ELECTRON RESONANCE SPECTROSCOPY OF FREE RADICALS

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Principles of Magnetic Resonance.—Although the subject of nuclear magnetic resonance and its wide potentialities is well known and has been the subject of an article in *Quarterly Reviews*,[1] the elder brother, electron magnetic resonance, is less well known and confusion of the two is not uncommon. The basic principle of the two subjects is the same, namely, the observation of spectroscopic transitions between different spin orientation levels.

Electrons have a spin of 1/2, that is their internal angular momentum is $(1/2) \times (h/2\pi)$. Many nuclei, including the proton, also have a spin of 1/2 and the principle of magnetic resonance can best be understood by concentrating on the important special case of particles of spin 1/2. Besides their spin, such particles also possess an inherent magnetic moment rigidly bound to the axis of the spin and usually designated by the symbol μ. In the presence of an external magnetic field these magnets will tend to align themselves along the field. The classical potential energy is that for a compass needle in a magnetic field, H, namely $-\mu H \cos\theta$, where θ is the angle between the magnet direction and the field. However, nuclei and electrons are all small particles and their behaviour is modified by the laws of quantum mechanics. These restrict the resolved spin angular momentum along the magnetic field to the two discrete values $+1/2$ and $-1/2$. This is equivalent to restricting the particle spin and magnetic moments to be parallel or antiparallel to the field, *i.e.*, to restricting $\cos\theta$ to $+1$ or -1. Each particle has then a lower, or ground state, orientational energy level of $-\mu H$ and a higher, or excited state, level of $+\mu H$. High-frequency magnetic fields are able to cause transitions between these levels and the effect can be observed in a magnetic resonance spectrometer.

For magnetic fields readily obtainable in the laboratory the energy difference is much less than kT and, although the two energy states are very nearly equally populated, very slightly over half the particles will be in the lower state. As a consequence the high-frequency energy absorbed by those in the lower level exceeds the energy released from the stimulated emission of those in the higher state and a net absorption of energy occurs. Such absorption is a resonance phenomenon and will only occur when there is an exact balance between the quantum of high-frequency radiation and the energy difference between the two states. In symbols this requires

$$2\mu H = h\nu$$

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[1] J. A. S. Smith, *Quart. Rev.*, 1953, **7**, 279.

where ν is the resonant frequency. This equation is a special case, for particles of spin 1/2, of the more general equation

$$\mu H/I = h\nu$$

where I is the spin of the nucleus in question.

Table 1 shows some relevant properties of the electron and a few of the more important nuclei. It is an inherent feature of nuclear structure that nuclei of zero spin have no magnetic moment. It follows that such nuclei cannot develop a nuclear resonance spectrum, nor can they contribute to electron-resonance hyperfine structure (see below). The more important nuclei in this inactive category are given at the foot of Table 1.

TABLE 1

Particle	Spin	Magnetic moment in 10^{24} ergs/gauss	Resonant frequency in kc./gauss
Electron	1/2	− 9270	2800·3
^{1}H	1/2	+ 14·1	4·26
^{2}H (D)	1	+ 4·3	0·65
^{13}C	1/2	+ 3·5	1·07
^{14}N	1	+ 2·0	0·31
^{17}O	5/2	− 9·6	0·57
^{19}F	1/2	+ 12·8	4·01
^{35}Cl	3/2	+ 4·1	0·42
^{37}Cl	3/2	+ 3·4	0·32

Nuclei with zero spin include ^{4}He, ^{12}C, ^{16}O, and ^{32}S.

The preceding paragraphs have merely outlined the nature of the spectroscopic transitions and those interested in a more complete approach should consult the more detailed literature.[1–7]

Differentiation of Electron Resonance from Nuclear Resonance.—In the preceding section the principles of electron resonance * and nuclear resonance † have been considered together and clearly the resemblance is considerable. The first distinction is a trivial one of nomenclature in that the symbol S is used for electron spin instead of I for the spin of a nucleus. Secondly, there is an important experimental feature resulting from the large moment of the electron. For a magnetic field of 10,000 gauss the

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[2] D. J. E. Ingram, " Spectroscopy at radio- and micro-wave frequencies ", Butterworths, London, 1955.

[3] N. F. Ramsey, " Nuclear moments ", Wiley, New York, 1953.

[4] E. R. Andrew, " Nuclear magnetic resonance ", Cambridge Univ. Press, Cambridge, 1955.

[5] J. E. Wertz, *Chem. Rev.*, 1955, **55**, 829.

[6] F. Bloch, *Phys. Rev.*, 1946, **70**, 460.

[7] N. Bloembergen, E. M. Purcell, and R. V. Pound, *ibid.*, 1948, **73**, 679.

* Alternative names and abbreviations include electron spin resonance, e.s.r., electron paramagnetic resonance, paramagnetic electron resonance, p.e.r., and electron magnetic resonance, e.m.r.

† Alternative names and abbreviations include nuclear magnetic resonance, n.m.r., nuclear paramagnetic resonance, nuclear spin resonance, n.s.r., and nuclear induction.

required frequency for electron resonance is 28,000 Mc./sec. which lies in the microwave range, whereas all nuclear resonances lie below 50 Mc./sec. at this field and require radiofrequency techniques for their observation. Nuclear-resonance spectrometers can be used to detect electron resonance in fields below 20 gauss, but the sensitivity is inherently poor.

