the distribution of the electron in a delocalized molecular orbital. This can hardly be the case for NH_2, and we suggest two possible alternative causes (*39*). Both relate to the fact that the upward trend in a_{iso} (^{14}N) is towards the value of 18 gauss found for NH_3^+ in various matrices. Since this represents the limit of very strong hydrogen bonding to the NH_2 lone-pair, it is reasonable that weaker bonding should also increase a_{iso}. It is tempting to assign one third of the coupling (6 gauss) for NH_3^+ to each N–H bond and hence to interpret the gradual rise purely in terms of increasing polarization of the lone-pair electrons. The alternative extreme would be to assign the whole increase to the change in *s–p* hybridization of the N–H orbitals as the bond angle opens from 103° for NH_2 to 120° for NH_3^+. This would have no overall

some Hal_2^- and Related σ-Radicals

Hyperfine tensor (gauss)					
$B_{\parallel}$	$B_{\perp}$	A_{iso}	a_s^2	a_p^2	*Ref.*
634	−317	274	0.016	0.586	*79*
61.2	−30.6	39.9	0.024	0.582	*79*
288	−144	162	0.019	0.586	*79*
240	−120	147	0.020	0.563	*79*
608	−304	198	0.011	0.562	*79*
73.6	−36.8	52.5	0.032	0.700	
582	−291	153	0.009	0.538	*79*
354	−177	247	0.030	0.720	
538	−269	98	0.006	0.498	*79*
300	−150	261	0.035	0.703	
558	−279	388	0.022	0.516	*43, 79*
696	−348	564	0.033	0.644	*44, 79*
74	−37	348	0.048	0.175	*50*
40	−20	27	0.016	0.40	
56.3	−28.2	48.2	0.03	0.54[a]	
or	or	or	or	or	
83.0	−41.5	21.5	0.013	0.80[b]	*16*
25.8	−12.9	27.9	0.0016	0.026[a]	
or	or	or	or	or	
45.8	−22.9	7.9	0.0005	0.042[b]	

effect on a_{iso} (^{14}N) if polarization of the "lone-pair" remained unchanged on bonding since the total 2*s*-electron density remains distributed between the σ-bonds and the lone-pair. If, however, polarization of the lone-pair is considerably enhanced on bonding, the combined trend could be as observed. This is reasonable since the outward attenuation of the lone-pair is expected to increase as θ increases.

[To test this, we have studied the effect of a wide range of solvents upon the ^{14}N isotropic hyperfine coupling for pyrazine anions and cations (*39*). Here the bond-angle is only able to change slightly on protonation so that changes in a_{iso} must be caused by changes in polarization of the lone-pair electrons provided the π-electron distribution is unaffected. In fact, the changes are very small, showing, we feel, that the dominating effect for NH_2 is associated with the change in bond angle.]

Recently the radical PH_2 has been obtained by radiolysis of PH_3 in rare-gas matrices, but unfortunately the lines are broad and partially hidden beneath more intense features assigned to phosphorus atoms. Thus, the results (*26*) in Table VI have to be treated with some reserve.

As they stand, the results show that the U-value for ^{31}P (2.2) is essentially identical with that for ^{14}N in NH_2, but that the coupling to the protons is appreciably reduced.

Table VI. Magnetic Parameters

		^{14}N, ^{15}N, ^{31}P, or ^{33}S *Hyperfine Coupling constants (gauss)*			
	Medium	B_{xx}	B_{yy}	B_{zz}	A_{iso}
NH_2	Argon				10.3
	NH_3				15.0
	aqueous NH_3 (5%)				31.0
	aqueous NH_3 (50%)				18.0
	Argon				10.7
	Argon				10.4
	Krypton				10.7
	Xenon				10.8
	KNH_2/NH_3				16.7
$^{15}NH_2$	KNH_2SO_3	34.9	−16.6	−18.3	18.61
PH_2	Krypton				80.0
SH_2^-	H_2S				60 ± 2
	KCl				

Two groups have recently claimed to have prepared the radical H_2S^-, which has two electrons more than NH_2 or PH_2 (*14, 56*). One group prepared their radical by photolysis of alkali halide crystals doped with HS^- ions. At 20°K. only trapped hydrogen atoms were detected, but after annealing at 110°K. for a few seconds and recooling, spectra assigned to S^- and H_2S^- were obtained. The results for the latter species, summarized in Table VI, show indeed that one sulfur and two equivalent protons are present. Since the protons remain magnetically equivalent for all orientations, the molecule was taken to be linear.

