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Appendix II: Introduction to EPR Spectroscopy

There are several general texts on this topic, and this appendix is only intended to give you a brief outline of the Electron Spin Resonance experiment (otherwise known as Electron Paramagnetic Resonance, EPR). A particularly useful reference, which is included in your experiment reference folder, is Bunce, N.J. *J. Chem. Educ.*, **1987**, 64, 907.

If an electronic spin system of $s = 1/2$ comes under the influence of a magnetic field, H , the energy of the system is immediately divided into two states, $m_s = +1/2$ and $m_s = -1/2$. This effect is known as Zeeman splitting and is also seen in nmr with respect to nuclear spins.

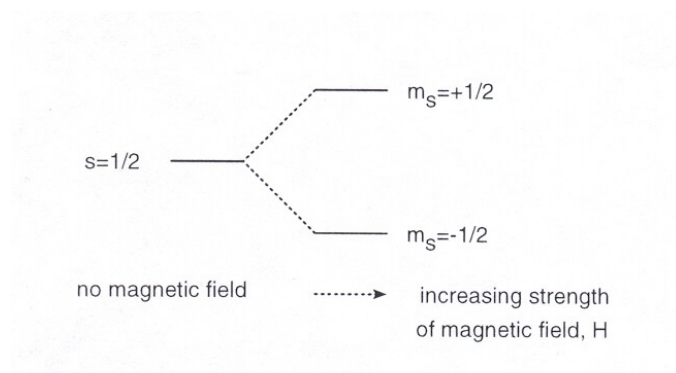


Figure 1: The splitting of the spin states of an unpaired electron

The energy gap between the two spin states is given by

$$\begin{aligned}\Delta E &= E_{+1/2} - E_{-1/2} \\ &= \frac{1}{2} g\beta H - (-\frac{1}{2}) g\beta H \\ &= g\beta H\end{aligned}$$

where β = a constant called the Bohr magneton, a unit of electron spin moment and has the value $\beta = 9.2741 \times 10^{-24} \text{ J.T}^{-1}$; g is the spectroscopic splitting factor (normally about 2).

Most of the spins will be in the lowest energy state, but can gain excitation to the upper state by absorbing energy, $h\nu$. This absorption of energy gives rise to the spectrum. Since the transition can be seen by either:

- (a) keeping the magnetic field fixed and scanning the range of energy supplied, or
- (b) keeping the energy supply constant and scanning the magnetic field.

The second option appears to be the most common, and is in fact that found on our instruments. The energy source is a microwave generator (Klystron) which emits a microwave of wavelength 3.2cm (called the X-band, corresponding to about 9.2 GHz) and this dictates that the magnetic field should be searched around 0.32 Tesla (3200 Gauss).

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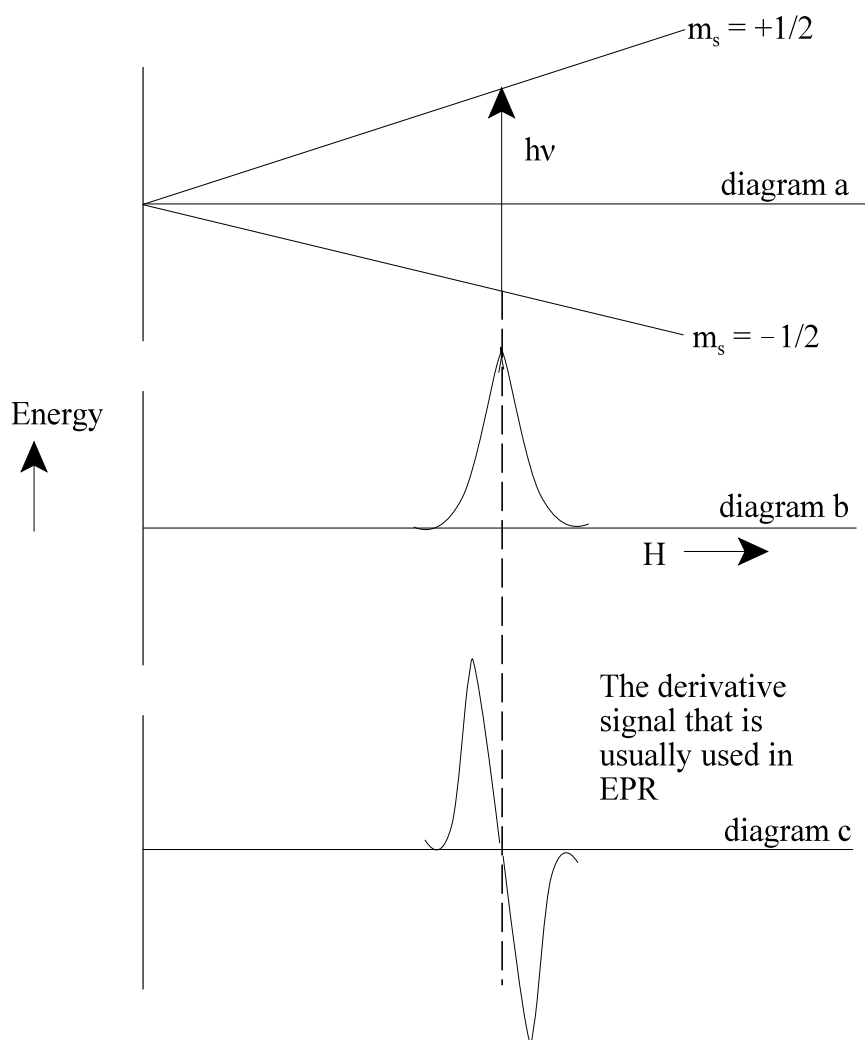