Henceforward attention will be confined to electron resonance. For this there are two fundamental features, both consequences of the small mass of the electron, which have no direct counterpart in nuclear resonance. First, the electrons in any molecule are not individually constrained to particular links and are indistinguishable from each other. The total electron wave function is required by a fundamental law of Nature to be antisymmetric to the interchange of any two electrons. As a consequence the individual electron spin should be replaced by the net electron spin for the whole molecule; this is zero for all spin-paired molecules and these do not show electron resonance. This same conclusion is reached by considering the two electrons in the same space orbital; these electrons necessarily have resolved angular momenta of $+ 1/2$ and $- 1/2$ since they obey the Pauli exclusion principle solely through differing in the spin part of their wave functions. It is then impossible to reverse the spin direction of only one of these two electrons without violating the exclusion principle and so no electron resonance transition is allowed. Should both the electron spin directions be reversed no distinguishable change would have occurred and no energy absorbed. Consequently, it is only molecular species for which spin pairing is incomplete that electron-resonance absorption is possible. Most non-metallic compounds with one unpaired electron are called radicals. With two parallel electrons $S = 1$, and the molecule is said to be in a triplet state or it may be a diradical. It is this absence of electron resonance spectrum for most molecules that makes electron resonance of far more limited application than nuclear resonance, but it does enable free radicals to be selectively examined in the presence of large amounts of other molecules. Since most free radicals are only encountered in small concentrations, this specificity is very valuable.

The second consequence of the small mass of the electron is the appearance of a magnetic moment related to the orbital motion of the electron as distinct from its internal spin. For a hydrogen atom the *s*, *p*, *d*, *f*, . . . states are associated with orbital angular momenta of 0, 1, 2, 3 . . . units, respectively, and corresponding magnetic moments. However, in the majority of molecules and radicals the spin orbital momentum is quenched and the corresponding magnetic moment no longer arises. This quenching is a consequence of the fact that molecular bonds emanating from any atom are strongly directional in character, being under the influence of the positive charges on the neighbouring atoms which occupy the other ends of the bonds. In order to contribute to the magnetic susceptibility, or to a resonance experiment, the orbitals must be capable of changing their direction in space so as to vary the resolved angular momentum and magnetic moment; this re-orientation is just what the second atom in the bond prevents. This can be seen for *p* orbitals which are normally required for molecule building in the three space-directed forms p_x, p_y, and p_z or hybrids constructed therefrom. Though the p_z orbital is that for which the resolved angular momentum, $l_z = 0$, the p_x and p_y are compounded equally from $l_z = +1$ and $l_z = -1$ orbitals. Even strong laboratory magnetic fields are too weak to undo the mixing of the $+1$ and -1 orbitals and allow orbital re-orientation effects to appear.

This orbital quenching does not arise for *s* electrons and is usually complete for *p* electrons, so that most organic molecules and radicals are of the orbital-quenched type. For *d* electrons in transition-metal ions, and even more for *f* electrons in rare-earth metal ions, the orientation effect of the surrounding ligands is often much weaker and the orbital momenta must be considered. The details of the consequent electron resonance spectra can become fairly complicated and their interpretation requires the use of crystal-field theory. There are two thorough reviews of this topic [8, 9] and the spectra of these metal-ion compounds have been omitted from the present account which relates only to free radicals.

Experimental.—The first detection of electron resonance was made in 1945 by Zavoisky [10] who used cupric chloride dihydrate and the first free-radical spectrum was observed in 1947 by Kozyrev and Salikhov [11] who used pentaphenyl*cyclo*pentadienyl. Since then the techniques of measurement have been greatly improved and a number of instruments of high sensitivity and resolution have been described.[12–16]

Fig. 1 shows the block diagram of a crude spectrometer which illustrates the basic features required. The klystron oscillator emits energy at a single frequency, say 28,000 Mc./sec., which is fed by a waveguide arrangement to a cavity containing the sample. This cavity is placed in a homogeneous magnetic field of 10,000 gauss * and provision is made to vary this field slightly by using subsidiary modulation coils fed with 50 c./sec. current. The signal transmitted by the cavity is modified by the sample absorption and this signal is detected with a crystal rectifier terminating the waveguide and is amplified. The presentation of the spectrum may take one of two forms, each of which is widely used. If the modulation coils are fed with so large a current that the resonance condition is only satisfied for part of a cycle of the 50 c./sec. field, the signal amplitude will vary in such a way that

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[8] B. Bleaney and K. W. H. Stevens, *Rep. Progr. Phys.*, 1953, **16**, 108.

[9] J. Owen and K. D. Bowers, *ibid.*, 1955, **18**, 304.

[10] E. Zavoisky, *J. Phys.* (*U.S.S.R.*), 1945, **9**, 245.

[11] B. M. Kozyrev and S. G. Salikhov, *Doklady Akad. Nauk S.S.S.R.*, 1947, **58**, 1023.

[12] H. A. Buckmaster and H. E. D. Scovil, *Canad. J. Phys.*, 1956, **34**, 711.

[13] J. M. Hirshon and G. K. Fraenkel, *Rev. Sci. Instr.*, 1955, **26**, 34.

