1 EPR Spectroscopy: The Basics

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1 THE BEGINNING

1.1 WHAT'S IN A NAME

This spectroscopy has several names. The name electron spin resonance (ESR) developed from the field of free radicals. Most free radicals have very little orbital angular momentum and thus, the spin of the system is dominated by the spin of the electron. The name electron paramagnetic resonance was preferred by researchers studying transition metals. In these systems, the unpaired electrons often have large values for their orbital angular momentum, thus the term paramagnetic is more appropriate. Electron magnetic resonance (EMR) has been offered as an incluse alternative. However, the name electron paramagnetic resonance is appropriate from a physics point of view for radicals, transition metals and solid state studies. Thus, the International EPR Society recommends the use of EPR. But students should keep in mind that, with respect to the spectroscopy, that is the instrumentation, EPR = ESR = EMR = epr = esr = emr.

1.2 WHAT IS EPR?

EPR is a spectroscopy that looks at the environment of unpaired electrons. Several textbooks deal with the physics of this spectroscopy [1–3]. Electrons have spin ($S = 1/2$; $m_s = \pm 1/2$); because they are particles with a charge (-1) and they have motion (spin), they produce a magnetic field and thus will behave as little magnets with quantum mechanical characteristics.

When placed in a magnetic field, these quantum properties dictate that there are only two possible orientations, either they are in a low energy state or a high energy state (Figure 1).

The difference in energy (ΔE) between these two states is directly proportional to the magnetic field strength (H):

$$\Delta E = h\nu = g\beta H \tag{1}$$

General Aspects of the Chemistry of Radicals, edited by Z. B. Alfassi.

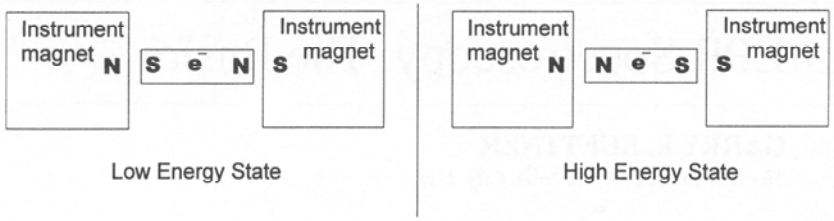

Figure 1 Low energy state and high energy state configurations for the electron spin when in the magnetic field of the EPR. An EPR spectrometer uses electromagnets to provide a variable magnetic field over the sample.

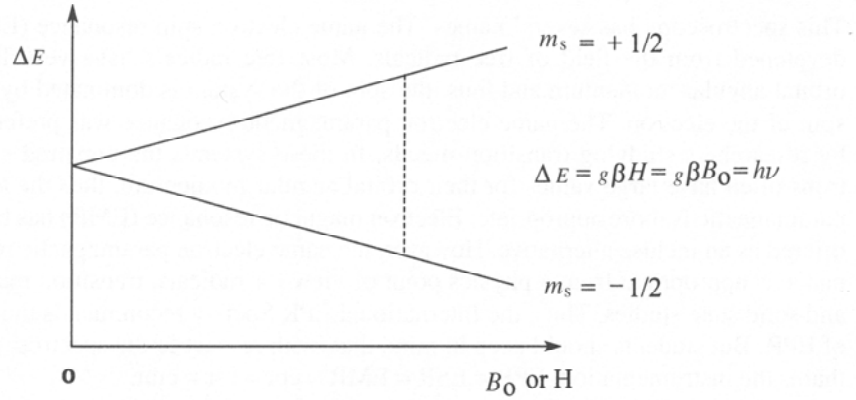

Figure 2 Separation in energy between the two spin states, often called the Zeeman splitting, is shown. The dashed vertical line represents the absorption of energy for the 'flipping' of the electron spin from the $m_s = -\frac{1}{2}$ to the $m_s = +\frac{1}{2}$ spin state.

where g is the g factor, a dimensionless constant for any given species; for a free electron $g = 2.002322$. Beta(β) is the Bohr magneton, equal to $eh/4\pi mc = 0.927\,31 \times 10^{-20}$ erg G^{-1}, where $-e$ and m are the charge and mass of the electron, h is Planck's constant and c the speed of light. Thus, the energy separation vs. H is as shown in Figure 2.

1.3 EPR IS A MICROWAVE EXPERIMENT

The actual magnitude of the energy separation in most EPR experiments lies in the microwave region of the spectrum. As seen in Table 1, the photon wavelength is very long, in the millimeter or centimeter range. This region of the spectrum is broken into 'bands', Table 2. The names of these bands, L, S, X, K, etc., arose when microwave research first began and was focused on the development and

Table 1 The electromagnetic spectrum.

Type	Wavelength range
γ rays	10^{-4}–10^{-1} nm
X rays	10^{-2}–10 nm
Vacuum UV	10–200 nm
UV	200–380 nm
Vis	380–800 nm
IR	0.8–1000 μm
Microwave	1 mm–100 cm

Table 2 Microwave frequency bands.