The species prepared by depositing alkali metal atoms and a stream of H_2S gas upon a rotating cold-finger (*14*) gave a rather poorly resolved spectrum which was interpreted in terms of the data in Table VI.

In our view, neither of these radicals has the magnetic properties to be expected for H_2S^-. The only radical bearing any resemblance to this species that has been unambiguously identified by ESR is PF_4 (*8, 68*). The unpaired electron is bound in a molecular orbital closely related to the lowest σ^*-orbital of the tetrahedral molecule, which distorts to reduce the antibonding character. Hence, there is a large *s*-character associated with the central atom. The lowest lying vacant orbital for H_2S is probably also σ^* in character. Hence, the radical H_2S^- is expected to have a very large isotropic proton hyperfine coupling, the situation being similar to that envisaged for deeply trapped hydrogen atoms (*6*) in—*e.g.*, a halide salt. In fact, HCl^- is closely related to H_2S^-, but nevertheless trapped H

for NH_2, PH_2, and SH_2^-

^1H Hyperfine Coupling constants (gauss)					
B_{xx}	B_{yy}	B_{zz}	A_{iso}	g_{av}	*Ref.*
			−23.9	2.00481	*20*
			−24.5		*75*
			−24.5		*75*
			−23.0		*3*
			−24.8		*32*
			−23.9	2.0038	*25*
			−23.95	2.0036	
			−24.0	2.003	
			−25.2		*24*
−4.0	+1.8	+2.3	−27.4		*69*
			18.0	2.0087	*28*
			7.7 ± 0.3	$g_{\parallel} = 2.0023$; $g_{\perp} = 2.0164$	*14*
−9.1	+4.5	+4.5	−24.2	$g_{\parallel} = 1.9865$; $g_{\perp} = 2.2055$	*56*

atoms have ESR spectra close to that of the gas-phase atoms. We would not expect to find a major contribution from sulfur 3*d* orbitals, but if the electron was primarily a *d*-electron, the *g*-value should be less than the free-spin, whereas in these species there are large positive deviations.

For these and other reasons it seems improbable that H_2S^- is a correct formulation for either of these radicals. Possible alternatives include H_2S^+, isoelectronic with PH_2, and species such as $H_2S_2^-$, $H_2S_2^+$, or more complex polysulfide radicals. The radical H_2S^+ is a possible candidate for the species in alkali halide crystals (*56*), which apparently contains only one sulfur atom, except that some restricted rotational motion would need to be invoked to explain the equivalence of the two protons. Rotation within the molecular plane would achieve this, and would also account for the form and magnitude of the anisotropic proton coupling. The ^{33}S tensor is also accommodated reasonably well, as also is the positive *g*-shift. However, the very large value for Δg is more difficult to reconcile with this formulation.

That the species formed by reaction between H_2S and alkali metal atoms could be more complex than originally envisaged (*14*) is supported by the observation of secondary "polymeric" sulfur radicals on annealing.

CS_2^-, PF_2, and Related Species. The former has not yet been detected as a product of irradiation, but has been unambiguously identified as the initial product in the reaction between alkali metal atoms and carbon disulfide. Its magnetic properties, summarized in Table VI, are quite in accord with expectation for this radical, which is isostructural with CO_2^- and NO_2. It is noteworthy that the calculated spin-densities on carbon are almost the same for CO_2^- and CS_2^-, whereas because of the lower electronegativity of sulfur relative to that of oxygen one would have expected a lower spin-density on carbon in CS_2^- than in CO_2^-. However, the p/s ratio for carbon is increased because of the greater bond angle in CS_2^- which offsets this trend. This situation is also found for AB_3 radicals, and is discussed later in detail.

The radical PF_2, isostructural with the stable NF_2, has been made by electron bombardment of solid SF_6 containing about 1% of PF_3 and has also been detected in γ-irradiated NH_4PF_6 (*15*).