[14] P. M. Llewellyn, *J. Sci. Instr.*, 1957, **34**, 237.

[15] A. C. Rose-Innes, *ibid.*, p. 276.

[16] M. W. Strandberg, M. Tinkham, I. H. Solt, and C. F. Davis, *Rev. Sci. Instr.*, 1956, **27**, 596.

* Strictly, magnetic fields should be expressed in oersteds and the unit of gauss reserved for the magnetic flux which is greater by a factor of the magnetic permeability. The units are identical in a vacuum and differ by less than 1 in 10^6 in air. Except for work of high precision or with ferromagnetic materials, the more euphonious gauss is often used for field or flux without distinction.

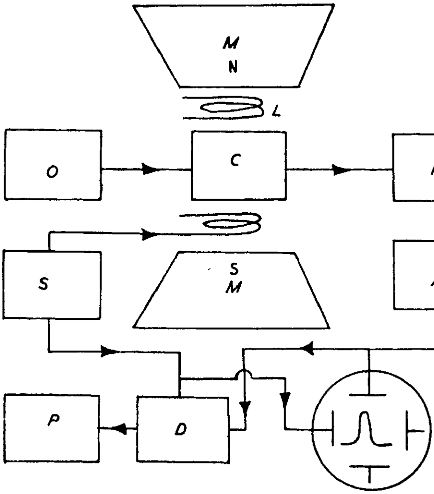

FIG. 1

Simplified block diagram of a typical electron resonance spectrometer.

M, 10,000 gauss magnet. *O*, Klystron oscillator, 28,000 Mc./sec. *C*, resonant cavity with sample. *R*, crystal rectifier. *A*, amplifier. *S*, 50 c./sec. supply. *D*, phase-sensitive detector. *P*, pen recorder. *L*, modulation coils. Connections to an oscilloscope are shown at the lower right-hand corner.

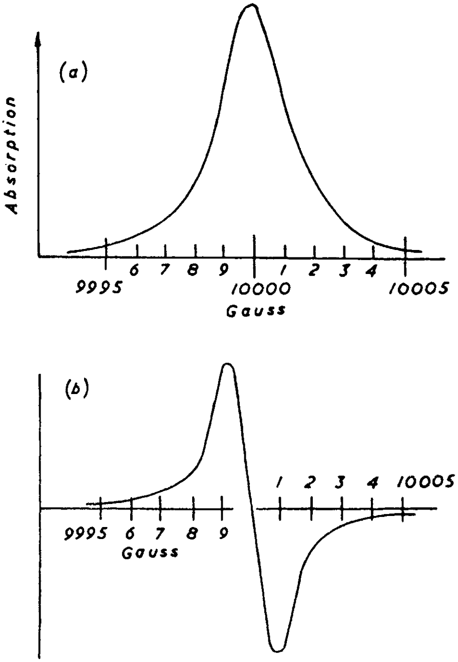

FIG. 2

(*a*) *Absorption spectrum and* (*b*) *its derivative for solid diphenylpicrylhydrazyl at* 28,000 *Mc./sec.*

if it is presented on the vertical plates of an oscilloscope screen whose horizontal plates are fed with a 50 c./sec. time base, then a picture of the absorption spectrum will appear on the screen. This may be photographed for permanent record. The alternative presentation, which has considerable advantages in sensitivity and resolution, requires the 50 c./sec. modulation field amplitude to be smaller than the width of the absorption line. The 50 c./sec. component of the resulting signal is proportional to the tangent

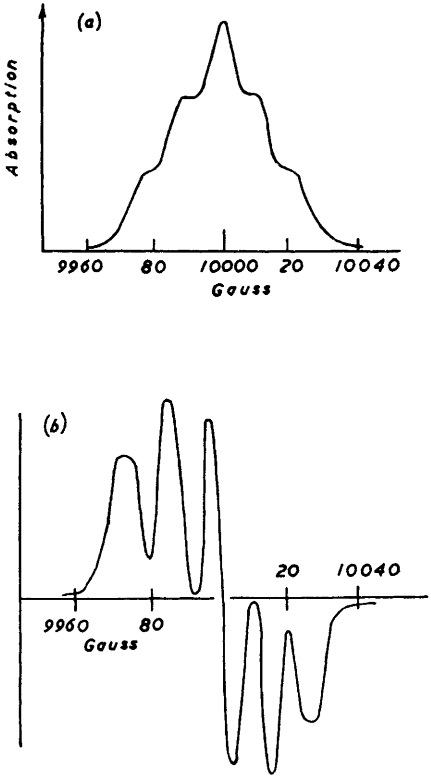

FIG. 3

(*a*) *Absorption spectrum and* (*b*) *its derivative for diphenylpicrylhydrazyl in benzene solution at* 28,000 *Mc./sec.*

to the absorption curve at the value of the static magnetic field. The signal is therefore fed to a phase-sensitive detector which picks out the 50 c./sec. Fourier component and its amplitude is displayed on a pen recorder. The main magnetic field of about 10,000 gauss is slowly varied so that the system passes from a field too low for resonance to a field too high for resonance in the course of about 15 minutes. The recorder pen will then trace out the complete derivative of the absorption curve. Fig. 2*a* shows an absorption curve and 2*b* the derivative curve such as would be obtained from a single-peak spectrum such as that of solid diphenylpicrylhydrazyl.