Band	Range (GHz)	≈EPR ν (GHz)	Field center (G)[a]
L	0.39–1.55	1.5	540
S	1.55–3.90	3.0	1100
C	3.90–6.20	6.0	2200
X	6.20–10.9	9.5	3400
K	10.9–36	23	8200
Q	36–46	36	13000
V	46–56	50	18000
W	56–100	95	34000

[a]For a free radical, i.e. a $g = 2$, species.

application of radar. In the area of EPR, this nomenclature is still used to designate the approximate frequency used by a specific instrument.

2 THE STANDARD CONTINUOUS WAVE EPR EXPERIMENT

2.1 THE EXPERIMENT

The most widely used frequency band for continuous wave (CW) EPR spectroscopy is X band, $\nu \approx 9.5$ GHz, $\lambda \approx 3$ cm. Thus, for free radical species with $g \approx 2$, the magnetic field required for resonance, absorption of energy, is ca. 3400 Gauss. X band, L band and Q band instrumentation are available commercially and other frequencies are used in specialized research centers.

2.2 MAGNETIC FIELD SWEEP—ν IS FIXED

In the EPR experiment, the energy of the microwave radiation is connected to resonance by equation (1):

$$\Delta E = h\nu = g\beta h \tag{1}$$

Upon examination of this simple relationship, we see that h and β are physical constants and g is a constant for any given species examined; thus, the only variables in the equation are v and H.

In a typical UV–vis experiment, the absorption spectrum of a species is presented as a plot of absorbance vs. wavelength. However, in the world of microwave EPR spectroscopy, it is not possible to vary the wavelength (frequency) of the instrument for an experiment. Thus, the frequency of each experiment is fixed and the magnetic field is varied. The sample is placed between the poles of the electromagnet of the spectrometer and the magnetic field is swept. In UV–vis spectroscopy, the ordinate is the absorbance, however, the circuitry of the EPR instrument presents the spectrum as the first derivative of the absorbance vs. magnetic field strength at the sample, Figure 3.

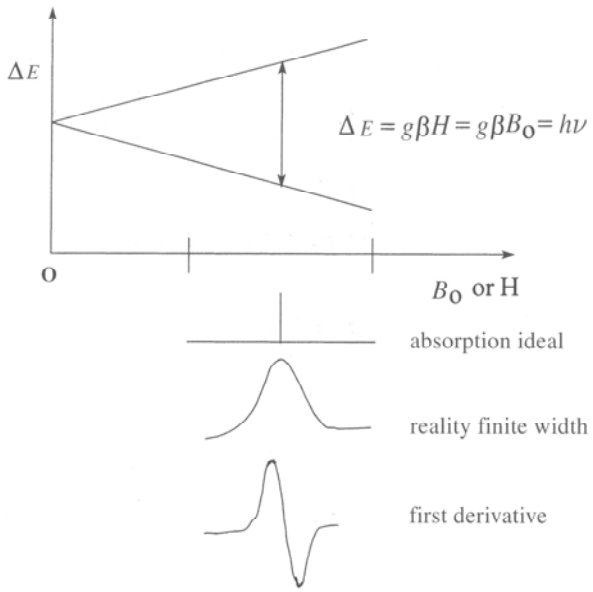

Figure 3 Schematic showing how the two energy levels of the unpaired electron separate as a function of magnetic field strength. The ideal absorption would be a line of infinitesimal width. However, energy levels within a molecule (free radical) are intrinscially 'fuzzy' due to internal motion, internal magnets (i.e. nuclei that have spin) and also potential external factors. Thus, in the real world, absorption lines have finite width. The spectra are presented as the first derivative of the absorption curve. If the species is a free radical with $g = 2$, then the center of this spectrum would be at 3500 G when the frequency of the instrument is 9.8 GHz.

3 WHERE CAN THE INFORMATION BE IN CW EPR DATA?

3.1 *g* FACTOR OR *g* VALUE

The *g* factor * is a constant for any given species but can vary considerably from species to species. From a mathematical point of view, *g* actually has many of the characteristics of a tensor. Because the actual value of *g* depends on both the spin of the electron as well as the orbital angular momentum of the electron, *g* will have information about the electronic structure as well as the symmetry of the system.

In the language of quantum mechanics, the spin Hamiltonian of the Zeeman term will appear as:

$$\hat{H} = \beta \vec{B}_t \cdot \mathbf{g} \cdot \hat{S}$$

$$\hat{H} = \beta(\vec{B}_x, \vec{B}_y, \vec{B}_z) \begin{pmatrix} g_{xx} & 0 & 0 \\ 0 & g_{yy} & 0 \\ 0 & 0 & g_{zz} \end{pmatrix} \begin{pmatrix} \hat{S}_x \\ \hat{S}_y \\ \hat{S}_z \end{pmatrix} \tag{2}$$

Thus, *g* has a directional character in that the diagonalized • *g* tensor will have elements g_{xx}, g_{yy} and g_{zz}. Because these *g* values are characteristic of the spin and orbital angular momentum of the unpaired electron in the species, they can provide information on the identity of the species or at least, the type of species observed.