Figure 2: The transition observed in an EPR experiment: (a) energy level diagram of a free electron in a magnetic field; (b) the absorption signal; (c) the traditional derivative signal ¹

Just as in nmr, multiple resonances can arise as a result of the electron interacting with another spin system. Predictions for the splitting pattern can be made by applying the multiplicity rule, $2nI + 1$ (n = number of nuclei to which the electron is coupling; I = nuclear spin). The magnitude of the coupling constant, a , depends upon whether the electron originates from an s, p or d-orbital. Since s orbitals have high electron density at the nucleus, a will be large, and because s orbitals are symmetrical, it will be independent of direction. This interaction is called the isotropic hyperfine coupling, a_{iso} .

In p or d orbitals, there is no electron density found at the centre of the nucleus but at some distance away. Thus, the interaction is smaller and very dependent upon the direction of the orbital with

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respect to the applied field. This gives rise to the anisotropic hyperfine coupling, a_{aniso} which may be resolved into the components for x, y and z. In a fluid solution, the anisotropic coupling is averaged to zero and the only observed coupling is due to a_{iso} . In a frozen matrix or a single crystal, one observes the combination of a_{iso} and a_{aniso} . The anisotropic contribution is calculated from the coupling along the three principal directions, x, y and z after the isotropic contribution has been subtracted. [x and y components may be combined as the perpendicular term; z becomes the parallel term]. Thus, from a spectrum obtained using fluid and frozen solutions, a_{iso} and a_{aniso} may be computed and consequently the unpaired electron population in s and p/d orbitals can be calculated enabling one to make an estimate of the degree of hybridisation.