Fig. 3 shows the more complicated pattern observed in dilute solution. In both styles of presentation the spectra are obtained as a function of magnetic field rather than of frequency, for reasons of experimental convenience. Since field and frequency are proportional to each other, the spectra would have the same shape with frequency plotted as the abscissa under conditions of fixed field. The conversion factor for electron spin resonance is 1 gauss = 2·80 Mc./sec.

Spectrometer sensitivities vary with the details of their construction, frequency, working temperature, and especially the nature of the sample. A spectrometer operating at room temperature will normally detect about $10^{15}\Delta H_{1/2}$ spins/g. in 0·2-g. samples, where $\Delta H_{1/2}$ is the width of the resonance at half the maximum intensity. Under the most favourable conditions possible the sensitivity limit for solid diphenylpicrylhydrazyl at 4° K is estimated [12] to be 10^9 radicals, that is 10^{-12} g.

Detection of Free Radicals.—Since the existence of unpaired electrons is essential for the observation of electron resonance, the technique is well suited to the detection of free radicals. In the past a number of compounds have been considered to exist exclusively as free radicals in the solid state and chemists have supported these beliefs with static magnetic-susceptibility measurements. When such compounds are studied by electron-resonance techniques very strong signals are obtained which confirm the free-radical nature of the solids. One very early experiment [17] used Banfield and Kenyon's radical, in such amount that over half the microwave energy was absorbed by the radical at resonance. A stable free radical commonly used is diphenylpicrylhydrazyl [18, 19] which gives a narrow resonance and is therefore suitable for testing and for demonstration purposes. The radicals may also be charged entities, and are then called radical ions, of which Wurster's Blue [20, 21] is an example.

Of greater interest are the compounds which exist only partly as free radicals in the solid. For these, the paramagnetic contribution to the total susceptibility is much smaller and may even be outweighed by diamagnetic contributions so that interpretation of the older static susceptibility measurements is ambiguous. If, however, there is any electron resonance spectrum, part at least of the material must be in the free-radical form. In this category is Chichibabin's hydrocarbon [22] (I) (p. 261) for which the spin-paired structure shown is quinonoid with fixed double bonds, whereas if the central link is reduced to a single bond each half of the molecule is a free radical, and aromatic character is restored to the rings. Chichibabin's hydrocarbon appears to exist as 4% diradical or triplet state in benzene solution at room temperature.

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[17] A. N. Holden, C. Kittel, F. R. Merritt, and W. A. Yager, *Phys. Rev.*, 1949, **75**, 1614.

[18] A. N. Holden, C. Kittel, F. R. Merritt, and W. A. Yager, *ibid.*, 1950, **77**, 147.

[19] C. H. Townes and J. Turkevich, *ibid.*, p. 148.

[20] A. N. Holden, W. A. Yager, and F. R. Merritt, *J. Chem. Phys.*, 1951, **19**, 1318.

[21] S. I. Weissman, *ibid.*, 1954, **22**, 1135.

[22] C. A. Hutchison, P. Kowalsky, R. C. Pastor, and G. W. Wheland, *ibid.*, 1952, **20**, 1485.

Free-radical resonance has been detected in coal,[23, 24] cokes,[25] graphite,[26] sugar chars,[27] etc. In the carbonised coals[25] there is a maximum radical concentration amounting to 3×10^{19}/g. or 1 in 1600 carbon atoms if the carbonisation is carried to 550° and no higher. At this temperature the peripheral fragments appear to be detached from the coal structure leaving radical centres, and the latter rearrange to predominantly spin-paired products at higher temperatures.

Radiation damage, whether caused by X-rays, γ-rays, electron bombardment, or neutron bombardment, commonly involves the rupture of bonds and the formation of free radicals which may remain trapped in a solid structure. Irradiated poly(methyl methacrylate),[28] polystyrene,[28] and amino-acids,[29] not to mention toe nails and fish scales,[29] have been shown to contain trapped radicals.

Quantitative Estimation of Free Radicals.—Once radicals have been detected it may be of interest to obtain a quantitative estimate of their concentration. The total integrated area of an absorption band is directly proportional to the number of free radicals present. The proportionality constant is a function of the spectrometer arrangement, sample size, temperature, and related experimental features, but not of the nature of the radical species involved. This result arises from the fact that the transition moment which governs the intensity depends only on the inherent magnetic moment of the electron. This means that an absolute spectrometer calibration should be possible, but like all absolute calibrations it would be extremely difficult. It is more practical to introduce weighed amounts of materials which are known to be exclusively free radicals and to relate other materials to the known radical concentration so introduced.

One use of this technique has been the study of the liquid sulphur equilibrium.[30] The cyclic S_8 molecules are spin paired, but the S_n chains have one unpaired electron at each end of the chain and the number of such ends can be counted at a series of temperatures. The results showed that the radical concentration was $1{\cdot}1 \times 10^{-3}$M at 300°, that the heat of scission was 33·4 kcal./link, that the maximum average chain length was $1{\cdot}5 \times 10^6$ links at 171°, and that the rate constant for replacement of chain ends was $2{\cdot}8 \times 10^8 \exp(-3100/RT)$ l. (g.-atom)$^{-1}$ sec.$^{-1}$. These figures show that the art of electron-resonance spectroscopy has reached the state where it can be used to obtain detailed chemical information.