3.1.1 Practical level

The practical determination of *g* value for EPR spectra boils down to:

$$g_{\text{observed}} = \frac{0.714\,4775\ \nu\ (\text{in GHz})}{H\ (\text{or } B \text{ in kG})} \tag{3}$$

where ν is the experimental frequency in GHz and *H* (or *B*)† is the magnetic strength in kgauss (kG). If tesla (T) is the preferred unit for magnetic field strength, then:

$$g_{\text{observed}} = \frac{0.071\,447\,75\ \nu\ (\text{in GHz})}{B\ (\text{in mT})} \tag{4}$$

Recall that $1\text{T} = 1 \times 10^4\,\text{G}$ and that for the simple approach above, *B* and *H* are used interchangeably.

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* Always use lower case *g* when referring to the *g* value or *g* factor.

† Magnetic fields are represented as *H* or *B*. *B* is now most often used, but in EPR they are still both used interchangeably.

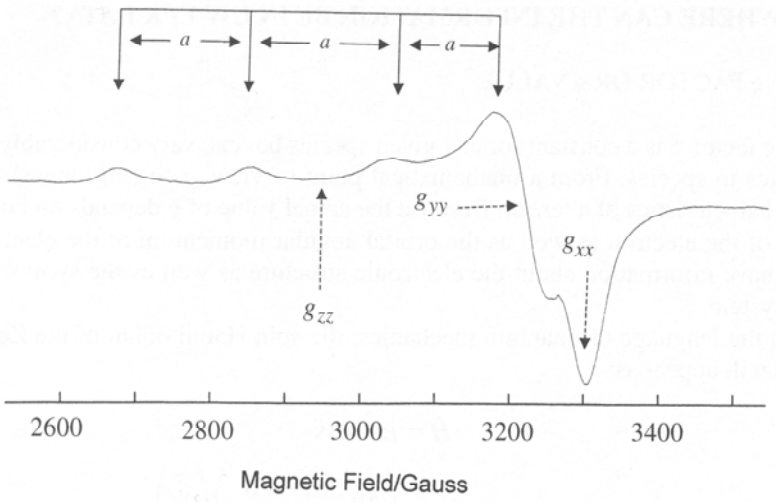


Figure 4 Typical x-band copper spectrum showing all three g values as well as hyperfine splitting in the 'Z' domain. $g_{zz} \sim 2.25$, $g_{yy} \sim 2.06$ and $g_{xx} \sim 2.01$; $a_{zz} \sim 175$ G.

3.1.2 Cu as an example

Transition metals can be identified by their unique g values and lineshapes. Cu^{2+}, Fe^{3+} and Mn^{2+} present different spectra and the exact nature of these spectra is dependent upon the ligand field environment. Examples of transition metal EPR spectra have been published [4–7]. Thus, not only identification of species, but the environment of the transition metal can be deduced from the EPR spectrum.

Spectra for Cu^{2+} can take many shapes, but they often are similar to Figure 4. This spectrum shows lines that are typical of Cu^{2+} hyperfine splitting at lower field plus a feature at ca. 3100 G consistent with g value separations.

3.2 HYPERFINE SPLITTINGS

Hyperfine splittings provide information on the structure of a species. Some nuclei have spin; because they have spin, they will behave as little magnets, adding to or subtracting from the larger magnetic field provided by the electromagnet of the instrument. Thus, a single resonance line can be split into two, three or more lines (Table 3). The distance on the 'x axis' or more correctly, the spacing in gauss (or Tesla) is the hyperfine coupling. There can be more than one nearby nucleus providing hyperfine splitting. Thus, the pattern can be complex. But analysis of the pattern provides the rich structural information wanted.

Table 3 Examples of spin states and EPR spectra.

Nuclei	Spin I (m_s)	Number of lines
^{12}C	0 (0)	1
^{13}C	$\frac{1}{2}$ $(-\frac{1}{2}, +\frac{1}{2})$	2
^{14}N	1 (−1, 0, +1)	3
^{15}N	$\frac{1}{2}$ $(-\frac{1}{2}, +\frac{1}{2})$	2
^{1}H	$(-\frac{1}{2}, +\frac{1}{2})$	2
^{2}H	1 (−1, 0, +1)	3
Cu	$\frac{3}{2}$ $(-\frac{3}{2}, -\frac{1}{2}, +\frac{1}{2}, +\frac{3}{2})$	4
Mn	$\frac{5}{2}$ $(-\frac{5}{2}, -\frac{3}{2}, -\frac{1}{2}, +\frac{3}{2}, +\frac{3}{2})$	6

3.2.1 Simple doublet hyperfine splitting

The analysis of an EPR spectrum that exhibits hyperfine splitting is most easily done using a 'splitting tree'. This technique allows the pattern of lines to be understood, as seen in a freely tumbling solution spectrum of a free radical. For example, a simple doublet spectrum is observed if a nuclei of spin 1/2 sees the unpaired electron of the radical. This nuclei will have two spin states, $m_I = \pm 1/2$, and thus the energy lines are split, Figure 5.

