

## CHAPTER 1

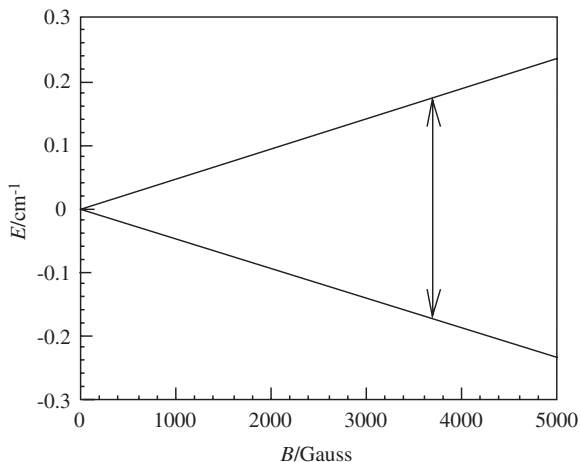
# *Introduction*

### 1.1 What is ESR Spectroscopy?

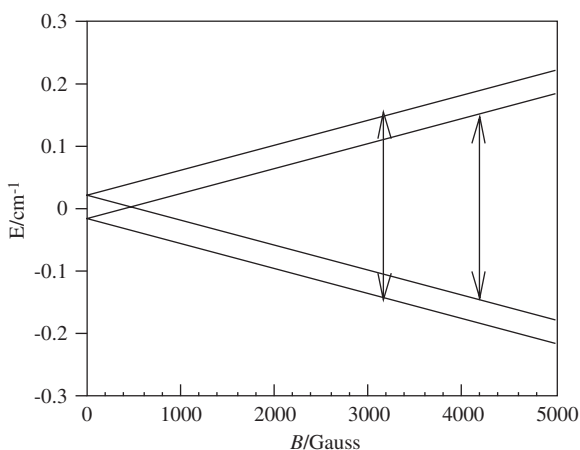
Electron spin resonance spectroscopy (ESR), also known as electron paramagnetic resonance (EPR) or electron magnetic resonance (EMR), was invented by the Russian physicist Zavoisky<sup>1</sup> in 1945. It was extended by a group of physicists at Oxford University in the next decade. Reviews of the Oxford group's successes are available<sup>2</sup> and books by Abragam and Bleaney and by Abragam<sup>3</sup> cover the major points discovered by the Oxford group. In the present book, we focus on the spectra of organic and organotransition metal radicals and coordination complexes. Although ESR spectroscopy is supposed to be a mature field with a fully developed theory,<sup>4</sup> there have been some surprises as organometallic problems have explored new domains in ESR parameter space. We will start in this chapter with a synopsis of the fundamentals of ESR spectroscopy. For further details on the theory and practice of ESR spectroscopy, the reader is referred to one of the excellent texts and monographs on ESR spectroscopy.<sup>3,5-36</sup> Sources of data and a guide to the literature of ESR up to about 1990 can be found in ref. 16*a*. The history of ESR has also been described by many of those involved in the founding and development of the field.<sup>37</sup>

The electron spin resonance spectrum of a free radical or coordination complex with one unpaired electron is the simplest of all forms of spectroscopy. The degeneracy of the electron spin states characterized by the quantum number,  $m_S = \pm 1/2$ , is lifted by the application of a magnetic field, and transitions between the spin levels are induced by radiation of the appropriate frequency (Figure 1.1). If unpaired electrons in radicals were indistinguishable from free electrons, the only information content of an ESR spectrum would be the integrated intensity, proportional to the radical concentration. Fortunately, an unpaired electron interacts with its environment, and the details of ESR spectra depend on the nature of those interactions. The arrow in Figure 1.1 shows the transitions induced by  $0.315 \text{ cm}^{-1}$  radiation.