Application has also been made to the detection and estimation of the number of free radicals trapped during polymerisation. With cross-linked

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[23] J. Uebersfeld, A. Étienne, and J. Combrisson, *Nature*, 1954, **174,** 614.

[24] N. S. Garif'yanov and B. M. Kozyrev, *Zhur. exp. teoret. Fiz.*, 1956, **30,** 272.

[25] D. J. E. Ingram, J. G. Tapley, R. Jackson, R. L. Bond, and A. R. Murnaghan, *Nature*, 1954, **174,** 797.

[26] J. G. Castle, *Phys. Rev.*, 1953, **92,** 1063.

[27] J. E. Bennett, D. J. E. Ingram, and J. G. Tapley, *J. Chem. Phys.*, 1955, **23,** 215.

[28] E. E. Schneider, *Discuss. Faraday Soc.*, 1955, **19,** 158.

[29] W. Gordy, W. B. Ard, and H. Shields, *Proc. Nat. Acad. Sci., U.S.A.*, 1955, **41,** 983.

[30] D. M. Gardner and G. K. Fraenkel, *J. Amer. Chem. Soc.*, 1956, **78,** 3279.

poly(methyl methacrylate) gels [31, 32] or precipitated polyacrylonitrile [33] about 2% of the radical chains initiated can result in trapped free radicals of indefinite life.

Hyperfine Splitting and Radical Structure.—The spectrum of diphenylpicrylhydrazyl in solution (Fig. 3) shows a well-developed hyperfine structure and this type of absorption with multiple peaks is typical of most radicals in dilute solution. It is necessary therefore to discuss whence such a structure arises and what information can be derived from its interpretation. It is now well established that the structure relates to the possible orientations of the nuclei and of the magnetic field associated with their magnetic moments.

Any nucleus has a definite orientation with respect to the external magnetic field, and the electron spin which is parallel to the field, so that the extra magnetic field due to the nuclear moment, appropriately averaged over the electron orbital, will not be zero. The average field from this cause will add to the external field perceived by the electron, so that resonance occurs at a lower value of the external field; it is the net field from the two sources which governs the resonance condition. If the nucleus is reversed in orientation the magnitude of its field is the same, but it will now subtract from the external field so that resonance occurs at a higher value of the latter. A hydrogen nucleus with spin 1/2 has just two such orientations and at temperatures above 1° K the two orientations are equally probable. In an experiment on a large assembly of molecules, half will show resonance absorption below the expected field position and half above, so that a pair of absorption peaks are obtained which are of equal intensity and symmetrically placed with respect to the centre. If there are two hydrogen atoms present which are in non-equivalent positions, then each of the two lines resulting from one hydrogen atom will be split again by the second, and four lines be obtained of equal intensity in a symmetrical pattern. If the two hydrogen atoms are equivalent they will interact equally and the two centre lines will coalesce and a three-line pattern with relative intensities 1 : 2 : 1 will result. In general n equivalent nuclei with spin 1/2 give a symmetrical $(n + 1)$ line pattern with relative intensities as the binomial coefficients in the expansion of $(1 + x)^n$. Nuclei with larger spins have $(2I + 1)$ equally probable orientations and split the resonance line into $(2I + 1)$ symmetrically placed lines of equal intensity. A rough measure of the relative importance of the coupling for different nuclei can be obtained from the nuclear resonance frequencies in the last column of Table 1. For the same electronic wave function the coupling would be proportional to this frequency.

A more formal treatment of the coupling would say that the spin part of the Hamiltonian contains a term $a\boldsymbol{I}\cdot\boldsymbol{S}$ which leads to diagonal energy contribu-

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[31] G. K. Fraenkel, J. M. Hirshon, and C. Walling, *J. Amer. Chem. Soc.*, 1954, **76**, 3606.

[32] N. M. Atherton, H. W. Melville, and D. H. Whiffen, in the press.

[33] C. H. Bamford, A. D. Jenkins, D. J. E. Ingram, and M. C. R. Symons, *Nature*, 1955, **175**, 894.

tions aI_zS_z. Since S_z changes from $+1/2$ to $-1/2$ the extra transition energy required by this coupling is aI_z as the selection rule $\Delta I_z = 0$ normally applies. The coupling constant, a, which governs the separation between the hyperfine peaks consists of two parts. One varies as the average of the inverse cube of the distance of the nucleus from the electron and also as $(3 \cos^2 \theta - 1)$, where θ is the angle between the line joining the electron to the nucleus and the magnetic field direction. For solids this contribution may be important but it does not seem to have been treated in detail for free radicals. Its influence has been shown experimentally by the marked change of hyperfine structure with orientation shown by single crystal of $K_2(SO_3)_2NOH$ with $(SO_3)_2NO^{2-}$ as a free-radical impurity.[34] The change of spectrum with crystal orientation for a γ-irradiated single crystal [35] of glycine must also be due to this direction-dependent term; it also implies that the trapped radicals are specifically oriented with respect to the crystal lattice of the host. For liquids the molecular-rotational motion is fast compared with the value of a in c./sec., and the energy levels of each individual radical depend only on the value of a averaged over all solid angles; the average of $(3 \cos^2 \theta - 1)$ is then zero and the direction-dependent term vanishes.