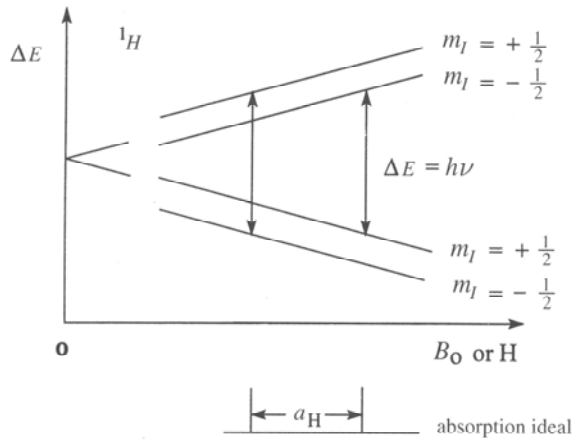


Figure 5 Schematic of the energy level diagram for hyperfine splitting brought about by a nuclei of spin $\frac{1}{2}$. The hyperfine splitting a^H would occur if a nearby proton provided the splitting.

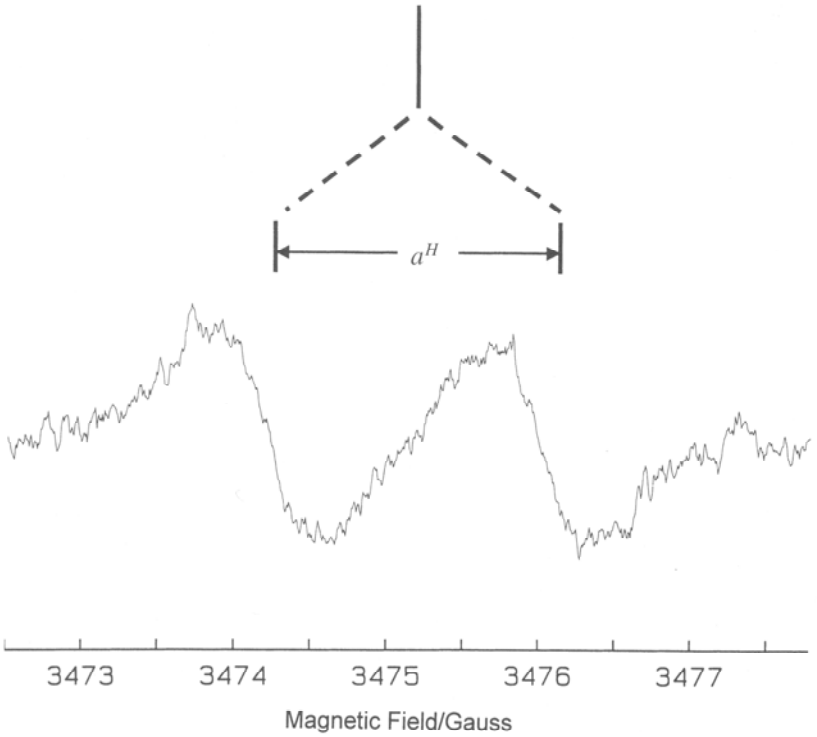


Figure 6 Simple splitting tree for a doublet spectrum, that is when a resonance line is split into two lines of equal intensity by a spin $\frac{1}{2}$ nucleus, such as ^{1}H, ^{13}C or ^{15}N.

The resulting splitting tree will consist of two lines of equal height. In Figure 6 the single line of the top of the splitting tree represents the EPR absorption with no splitting. The length of this line represents the intensity of the line, that is the line height. When the line is split, each resulting line has one-half the height (intensity) of the theoretical original line. These are centered on the original line and the hyperfine splitting, a^H in this example, is the hyperfine splitting constant.

3.2.2 A triplet

If a spin 1 nuclei is nearby, such as ^{14}N, and is 'seen' by the unpaired electron, then three lines of equal height will be observed; Figure 7 shows the energy level splittings. A splitting tree would have each line at $\frac{1}{3}$ the height of the 'original' single line spectrum.

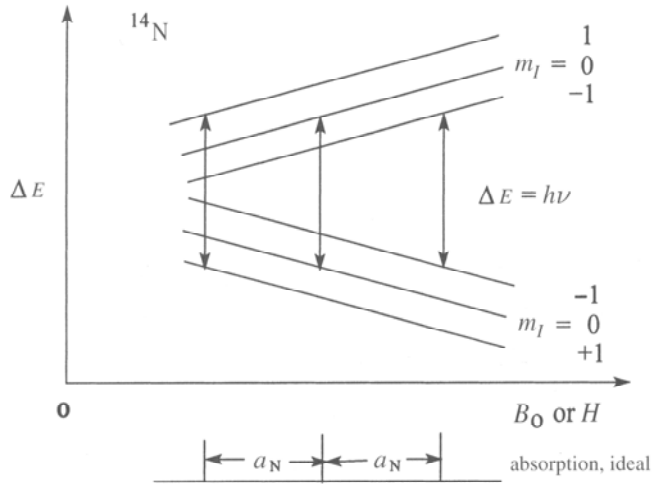


Figure 7 Example of a triplet energy level diagram formed from hyperfine interaction with a spin 1 nucleus, such as ^{14}N.