Only the isotropic ^{19}F and ^{31}P hyperfine coupling constants were obtained and hence it is difficult to draw any firm conclusions about the structure of this π-radical. The parameters are quite similar to those for NF_2 except if one assumes that, as with NF_2, the spin-density is almost 100% on the central atom, the U-value for ^{31}P is lower than that for ^{14}N. This probably means that the bond angle for PF_2 is less than that for NF_2.

The radicals S_3^- and Se_3^-, which are isostructural with PF_2, have been detected in alkali halides doped with sulfur or selenium, the identification being based upon the appearance of two different ^{33}S or ^{77}Se coupling constants (Table VII). Because of sign ambiguity in the tensor, two sets of data result. However, we favor set (ii) because we expect the spin-density on the central atom to be less than that on the corresponding oxy-radicals SO_2^- and SeO_2^-.

Table VII. Magnetic Parameters

Radical	*Matrix*	*Nucleus*	g-*tensor*		
			g_{xx}	g_{yy}	g_{zz}
CS_2^-	CS_2	^{13}C	2.0079	1.9661	1.9993
CO_2^-	$NaHCO_2$	^{13}C	2.0032	1.9975	2.0014
PF_2	ND_4PF_6	^{31}P		$g_{iso} = 2.0108$	
		^{19}F			
NF_2	Ne	^{14}N	2.0011	2.0079	2.0042
		^{19}F			
S_3^-	KCl	^{33}S	2.0499	2.0319	2.0026
		^{33}S[c]			[a]
					[b]
Se_3^-	KCl	^{77}Se	2.2205	2.1545	1.9885
		^{77}Se[c]			[a]
					[b]
SO_2^-	KCl	^{33}S	2.0110	2.0071	2.0025

[a] a_{xx} + ve.
[b] a_{xx} − ve.

The Radicals FOO and ClOO. It has recently been proposed that a radical containing one chlorine atom, previously thought to be the monoxide, ClO (*4*), is more likely to be the peroxide, ClOO (*38*). The radical is readily formed on photolysis of chlorine dioxide in γ-irradiated $KClO_4$ at room temperature and also from rigid solutions of chlorine dioxide in sulfuric acid at 77°K. However, photolysis of ClO_2 in a chlorate lattice does not result in the formation of this species. If the radical is indeed ClOO, this can be understood since chlorate is an extremely efficient oxygen atom acceptor, which would favor formation of ClO rather than ClOO. Also, many details of the ESR spectra are readily accommodated if ClOO is the correct formulation but very hard to understand if the species is ClO.

The properties of this radical are similar to those of the stable fluorine analogue, FOO, and they are compared in Table VIII. In general, the radical ABO will be more stable than BAO when the electronegativity of A is greater than that of B. Hence, FO_2 is not detected in solutions containing FOO, but ClO_2 is more stable than ClOO. Our results (*38*) show that ClOO isomerizes to ClO_2 in $KClO_4$ at room temperature.

Another example of a peroxy-oxyradical is O_3SOO^-, which is formed on photolysis or radiolysis of potassium persulfate crystals (*10*). It seems probable that peroxy radicals of this type, including XOO, OXOO, O_2XOO, and O_3XOO, ought to be considered as possible species in radiation-damage studies of oxy-salts.

The Radical Be_2F^{2+}. The detection of a widely spaced doublet having extra hyperfine splitting for each component in X-irradiated BeO

for CS_2^-, PF_2, and Related Radicals

Hyperfine tensor (gauss)							
a_{xx}	a_{yy}	a_{zz}	a_s^2	$a_{p_z}^2$	$a_{p_x}^2$	*p/s*	*Ref.*
73.1	67.0	121.6	0.077	0.560	0.06	7.3	13
155.8	150.8	195.1	0.15	0.50	0.08	3.3	*74*
$a_{iso} = 36$			0.01				*15*
$a_{iso} = 60.5$			0.004				
49 ± 0.5	0 ± 1.0	0 ± 1.0	0.03	0.94			*61*
212 ± 2.0	−16.9 ± 1.0	−16.9 ± 1.0	0.004	0.14			
−10	−2	+52	0.013	0.69			*37*
+1	0	+19	0.007	0.21			
−1	0	+19	0.006	0.23			
−48	−59	+247	0.010	0.74			*37*
+17	0	+72	0.006	0.16			
−17	0	+72	0.004	0.20			
−7.1	−8.6	+52.5	0.013	0.71			*37*

[a] outermost atoms.