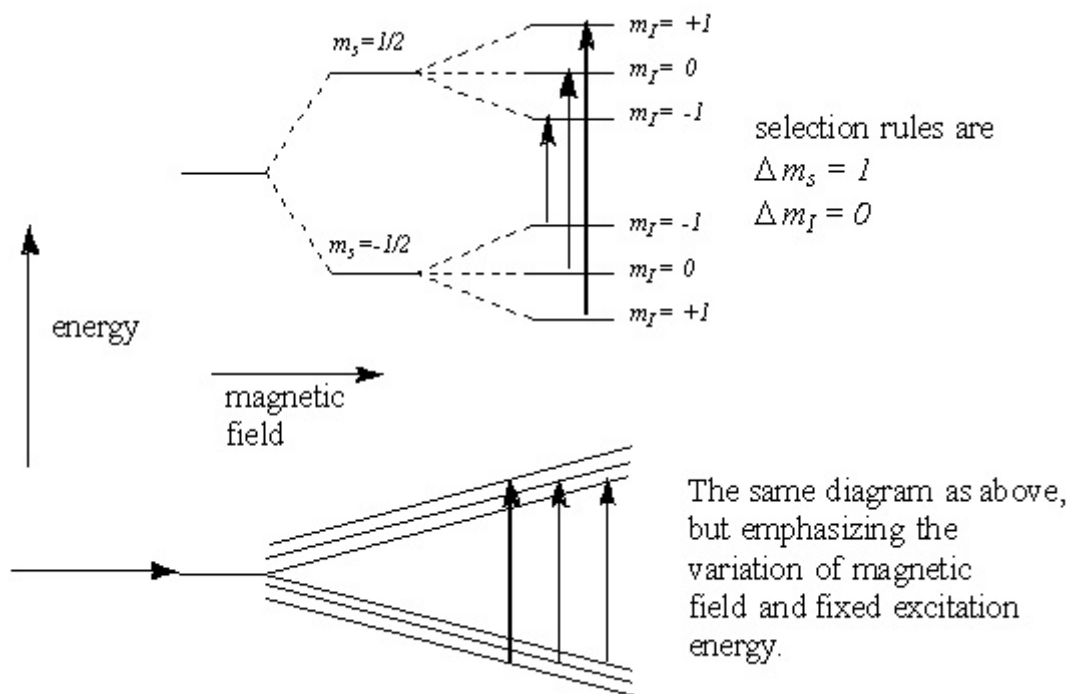


Figure 3: Interaction of the unpaired electron with a nuclear spin of $I = 1$

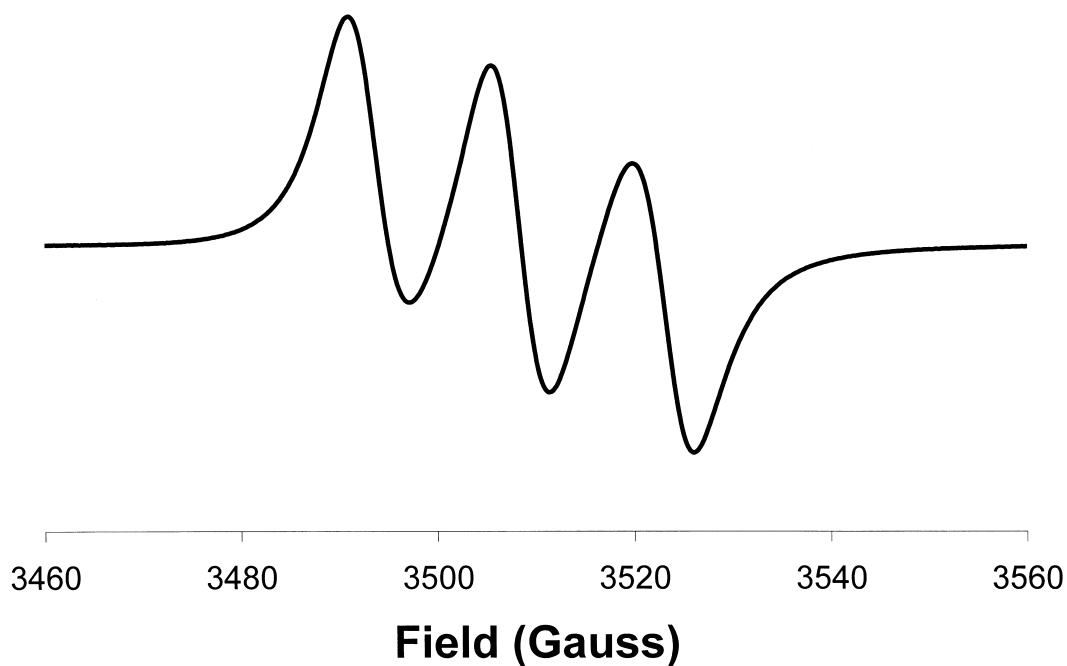


Figure 4: The EPR spectrum of the TEMPO radical. ($I = 1$ for ^{14}N)

The TEMPO radical is 2,2,6,6-tetramethylpiperidinyloxy as in Figure 5.

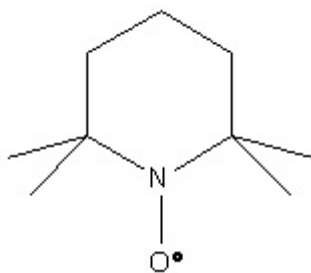


Figure 5: The TEMPO radical

The value of the hyperfine splitting constant, a , is often quoted in MHz or cm^{-1} . The conversion can be made using:

$$a = a \text{ (in Gauss)} \times g \times \beta$$

where $\beta = 1.40 \times 10^6 \text{ Hz.G}^{-1}$ or $\beta = 4.67 \times 10^{-5} \text{ cm}^{-1}.\text{G}^{-1}$.

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The chart calibration standard used for most spectra is the stable solid organic radical, dpph (2,2-diphenyl-1-picrylhydrazyl) for which $g = 2.0037$. The Bohr magneton for an electron has the value $9.2741 \times 10^{-24} \text{ J.T}^{-1}$. (1 gauss = 0.1 mT).

1. Diagrams redrawn from Herak, J.N.; Adamić, K.J. *Magnetic Resonance in Chemistry and Biology*; Marcel Dekker Inc.: New York, 1975