A three-line spectrum can also result when two spin $=\frac{1}{2}$ nuclei provide identical hyperfine interactions with the unpaired electron. The most common example would be two hydrogens that are equivalent by symmetry, such as in a $-CH_2-$ group or on a benzene or similar ring system. However, identical interaction can also arise by accident. No matter what the reason, a triplet signal will be observed, but rather than a 1:1:1 intensity ratio as observed with ^{14}N, a 1:2:1 ratio will be observed. The splitting tree of Figure 8 shows how each nuclei splits the resonance into two lines of half height, but the identical coupling results in overlap of the two middle lines of the four lines possible. This overlap brings about the three-line 1 : 2 : 1 intensity ratio observed.

3.2.3 A triplet of doublets

The example of Figure 9 shows a spectrum when both a spin 1 and a spin $\frac{1}{2}$ are providing hyperfine splitting. In this spectrum, the spin 1 is on ^{14}N and the spin $\frac{1}{2}$ is a ^{1}H. The nitrogen splitting is greater than the hydrogen splitting. Note that in the splitting tree, the three lines that result after the ^{14}N splitting is applied are $\frac{1}{3}$ the height of the original. The ^{1}H splits each of these lines into two; the intensity is decreased by a factor of two, thus each line is $\frac{1}{6}$ the height of the original line.

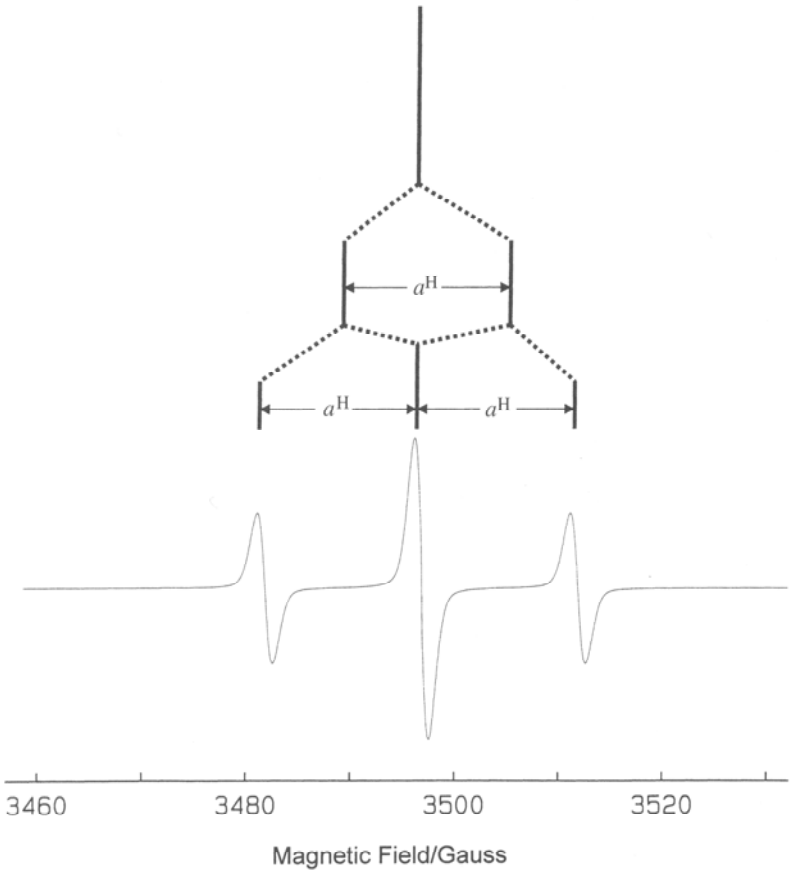


Figure 8 Hyperfine splitting tree for a spin system that has two identical spin $\frac{1}{2}$ nuclei providing the splitting. This shows how the 1:2:1 intensity ratio is achieved.

3.3 LINEWIDTH

The linewidth observed is a composite of many factors. There is the intrinsic linewidth that is a function of the spin relaxation time, but there can be much additional information in line broadening beyond this intrinsic width. Examples of effects that produce broadening are: unresolved hyperfine structure; dipolar interaction with paramagnetic species such as O_2, $^{\bullet}NO$, or metal complexes; motion, slow tumbling can broaden or completely change the character of an EPR spectrum depending upon the rotational correlation time.