Table VIII. Magnetic Parameters for FOO and ClOO

		A tensor (^{35}Cl or ^{19}F) in gauss			*g-tensor*			
Radical	*Medium*	a_{11}	a_{22}	a_{33}	g_{11}	g_{22}	g_{33}	*Ref.*
ClOO	H_2SO_4	[a]	[a]	15.3	[a]	[a]	2.0115	*38*
	$KClO_4$	(−)5.3	(+)7.2	(−)14.9	1.9983	2.0017	2.0130	*38*
FOO	Argon	(∓)50	(∓)14.0	(±)103	2.0008	2.0022	2.0080	2

[a] These values were not obtained.

powder led to the postulate (*73*) that an unpaired electron was trapped in the 3*s* level of a substitutional fluoride ion. The structure of this center has been discussed in terms of bonding to neighboring beryllium cations (*19, 83*) which led to the idea that the large isotropic coupling to fluorine involved the 2*s*-rather than the 3*s*-orbital. The model postulated involved an unpaired electron in a σ^*-orbital between fluoride and one of the three equivalent beryllium ions adjacent thereto. This orbital closely resembles that for the unpaired electron in nitrogen centers in diamond (*18, 49*), and the electron should have a high density on the beryllium 2*s* orbital and a low density on fluorine. A rapid fluctuation between the three beryllium ions would then give the required equivalence.

Many features of this model have been confirmed by a recent study of fluoride-doped single crystals of beryllium oxide (*42*). The basic unit is Be_2F^{2+} rather than BeF and hopping then occurs between the three possible states involving the three beryllium ions. However, the normal model for such a hopping process was incompatible with the temperature dependence, and a model involving quantum mechanical coupling between the three states was devised to account for the behavior (*42*).

Some Tetra-atomic Radicals

BH_3^-, SiH_3, and Related Species. The radical BH_3^- has been identified as one of the products in potassium tetrahydridoborate, after γ-irradiation at 77°K. (*84*). The results, given in Table IX, show that the proton coupling is somewhat lower than that for the isoelectronic radicals CH_3 and NH_3^+, but that the U-value for boron is very close to those for ^{13}C and ^{14}N. There is a steady trend to lower g_{av} values on going from NH_3^+ to BH_3^- (Table IX).

That the proton hyperfine coupling for SiH_3 radicals was much smaller ($\sim \pm 8$ gauss) has been known for some time (*29*) and it was surmised that this was because the radical could well be pyramidal with a positive coupling (*80*). The detection of a large ^{29}Si hyperfine coupling has confirmed this postulate (*27*). This trend from planar CH_3 to pyramidal SiH_3 follows the decrease in bond angle on going from NH_3 to PH_3.

The Radicals NO_3^{2-}, CO_3^{3-}, and Related Species. The radical NO_3^{2-}, identified originally in irradiated nitrates and nitrate-doped alkali halides (*33*, *59*), has now been prepared in nitrate-doped calcite (*40*). Its properties are interesting in that its bond angle, as deduced from the ^{14}N hyperfine tensor (*7*) (115°), is almost midway between that for the planar radical (120°) and the strongly pyramidal isostructural radicals such as PO_3^{2-} ($\sim$ 110°).

The detection of CO_3^{3-} in irradiated calcite (*40*, *64*) enables us to draw some conclusions regarding the overall factors which control the degree of bending in these 25-electron radicals. The situation we envisage is depicted in Figure 2 in which the difference in electronegativity between the central and outer atoms is plotted against total spin-density on the central atom. There is a steady decrease in the p/s ratio on going from NO_3^{2-} (7.8) to CO_3^{3-} (5.25) and CF_3 ($\sim$ 3) as the spin-density on the central atom rises.