The second part of a is direction-independent, persists in the liquid state, and is responsible for the observed hyperfine structure. Its value is proportional to the probability of the unpaired electron's being at the nucleus responsible for the coupling. If the wave function for the molecule were expanded in one-electron atomic wave functions centred on this nucleus, only the spherical s wave functions would contribute to this probability since other wave functions all have a node at the nucleus.

The interpretation of the hyperfine structure is of importance in identifying the radical and for locating the unpaired electron. We will consider diphenylpicrylhydrazyl (II) in detail. The spectrum in Fig. 3*a* shows 5 lines of intensity ratio 1 : 2 : 3 : 2 : 1 separated from each other by 10 gauss.[36] The structure of the radical (II) suggests that the unpaired electron is unlikely to be on the hydrogen atoms or the nitro-groups, but may be largely on one or both of the central nitrogen atoms. Location on the ring carbon atoms would not affect the shape of the hyperfine pattern since ^{12}C has zero spin and cannot couple. If the electron were located predominantly on one of the nitrogen atoms, three equally intense hyperfine lines would be expected, since ^{14}N has a spin of 1. If the adjacent nitrogen atom were also to couple, a further three-fold splitting would result to give a total of nine lines. But in the special case that the two nitrogen atoms couple equally, some of the lines overlap each other and the observed five-line spectrum is to be expected. Table 2 shows how this result is obtained in terms of the resolved spin angular momenta, I_{za} and I_{zb}, of the two ^{14}N nuclei. The possibilities for the individual spin momenta are indicated in the first and the second column, and the total addition to the transition

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[34] S. I. Weissman, T. R. Tuttle, and E. de Boer, *J. Phys. Chem.*, 1957, **61,** 28.

[35] J. Uebersfeld and E. Erb, *Compt. rend.*, 1956, **242,** 478.

[36] C. A. Hutchison, R. C. Pastor, and P. Kowalsky, *J. Chem. Phys.*, 1952, **20,** 534.

energy by virtue of the coupling term $aS_z(I_{za} + I_{zb})$ in the third. The total intensities of the transitions are proportional to the figures in the fourth column since each I_z combination is of equal probability at room temperature. In this case the result that the odd electron is equally likely to be on each of the central nitrogen atoms is unexpected from the chemical structure and is not dictated by symmetry grounds as in many other cases. Indeed if the two phenyl groups are joined in their *ortho*-positions, as in *N*-9-carbazolylpicrylaminyl (III), the coupling becomes unequal,[37] being 6·6 and 13·3 gauss for the two nitrogen atoms.

TABLE 2. *Coupling scheme for diphenylpicrylhydrazyl* (II)

I_{za}	I_{zb}	Extra transition energy	Relative intensity
$+1$	$+1$	$+2a$	1
$+1$	0	$+a$	2
0	$+1$	$+a$	
$+1$	-1	0	3
0	0	0	
-1	$+1$	0	
0	-1	$-a$	2
-1	0	$-a$	
-1	-1	$-2a$	1

An interesting pair of compounds [38] are triphenylmethyl, $Ph_3C\cdot$, and the isoelectronic triphenylnitrogen positive ion, $Ph_3N^{\cdot+}$. With triphenylmethyl there is very narrow hyperfine structure resulting from interactions with the hydrogen nuclei, but when the central carbon atom, normally ^{12}C of zero spin, is replaced by ^{13}C of spin 1/2, an appreciable coupling of 22 gauss is observed; this is in marked contrast to the absence of coupling on replacement with $^{14}N^+$. This difference is not wholly accounted for by the difference in the nuclear moments (see Table 1) but must indicate that the unpaired electron is partly on the C atom but not appreciably on the N^+ ion. This may be reconciled with the greater electronegativity of N^+ since this will tend to complete its valency shell with an electron pair and leave the odd electron to be distributed over the phenyl rings.

It is possible to calculate the numerical value of the coupling constant for a given nucleus and a specified electron wave function, and the ratio of this quantity to the observed coupling gives the fractional occupation of the corresponding orbital. For 2*s* and 3*s* wave functions the calculations are only approximate, in view of inexact knowledge of inner-shell shielding, etc., appropriate to the wave function near the nucleus. But for 1*s* wave functions of hydrogen the property required refers to the atom in the ground state and can be calculated and also measured by an atomic-beam experiment; [39] the coupling is found to be 507 gauss, which is 1420·41

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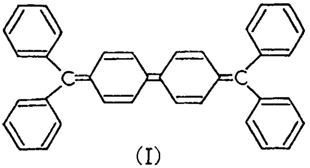
[37] H. S. Jarrett, *J. Chem. Phys.*, 1953, **21**, 761.

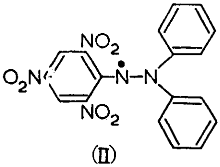
[38] G. E. Pake, S. I. Weissman, and J. Townsend, *Discuss. Faraday Soc.*, 1955, **19**, 147.

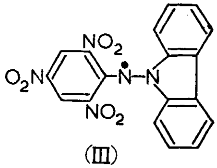
[39] J. E. Nafe and E. B. Nelson, *Phys. Rev.*, 1948, **73**, 718.