Two kinds of environmental interactions are commonly important in the ESR spectrum of a free radical: (i) To the extent that the unpaired electron has residual, or unquenched, orbital angular momentum, the total magnetic moment is different from the spin-only moment (either larger or smaller,



**Figure 1.1** Energy levels of an electron placed in a magnetic field.



**Figure 1.2** Energy levels of an unpaired electron in a magnetic field interacting with a spin-1/2 nucleus. The arrows show two allowed transitions.

depending on how the angular momentum vectors couple). It is customary to lump the orbital and spin angular momenta together in an effective spin and to treat the effect as a shift in the energy of the spin transition. (ii) The electron spin energy levels are split by interaction with nuclear magnetic moments – the nuclear hyperfine interaction. Each nucleus of spin  $I$  splits the electron spin levels into  $(2I + 1)$  sublevels. Since transitions are observed between sublevels with the same values of  $m_J$ , nuclear spin splitting of energy levels is mirrored by splitting of the resonance line (Figure 1.2).

## 1.2 The ESR Experiment

When an electron is placed in a magnetic field, the degeneracy of the electron spin energy levels is lifted<sup>†</sup> as shown in Figure 1.1 and as described by the *spin Hamiltonian*:

$$\hat{H}_s = g\mu_B B \hat{S}_z \quad (1.1)$$

In eqn (1.1),  $g$  is called the  $g$ -value (or  $g$ -factor), ( $g_e = 2.00232$  for a free electron),  $\mu_B$  is the Bohr magneton ( $9.274 \times 10^{-28} \text{ J G}^{-1}$ ),  $B$  is the magnetic field strength in Gauss<sup>‡</sup>, and  $\hat{S}_z$  is the  $z$ -component of the spin angular momentum operator (the magnetic field defines the  $z$ -direction). The electron spin energy levels are easily found by application of  $\hat{H}_s$  to the electron spin eigenfunctions corresponding to  $m_s = \pm 1/2$ :

$$\hat{H}_s |\pm \frac{1}{2}\rangle = \pm \frac{1}{2} g\mu_B B |\pm \frac{1}{2}\rangle = E_{\pm} |\pm \frac{1}{2}\rangle$$

Thus

$$E_{\pm} = \pm \left(\frac{1}{2}\right) g\mu_B B \quad (1.2)$$

The difference in energy between the two levels:

$$\Delta E = E_+ - E_- = g\mu_B B = h\nu \quad (1.3)$$

corresponds to the energy,  $h\nu$ , of a photon required to cause a transition; or in wavenumbers by eqn (1.4), where  $g_e\mu_B/hc = 0.9348 \times 10^{-4} \text{ cm}^{-1} \text{ G}^{-1}$ :

$$\tilde{\nu} = \lambda^{-1} = \nu/c = (g\mu_B/hc)B \quad (1.4)$$

Since the  $g$ -values of organic and organometallic free radicals are usually in the range 1.9–2.1, the free electron value is a good starting point for describing the experiment.

Magnetic fields of up to *ca.* 15000 G are easily obtained with an iron-core electromagnet; thus we could use radiation with  $\tilde{\nu}$  up to  $1.4 \text{ cm}^{-1}$  ( $\nu < 42 \text{ GHz}$  or  $\lambda > 0.71 \text{ cm}$ ). Radiation with this kind of wavelength is in the microwave region. Microwaves are normally handled using waveguides designed to transmit radiation over a relatively narrow frequency range. Waveguides look like rectangular cross-section pipes with dimensions on the order of the wavelength

<sup>†</sup>Energy level splitting in a magnetic field is called the *Zeeman effect*, and the Hamiltonian of eqn (1.1) is sometimes referred to as the electron Zeeman Hamiltonian. Technically, the energy of a magnetic dipole in a magnetic field is the negative of that shown in eqn (1.1). For electron spins, however, the parameter  $g$  is negative, *i.e.*, the magnetic moment and spin angular momentum vectors are anti-parallel, and both negative signs may be combined to give the formula as written. This has the advantage of allowing  $g$ -values to be tabulated as positive numbers.