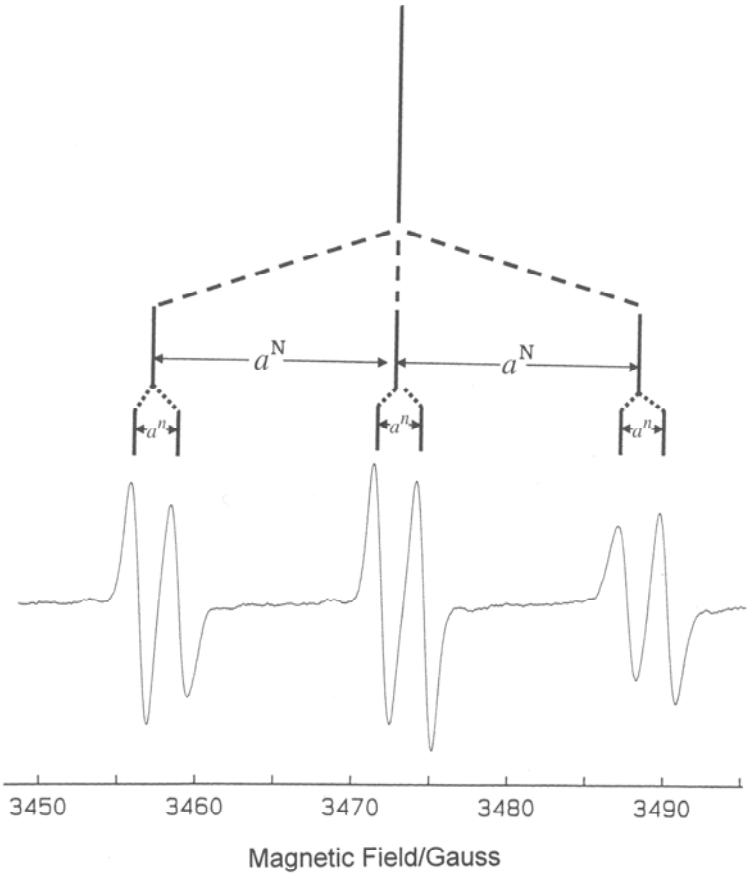


Figure 9 Example showing how two nuclei provide a splitting pattern. Although there is some lack of symmetry in the lines, the areas under each of the six lines are identical. Note that the two lines that are somewhat shorter are a bit broader; thus the areas are the same.

3.4 'LINE HEIGHT' CAN GIVE CONCENTRATION OF SPECIES

3.4.1 Concentration is proportional to absorption area

The concentration of a species observed in an EPR spectrum is proportional to the area under the absorption curve. Because the typical spectral display is presented as the first derivative of the absorption curve, it is necessary to double integrate an EPR spectrum to determine its relative area:

$$[R^{\bullet}] \propto \int_{H_1}^{H_2}\int_{H_1}^{H_2} \text{spectrum}\, d^2H \qquad (5)$$

Thus, it is possible to determine the absolute concentration of a species, or number of species in the sample, if appropriate standards are used [1, 8].

3.4.2 The Standard

Although there are numerous 'stable' species that can be used as standards, on a practical level, a species similar to the species being studied should be chosen. Because the EPR signal intensity is proportional to (g factor)^2, as well as instrument conditions, and the physical arrangement of the sample, quantitation is easier if:

1. The same solvent and sample geometry are used.
2. The power being applied is the same *and* is below that which would produce saturation effects.
3. The instrument modulation amplitude can be on the order of or even somewhat greater than ($\times$ 2–4) the linewidth of the species, but for simplicity, kept the same for sample and standard.
4. Samples are at the same temperature.
5. The receiver gain need not be the same, as this is easily corrected, assuming linearity.

Although the integration result will be in arbitrary units, it is easy to connect these area units for the unknown (X) with the concentration of the standard:

$$[X] = \frac{[\text{STD}]\ (\text{area of } X)(\text{receiver gain for } X)}{(\text{area STD})\ (\text{receiver gain for Std})} \tag{6}$$

This assumes: (i) The scan width is the same. (ii) The modulation amplitudes used for each are the same. (iii) The same non-saturating power was used. (iv) The g factors are essentially similar.* (v) The entire spectrum was integrated and not just one line.

If the area under the absorption curve for only one line of each species was determined, then the total area can be determined by use of a splitting tree, *vide supra*, and scaling as appropriate.

3.4.3 [R$^\bullet$] α EPR signal heights, but with restrictions

If only relative concentrations for a single species are needed, that is, if there is twice as much radical in sample 1 compared to sample 2, then line height can be used.

If the instrumental conditions are the same and the same species is being examined, then a simple examination of line height is all that is needed. Line

* An error of less that 5% would require that $0.95 < (g_{STD}/g_x)^2 < 1.05$.

height can be compared to determine relative radical concentration. However, if different species are to be compared using line height, then corrections must be made for linewidth, *g* value and power saturation as appropriate.

3.5 POWER SATURATION CURVES

3.5.1 What is a power saturation curve?

EPR instrumentation allows for different microwave power to be provided for the sample. In theory, the intensity of the EPR signal is proportional to the square root of the power, see Figure 10.

In Figure 10, 'Power' represents nominal power supplied to the sample. This is the power of the microwaves released from the microwave source and allowed to be conducted to the sample. It does not represent the actual power at the sample. The actual power at the sample is a function of many things, including the type of EPR sample holder (i.e. the type of resonance structure), the geometry of the sample and the solvent system. Thus, a power saturation curve for a species may not look identical if any of the above conditions change, because what is easiest to plot is the power provided by the instrument. The power saturation curves would be identical if power at the sample were known. But, as with quantitation, most experiments are done comparing species in the same environment. Thus, knowing the power at the sample is not a hinderance.