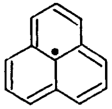
Mc./sec. For hydrogen atoms trapped in solid hydrogen[40] the coupling is 1417·13 Mc./sec., which shows that the wave function is slightly distorted in this state. Couplings in the range 1405—1425 Mc./sec. were found [41] for solutions of perchloric acid, sulphuric acid, and phosphoric acid in ice at 77° K which had been irradiated with γ-rays ; there can be no doubt that free hydrogen atoms are trapped in these materials.

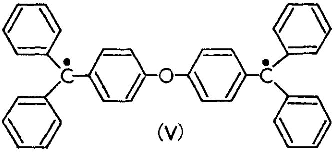
Much smaller hydrogen couplings are found when the odd electron is on a carbon skeleton. The spectra of the naphthalene negative ion, $C_{10}H_8^-$, and its deuterated derivatives have been interpreted.[42] There is a coupling of 5·01 gauss to each α-hydrogen atom, indicating 0·99% of odd-electron character on these atoms and a coupling of 1·77 gauss, which is equivalent to 0·35% of odd-electron character, at each β-hydrogen atom. In other cases, resolution and interpretation of the hyperfine structure can give strong support to the nature of the radical present. Thus, the action of ionising X-rays on dimethylzinc, $ZnMe_2$, at 77° K gives a spectrum [43] with four equally spaced lines of intensity ratio 1 : 3 : 3 : 1, which leaves a strong presumption that the spectrum is due to trapped methyl groups. Similarly ultraviolet irradiation of hydrogen peroxide in solid propan-2-ol leads to a spectrum of seven lines [44] attributable to the radical $HO{\cdot}CMe_2{\cdot}$.


(I)


(II)


(III)


(IV)


(V)

Nicely resolved hyperfine structure has been observed with semiquinone radicals,[45] and elucidation of the pattern of many of the substituted compounds has proved possible ; the chloro-semiquinone series proves to be specially simple [46] with one more hyperfine line than the number of hydrogen atoms in the ring. Many aromatic radicals and radical ions show coupling to the hydrogen atoms, and high resolution is required to obtain the completely resolved spectrum. Triphenylmethyl shows at least 70 lines

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[40] C. K. Jen, S. N. Foner, E. L. Cochran, and V. A. Bowers, *ibid.*, 1956, **104,** 846.

[41] R. Livingston, H. Zeldes, and E. H. Taylor, *Discuss. Faraday Soc.*, 1955, **19,** 166.

[42] T. R. Tuttle, R. L. Ward, and S. I. Weissman, *J. Chem. Phys.*, 1956, **25,** 189.

[43] W. Gordy and C. G. McCormack, *J. Amer. Chem. Soc.*, 1956, **78,** 3243.

[44] S. F. Gibson, D. J. E. Ingram, M. C. R. Symons, and M. G. Townsend, *Trans. Faraday Soc.*, 1957, **53,** 914.

[45] B. Venkataraman and G. K. Fraenkel, *J. Amer. Chem. Soc.*, 1955, **77,** 2707.

[46] J. E. Wertz and J. L. Vivo, *J. Chem. Phys.*, 1955, **23,** 2441.

spread over less than 30 gauss,[47] while the anthracene negative ion [48] and the perinaphthenyl radical (IV) [49] are among others that show impressive, multi-line spectra.

Triplet States and Diradicals.—Any molecule which contains two unpaired electrons may be in a triplet state or it may be a diradical. The distinction lies in that in the former the electrons couple strongly to each other to give a state with $S = 1$ and three component states corresponding to $S_z = 0, \pm 1$ in a magnetic field. For a diradical the mutual electron interaction is weaker than that of each with the magnetic field, and each electron has an orientation uncorrelated with that of the other. Such a diradical nature must be presumed for the long chains of sulphur [30] where the radical sites may be several hundred Å apart. There is one interesting example where an experimental distinction has been made and the ether (V) shown [50] to be a diradical: ^{13}C was introduced into the two methyl-carbon positions and the hyperfine-structure pattern shown to be that expected for each electron interacting with only one ^{13}C atom. For a triplet state the electron-exchange process would result in each electron effectively coupling to both ^{13}C atoms, contrary to experiment.

Most molecules with spin-paired singlet ground states will have triplet, as opposed to diradical, excited states. Configurational interaction with the ground state causes the singlet and the triplet excited state to be well separated in energy, whereas a diradical corresponds to essentially degenerate singlet and triplet states. This argument does not apply if the excited states are of very different geometrical shapes. Well-known and well-established triplet states in organic molecules are the phosphorescent states, many of which are easily formed by ultraviolet irradiation and have appreciable half-lives. Although several searches for electron resonance have been made, none has been reported for such systems. There exist [51] electron spin–spin and spin–orbit interactions which can remove the zero-field degeneracy of the $S_z = 0$ from the $S_z = \pm 1$ states. In a magnetic field the value of these interactions depends on the direction of that field with respect to the molecule, and as a consequence the transition frequency for electron resonance is different for different individual molecules in an amorphous or polycrystalline material. Extremely broad, and therefore extremely weak, lines will result and these are not detected by the spectrometers employed. The interactions involved are incapable of affecting the relative energies of $S_z = \pm 1/2$ states which form a Kramers doublet, and the radical resonances are therefore narrow.