It seems that there is a greater tendency for the first row radicals to be planar, possibly for steric reasons, and it is particularly those radicals with intermediate bond angles that are sensitive to changes in electronegativity. The increase in 2*s*-character on the central atom leads to an increase in its effective electronegativity and hence to a fall in the spin-density thereon. The result for the isoelectronic radical CF_3 has been included in Figure 2. The p/s ratio for carbon in this radical must be close to three and so it has the same shape as the second and third row radicals. We conclude that, when a series of radicals have shapes which are intermediate between the normal extremes, an increase in the electronegativity difference between the outer and central atoms will lead to an increased bending and to a decrease in the normal growth of the spin-density on the central atom.

$C_2N_2^-$, $S_2N_2^+$, and Related Species. The radical $C_2N_2^-$ is thought to bear a structural resemblance to the cyanogen molecule, and is related to the V_K centers in being the simplest hole-center in cyanide salts (*78*). It is formed on exposure of alkali metal cyanides or cyanide-doped halides to γ-radiation and analysis of the ESR spectrum strongly supports a *trans*-bent structure.

This is a 19-electron radical and can be contrasted with the radical N_4^-, a 21-electron radical, which is thought to have a distorted square-planar structure, with all the nitrogen atoms equivalent (*81*). Another center, with four equivalent sulfur atoms, has recently been described, although details are not given (*37*). A square-planar structure again seems possible and it would be of interest to discover the nature of the orbital of the unpaired electron. Certainly the factors which determine the most stable geometry of these tetra-atomic radicals are a matter of some interest.

Table IX. Magnetic Parameters

			Anisotropic Hyperfine tensor (gauss)		
Radical	*Matrix*	*Nucleus*	*A_1*	*A_2*	*A_3*
BH_3^-	KBH_4	^{11}B			
		^{1}H			
CH_3	CH_3I CH_4 Krypton	^{13}C			
		^{1}H			
NH_3^+	NH_4ClO_4	^{14}N			
		^{1}H			
SiH_3	Krypton	^{29}Si		46–52	
		^{1}H			

Some 31 Electron Penta-atomic Radicals

Although radicals such as PO_4^{2-} or SO_4^- have often been reported, many aspects of their structure remain obscure. Some time ago it was suggested that the unpaired electron would be expected to be in a t_1 orbital in the undistorted tetrahedral radicals, which is purely non-bonding on oxygen (*80*). All the species to which this structure has been assigned have markedly asymmetric *g*-tensors with near axial symmetry, but the nature of the distortions which cause this deviation from symmetry remain obscure.

Perhaps the most characteristic feature is the small, nearly isotropic hyperfine coupling to the central atom, which corresponds to a U-value in the range 0.6 to 0.8. This fits in well with the proposed correlation between U-values and σ-bond hybridization (*57*), but the results recently assigned to ClO_4 do not (*72*). The species under consideration is formed by exposure of $KClO_4$ crystals to γ-rays at 77°K. and is lost irreversibly on warming to above 100°K. The magnetic properties are given together with those assigned to PO_4^{2-} and SO_4^- in Table X and it can be seen that both the total 3*s*-character and the *p*/*s* ratio are larger than expected. Furthermore, the form of the *g*-tensor is quite different from that for the other radicals. Whilst these differences may well be a consequence of a different form of distortion preferred by ClO_4, it seems possible that the species involved is not the normal ClO_4. However, its identity then poses a problem, since most of the "normal" monochlorine radicals are known. One alternative which bears scrutiny is the peroxy-radical O_2ClOO. The orbital of the unpaired electron would be considerably delocalized on to the peroxy-oxygens, but nevertheless the basic structure should be closely related to that of the σ-radical ClO_3 (*5*).

for BH_3^-, CH_3, NH_3^+, and SiH_3

A_{iso}	g_{av}	a_s^2	U^X	*Ref.*
(+)24	2.0013	0.033	3.3	*84*
(−)16.5		0.033		*84*
(+)41	2.0026	0.037	3.7	*27, 31,*
(−)23.0		0.045		*and 46*
(+)19.5	2.0035	0.036	3.6	*30*
(−)25.9		0.051		
200–300	2.006	0.2		*27*
−8.1		0.016		