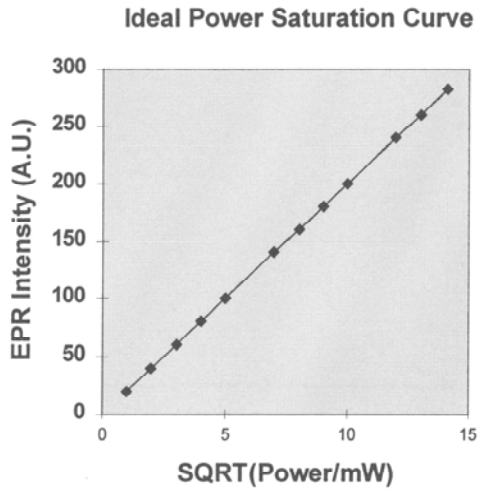


Figure 10 Ideal power saturation curve for an EPR sample. The abscissa represents the nominal power supplied to the sample.

3.5.2 What information is in a power saturtion curve?

Knowledge of the power saturation curve for a species under the experimental conditions allows for optimal instrument settings. With many EPR-active species, providing too much power can result in saturation effects. Saturation effects occur when the population of the two spin states, spin 'up' and spin 'down', begin to equalize. It must be remembered that the energy in a photon for a typical X band experiment is $E = hc/\lambda = 6.6 \times 10^{-24}$ J photon^{-1}. However, the thermal energy available at room temperature is $kT = 4.4 \times 10^{-21}$ J at 298 K. Thus, thermal energy is 1000 times the energy separation being spanned in the EPR transition and the difference in population of the two spin states, as dictated by the Boltzmann distribution, is very small. This small difference in energy means that the population difference of the two spin states is very small, thus even in a continuous wave experiment, it may be possible to equalize these populations and saturate the spectrum.

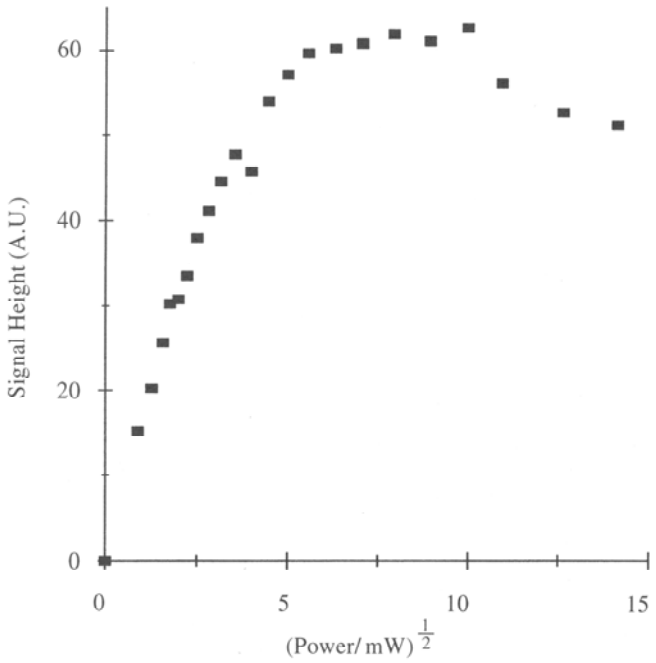


Figure 11 Experimental power saturation curve of the ascorbate free radical in aqueous solution.

3.5.3 Ascorbate radical as an example

The ascorbate radical power saturation curve for an aqueous sample in a TM-flat cell in a Bruker TM cavity, shows deviation from the ideal. If maximum signal height is needed for weak samples, a nominal power of ca. 40 mW with this sample configuration could be used, Figure 11. But, if quantitation is desired, the correction must be made for the deviation from the ideal curve or a lower power setting should be used.

3.5.4 Species information

Power saturation curves for similar species will be similar, but quite different species may be very different. Thus, power saturation curves can be used to provide evidence about the nature of an unknown species or more often they are used to determine the nature of species in a sample in which several species are present. For example, in a frozen sample containing both a metal complex and a free radical, power saturation curves will permit the identification of those features in the observed spectrum that belong to each species, making interpretation easier and more definitive.

4 SPIN TRAPPING

Many free radicals are not detectable or are very difficult to detect in aqueous solution. Diatomic radicals, such as $HO^{\bullet}$, $O_2^{\bullet -}$ and $^{\bullet}NO$ are simply not detectable in room temperature aqueous solution because of their very broad linewidths and the extremely low steady state concentrations. In addition, most sulfur-centered radicals, such as the thiyl radical of glutathione ($GS^{\bullet}$), also have very broad lines, making their detection possible only at very low temperatures. To overcome this kind of problem the technique of spin trapping has been developed.

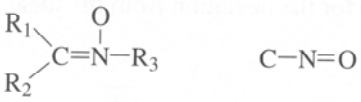
4.1 THE REACTION

Spin trapping involves the addition reaction of the free radical of interest to a diamagnetic compound, a spin trap, to produce a relatively long-lived free radical product, a spin adduct (usually a nitroxide), which hopefully accumulates in a concentration high enough to be studied by EPR. Nitroxides are relatively stable because the unpaired electron is resonance stabilized. Spin traps do not readily react with resonance-stabilized radicals and thus are of little help in increasing their visibility; however, resonance-stabilized radicals are the easiest to observe directly by EPR. Thus, spin trapping is a valuable tool for the study of

free radical processes:

$$R^{\bullet} + \text{spin trap} \longrightarrow \text{spin adduct}$$

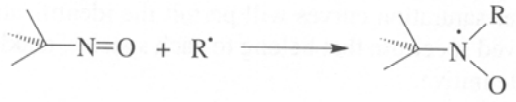
There are two general classes of spin traps, nitrone and nitroso compounds.