<sup>‡</sup>Using the symbol “ $B$ ” for the magnetic field technically implies we are using the MKS system of units in which  $B$  is given in Tesla (T). Many spectroscopists still express the magnetic field in Gauss (G) =  $10^{-4}$  T, however, and we will continue that practice here.

**Table 1.1** Common frequencies used for ESR

<i>Designation</i>	$\nu$ (GHz)	$\lambda$ (cm)	$B$ (electron) (G)
L	1.1	27	390
S	3.0	10	1070
<b>X</b>	<b>9.5</b>	<b>3.2</b>	<b>3400</b>
K	24	1.2	8600
Q	35	0.85	12500
W	95	0.31	34000
–	360	0.083	128000

to be transmitted. As a practical matter for ESR, waveguides can not be too big or too small – 1 cm is a bit small and 10 cm a bit large; the most common choice, called X-band microwaves, has  $\lambda$  in the range 3.0–3.3 cm ( $\nu \approx 9$ –10 GHz); in the middle of X-band, the free electron resonance is found at 3390 G.

Although X-band is by far the most common, ESR spectrometers are available commercially or have been custom built in several frequency ranges (Table 1.1).

### 1.2.1 Sensitivity

As for any quantum mechanical system interacting with electromagnetic radiation, a photon can induce either absorption or emission. The experiment detects net absorption, *i.e.*, the difference between the number of photons absorbed and the number emitted. Since absorption is proportional to the number of spins in the lower level and emission is proportional to the number of spins in the upper level, net absorption, *i.e.*, absorption intensity, is proportional to the difference:

$$\text{Net absorption} \propto N_- - N_+$$

The ratio of populations at equilibrium is given by the Boltzmann distribution:

$$N_+/N_- = \exp(-\Delta E/kT) = \exp(-g\mu_B B/kT) \quad (1.5)$$

For ordinary temperatures and ordinary magnetic fields, the exponent is very small and the exponential can be accurately approximated by the expansion,  $e^{-x} \approx 1 - x$ . Thus

$$N_+/N_- \approx 1 - g\mu_B B/kT$$

Since  $N_- \approx N_+ \approx N/2$ , the population difference can be written:

$$N_- - N_+ = N_- [1 - (1 - g\mu_B B/kT)] = Ng\mu_B B/2kT \quad (1.6)$$

This expression tells us that ESR sensitivity (net absorption) increases with the total number of spins,  $N$ , with decreasing temperature and with increasing magnetic field strength. Since the field at which absorption occurs is proportional to microwave frequency, in principle sensitivity should be greater for

higher frequency K- or Q-band spectrometers than for X-band. However, the K- or Q-band waveguides are smaller, so samples are also necessarily smaller and for the same concentration contain fewer spins. This usually more than cancels the advantage of a more favorable Boltzmann factor for samples of unlimited size or fixed concentration.

Under ideal conditions, a commercial X-band spectrometer can detect about  $10^{12}$  spins (*ca.*  $10^{-12}$  moles) at room temperature. This number of spins in a  $1 \text{ cm}^3$  sample corresponds to a concentration of about  $10^{-9} \text{ M}$ . By ideal conditions, we mean a single line, on the order of 0.1 G wide, with sensitivity going down roughly as the reciprocal square of the line width. When the resonance is split into two or more hyperfine lines, sensitivity decreases still further. Nonetheless, ESR is a remarkably sensitive technique, especially compared with NMR.