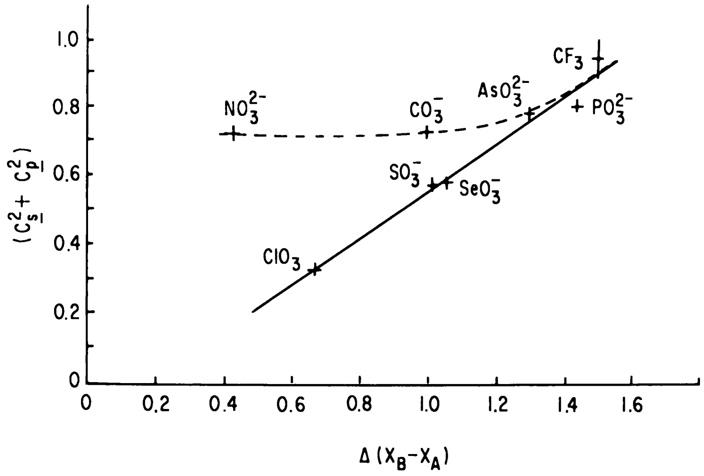

Figure 2. Dependence of the spin-density on A for certain AB_3 radicals as a function of the difference in the electronegativities of A and B $\Delta(\chi_B - \chi_A)$

One curious feature of the results is the appearance of two rather similar radicals: it seems that further studies are needed before firm conclusions about their structure can be drawn.

Another class of radical which seems to be readily formed on radiolysis consists of transition-metal XO_4 analogues such as VO_4^{2-} and WO_4^-. Again, however, the results are not clear-cut. The radical WO_4^- is not itself detected in irradiated tungstates, but rather a two-tungsten center is found which could be the WO_4^-–WO_4^{2-} (*62*) analog of the V_K centers.

Table X. Magnetic Parameters

Radical	Medium	Nucleus	g-tensor g_{xx}	g_{yy}	g_{zz}
PO_4^{2-}	Calcite	^{31}P	2.0072	2.0033	2.0122
SO_4^-	$K_2S_2O_8$	^{33}S	2.0047	2.0034	2.0142
ClO_4	$KClO_4$	a) ^{35}Cl	2.0024	2.0548	2.0553
		b) ^{35}Cl	2.005	2.036	2.038
VO_4^{2-}	$CaMoO_4$	^{51}V		$g_{av} = 2.023$	
$(WO_4^--WO_4^{2-})$	$CaWO_4$	^{183}W	2.0013	2.0064	2.0352

Radicals having rather similar properties (Table X) containing one vanadium atom are formed on exposure of molybdates doped with vanadate to γ-rays (*41*). We have also prepared radicals which could well be NbO_4^{2-} and MoO_4^-.

The difficulty with the formulation XO_4–XO_4^- can be understood if one envisages its formation from the peroxide O_3XOOXO_3 by adding an extra electron. While this could possibly be accommodated in the O–O σ^*-orbital, it is far more likely to go into one of the π-d metal orbitals, probably with an equal distribution between the two metal atoms. The magnetic properties of the two-tungsten center in calcium tungstate do not accord with either of these formulations, so it may be that the center is better described as WO_4^-, there being a fortuitously rapid electron transfer between two tungstates having identical environments.

If it is accepted that the vanadium species is indeed VO_4^{2-}, then the way in which the vanadium atom acquires an isotropic hyperfine coupling, remains obscure. The latter is almost three times larger than would be predicted from the U-value of PO_4^{2-}, but is much smaller than the "normal" value of about 100 gauss resulting from spin polarization of inner *s*-electrons by an unpaired 3*d*-electron.

Some Conclusions and Aspects of Mechanism

Despite the rapid rise in understanding the factors involved, the task of interpreting ESR spectra remains formidable in many cases, especially when only powder spectra are available. In that case, the use of two frequencies (say X- and Q-band) can be a great help in unravelling the difference between hyperfine and *g*-features, as can the use of different isotopes. Extracting the hyperfine and *g*-tensors from single-crystal spectra is more satisfactory than the use of powders, and gives, of course, directions, which cannot be deduced from powders. However, pitfalls again abound and we strongly recommend the parallel study of powders, which will give an overall guide to the sort of results to be expected from the crystal.

for Some XO_4 Radicals

Hyperfine tensor (gauss)					
A_{xx}	A_{yy}	A_{zz}	a_s^2	a_p^2	*Ref.*
18.76	20.06	18.61	0.0053	0.004	*63*
ca 4	*ca* 4	*ca* 4	*ca* 0.004		*11*
	$A_{iso} = 57$		0.034		*72*
69	71	83	0.044	0.09	
	$A_{iso} = 19.5$				*41*
9.5	10.5	9.0			*41*

Magnetic "centers" are frequently normal "molecules" unless they are part of a polymeric network, but their characteristic spectra may be greatly modified by minor interaction with their environment, which can nevertheless give rise to extra features.