Line Widths, Relaxation Times, Exchange Rates, etc.—Many measurements have been performed of exact line widths, line shapes, relaxation times and exact resonance frequencies. The original papers * must be consulted

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[47] H. S. Jarrett and G. J. Sloan, *J. Chem. Phys.*, 1954, **22**, 1783.

[48] E. de Boer, *ibid.*, 1956, **25**, 190.

[49] P. B. Sogo, M. Nakazaki, and M. Calvin, *ibid.*, 1957, **26**, 1343.

[50] D. C. Reitz and S. I. Weissman, *ibid.*, 1957, **27**, 968.

[51] H. S. Jarrett, G. J. Sloan, and W. R. Vaughan, *ibid.*, 1956, **25**, 697.

* For a comprehensive bibliography see ref. 5.

for the detailed theories which will not be treated here; the mechanisms of line broadening vary considerably with the type of system involved. The line widths at half height vary widely, extreme values being "tetraphenylstibonium peroxylaminedisulphonate",[52] $[(C_6H_5)_4Sb^+]_2NO(SO_3)_2^{2-}$, 100 gauss, and solvated electrons as present in solutions of sodium in liquid ammonia,[53] 0·02 gauss.

There is one contribution to the line width which must be discussed since it enables kinetic rate constants to be determined for electron-exchange reactions. A well-studied case is the reaction [54]

$$C_{10}H_8^- + C_{10}H_8 \longrightarrow C_{10}H_8 + C_{10}H_8^-$$

The radical ion is made by the action of metallic sodium on naphthalene in tetrahydrofuran solution and at low concentrations a well-resolved hyperfine structure is observed which results from coupling to the hydrogen atoms. On addition of more naphthalene, in the absence of excess of sodium, the individual lines broaden. To understand this phenomenon consider the Heisenberg uncertainty principle as applied to the conjugate quantities energy and time, namely $\Delta t \Delta E \sim h$. If an absorbing radical loses its identity, by virtue of the exchange reaction displayed above, after an average time interval Δt, this exchange breaks off the spectroscopic absorption process and leaves an uncertainty in the size of the energy quantum absorbed $\sim h/\Delta t$. This appears as an uncertainty in the absorption frequency $\sim 1/\Delta t$, which is the width of the band in cycles/sec. Δt is thus measurable from the observed line widths, and it has been shown [54] that the bimolecular rate constant for the naphthalene ion exchange is $1{\cdot}0 \times 10^6$ l. mole^{-1} sec.$^{-1}$ at 30°.

Conclusion.—A number of aspects have been omitted from this Review since their interpretation is not fully clear; this category includes small frequency, or g value, variations and incomplete orbital quenching. Also, as stated above, results [8, 9] on metallic ions with d and f electrons have been omitted as well as applications to solid-state physics,[55] especially F centres [56] and semiconductors. There are also applications to magnetic field measuring devices and to low-noise, stimulated emission or maser amplifiers.[57]

From this survey of the more chemical topics, it is clear that electron-resonance spectroscopy has reached the stage where in most future applications systems will be studied for the inherent interest in the end result, rather than for the interest in the techniques of measurement and the principles of interpretation. The technique will be an essential tool in the study of radiation damage and there are likely to be applications to the study of biological and botanical systems, following the initial successes in detecting free radicals in frogs' eggs, firefly lanterns,[58] and oak-leaf stems.[59]

[52] T. L. Chu, G. E. Pake, D. E. Paul, J. Townsend and S. I. Weissman, *J. Phys. Chem.*, 1953, **57**, 504. [53] R. Bieler and D. Roux, *Helv. Phys. Acta*, 1957, **30**, 216.

[54] R. L. Ward and S. I. Weissman, *J. Amer. Chem. Soc.*, 1954, **76**, 3612.

[55] D. M. S. Bagguley and J. Owen, *Rep. Progr. Phys.*, 1957, **20**, 304.

[56] A. F. Kip, C. Kittel, R. A. Levy, and A. M. Portis, *Phys. Rev.*, 1953, **91**, 1066.

[57] H. E. D. Scovil, G. Feher, and H. Seider, *ibid.*, 1957, **105**, 762.

[58] B. Commoner, J. Townsend, and G. E. Pake, *Nature*, 1954, **174**, 689.

[59] H. Shields, W. B. Ard and W. Gordy, *ibid.*, 1956, **177**, 985.

There is a need to obtain more spectra of simple radicals of known structure, so that the nature of uncertain radicals can be deduced from the hyperfine pattern in their spectra. On the interpretational side there is need for a more precise understanding of the relation between the hyperfine coupling constants and electronic wave functions, especially for the non-aromatic radicals. Experimental sensitivities may be improved to the point at which measurement of radical concentration can be used to follow the kinetics of simpler free-radical reactions than those of cross-linking and heterogeneous polymerisations. Co-ordination with flash photolysis and other photochemical techniques appears promising. Also the field of coal, charcoal, and graphite structure will doubtless receive further study, especially in connection with adsorption and catalytic properties. Even if this list of applications is overshadowed by that for nuclear resonance, it is still so varied and large that chemists cannot afford to neglect it.