Nitrone

Nitroso

Nitroso compounds provide considerably more information than nitrones since the radical to be trapped adds directly to the nitroso nitrogen, thereby increasing the amount of information in the hyperfine splittings. An example of a nitroso trapping reaction is shown:



Nitrones are the most popular spin traps because of the stability of both the trap and the resulting adduct. An example of a nitrone trapping reaction is shown:

DMPO
(nitrone spin trap)

nitroxide radical
(aminoxyl spin adduct)

Example structures of spin traps are provided in Figure 12.

4.2 WHY IS SPIN TRAPPING SO POPULAR?

1. Spin trapping is widely used because of the ability to detect radical formation in real time in room or physiological temperature aqueous solutions. Many of the radicals of interest could only be observed directly in frozen solution, thus only snapshot pictures of ongoing processes could be observed. The real time detection ability with spin trapping opens many new windows for observation.

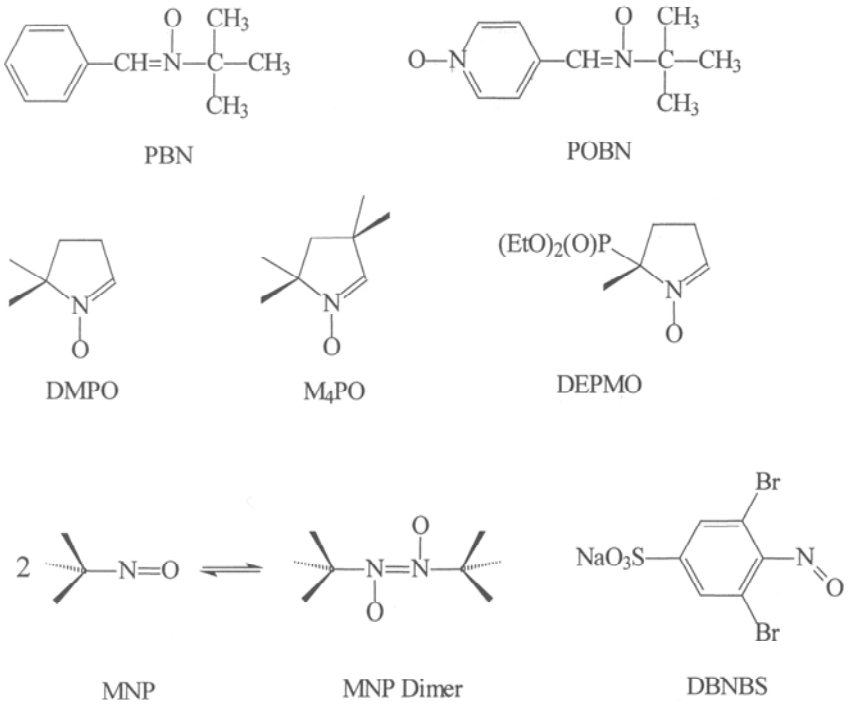


Figure 12 A few examples of the many spin traps being used in research.

2. Spin trapping allows the detection of radicals that cannot be detected directly in aqueous solutions. For example: $HO^{\bullet}$, $O_2^{\bullet-}/HO_2^{\bullet}$, $GS^{\bullet}$, $ROO^{\bullet}$, $RO^{\bullet}$, $L^{\bullet}$ (lipids).
3. Spin trapping is integrative. Because the lifetime of the spin adduct is typically much greater than that of the original radical, the steady-state concentration of spin adduct is much greater, allowing detection, that is,

$$[\text{spin adduct}]\bullet_{SS} >>> [R^{\bullet}]$$

because

$$t_{1/2}\,(\text{spin adduct}) >>> t_{1/2}\,[R^{\bullet}]$$

4. The hyperfine splittings (a) provide information about the identity of the radical being studied. Table 4 provides an example of the range of hyperfine splitting constants observed for various spin adducts of DMPO in aqueous solution. It must be kept in mind that splitting constants will change with solvent.

Table 4 Spin adduct hyperfine splittings.[a]

Spin adduct	a^N/G	a^H/G
DMPO/$^{\bullet}$OH	14.9	14.9
DMPO/$^{\bullet}$OOH	14.3	11.7 1.3
DMPO/GS$^{\bullet}$	15.3	16.2
DMPO/$CO_2^{\bullet-}$	15.6	18.8
DMPO/$CH_3{}^{\bullet}CHOH$	15.8	22.8
DMPO/$^{\bullet}CH_3$	16.4	23.4
DMPO/H$^{\bullet}$(e_q^-)	16.7	22.4[b](2)

[a]Data demonstrating the wide range of hyperfine splitting constants that might be observed from a spin adduct. This information coupled with the spin trapping data base can give researchers a great deal of information about the radical trapped [9–11]. [b]Two hydrogens.

5 SUMMARY

This chapter is intended to provide the reader with an idea of what kinds of information are available from an EPR experiment; a few examples of where this information is found in an EPR spectrum are provided. It is hoped that information has opened a door to more learning.

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