The characteristic magnetic properties of a particular radical may be so greatly modified by various possible modes of restricted rotation that, unless this is appreciated, the spectrum may be assigned to a new radical. The results for the fluorine center in BeO comprise an interesting variation on this theme.

The task of identification may be aided by the following general points—

(1) If a given nuclear hyperfine coupling tensor on analysis shows that there is a large atomic *s*-character in the orbital, then this atom is probably a "central" atom in a σ-radical.

(2) If the hyperfine coupling clearly indicates *p*-character (or *d*-character) only, then it is either a central or "ligand" atom in a π-radical. The "ligand" atoms in σ-radicals may show a large or small percentage of *s*-character depending upon the *s*-contribution to the σ-orbital and the dominating mechanism of delocalization. This has been discussed in detail elsewhere (*19*).

Attempts to prepare simple electron-deficient species by γ-irradiation of suitable solids may be frustrated by their tendency to bond, weakly, or strongly, to neighboring molecules. Thus, our attempts to prepare the CN radical from cyanide ions have always been frustrated by the formation of $C_2N_2^-$ radicals.

Another way in which the spectra of trapped radicals can be greatly modified is by spin-spin coupling to neighboring radicals. Radical pairs may be formed in relatively low abundance, in which case weak satellite lines may be found at high gain, which can be confused with traces of secondary radicals, or with features from molecules containing low-abundant isotopes. For example, the features assigned to $N_2O_2^+$ in irradiated sodium nitroprusside crystals (*34*) were in fact a property of pairs of the highly-abundant "parent" radicals (*51*).

Sometimes the mechanism of damage is such that these pairs dominate the spectra, in which case the basic pattern will be that of a triplet-state radical.

We conclude with a brief survey of some of the mechanistic features which emerge from these studies. After ejection, electrons will be rapidly trapped, not necessarily at the deepest traps available, but rather at the most abundant, which are deep enough to lead to a stationary state for the electron at the temperature involved. Then the residual "hole" must be sufficiently immobile to prevent migration and recombination.

The situation can be exemplified by considering our results for calcite doped with nitrate ions. Exposure to γ-rays at 77°K. gives CO_3^- and NO_3 as hole-centers, and CO_3^{3-} and NO_3^{2-} as electron-excess centers. The radical NO_3 readily gains electrons from neighboring carbonate ions which are relatively "mobile" because of electron-transfer, but which presumably distort sufficiently at low temperature to act as traps. On annealing these centers decay, as does the CO_3^{3-} center which is stabilized with respect to electron-transfer by its pyramidal distortion. The NO_3^{2-} center is stable to above 150°K. because there is now no tendency for electron-transfer and charge-neutrality is achieved. Similarly, phosphate-doped calcite gives the hole-center on exposure to high energy radiation, which is again remarkably stable because of charge neutrality (*63*).

Often these centers are "fixed" or stabilized by chemical reaction rather than by simple distortion, and if protons are present in hole-centers it often comprises proton loss to the medium (*83*). Alternatively, holes and electrons may re-combine but the resulting excited parent molecule may decompose before dropping to the ground-state, in which case the decomposition resembles a photolysis.

The pair-wise trapping of radicals is probably a more common occurrence than was originally appreciated, though it remains difficult to predict when it is likely to be sufficiently specific to do more than broaden ESR lines. That solid-state photolysis might be expected to give pairs of radicals has long been appreciated, a clear-cut example of this being the photolysis of potassium persulfate crystals (*10*). However, high energy radiation may also give rise to such pair-trapping, the pairs being either a minor product (*51*), or occasionally almost the sole radical product (*35*). At least in certain cases it seems probable that when this happens it is the result of normal bond homòlysis (*35*), although mechanisms involving further reactions of initially formed neighboring holes and electron-excess centers can be envisaged (*83*).

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