### 1.2.2 Saturation

Because the two spin levels are affected primarily by magnetic forces, which are weaker than the electric forces responsible for most other types of spectroscopy, once the populations are disturbed by radiation it takes longer for equilibrium population differences to be established. Therefore an intense radiation field, which tends to equalize the populations, leads to a decrease in net absorption which is not instantly restored once the radiation is removed. This effect is called “saturation”. The return of the spin system to thermal equilibrium, *via* energy transfer to the surroundings, is a rate process called *spin–lattice relaxation*, with a characteristic time ( $T_1$ ), the spin–lattice relaxation time (relaxation rate constant =  $1/T_1$ ). Systems with a long  $T_1$  (*i.e.*, spin systems weakly coupled to the surroundings) will be easily saturated; those with shorter  $T_1$  will be more difficult to saturate. Since spin–orbit coupling provides an important energy transfer mechanism, we usually find that odd-electron species with light atoms (*e.g.*, organic radicals) have long  $T_1$ s, those with heavier atoms (*e.g.*, organo-transition metal radicals) have shorter  $T_1$ s. The effect of saturation is considered in more detail in Chapter 5, where the phenomenological Bloch equations are introduced.

### 1.2.3 Nuclear Hyperfine Interaction

When one or more magnetic nuclei interact with the unpaired electron, we have another perturbation of the electron energy, *i.e.*, another term in the spin Hamiltonian:

$$\hat{H}_s = g\mu_B B \hat{S}_z + A \hat{I} \cdot \hat{S} \quad (1.7)$$

where  $A$  is the hyperfine coupling parameter in energy units (joule). Strictly speaking we should include the nuclear Zeeman interaction,  $\gamma B I_z$ . However, in most cases the energy contributions are negligible on the ESR energy scale, and,

since observed transitions are between levels with the same values of  $m_I$ , the nuclear Zeeman energies cancel in computing ESR transition energies.<sup>§</sup>

The eigenfunctions of the spin Hamiltonian [eqn (1.7)] are expressed in terms of an electron- and nuclear-spin basis set  $|m_S, m_I\rangle$ , corresponding to the electron and nuclear spin quantum numbers  $m_S$  and  $m_I$ , respectively. The energy eigenvalues of eqn (1.7) are:

$$E\left(\frac{1}{2}, \frac{1}{2}\right) = \frac{1}{2}g\mu_B B + \frac{1}{4}A \quad (1.8A)$$

$$E\left(-\frac{1}{2}, -\frac{1}{2}\right) = -\frac{1}{2}g\mu_B B + \frac{1}{4}A \quad (1.8B)$$

$$E_+ = \frac{1}{2}g\mu_B B [1 + (A/g\mu_B B)^2]^{\frac{1}{2}} - \frac{1}{4}A \quad (1.8C)$$

$$E_- = -\frac{1}{2}g\mu_B B [1 + (A/g\mu_B B)^2]^{\frac{1}{2}} - \frac{1}{4}A \quad (1.8D)$$

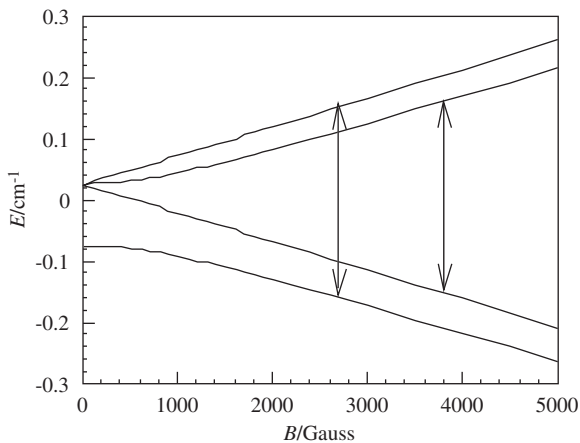
The eigenfunctions corresponding the  $E_+$  and  $E_-$  are mixtures of  $|\frac{1}{2}, -\frac{1}{2}\rangle$  and  $|\frac{1}{2}, \frac{1}{2}\rangle$ .

If the hyperfine coupling is sufficiently small,  $A \ll g\mu_B B$ , the second term in brackets in eqns (1.8C) and (1.8D) are negligible, which corresponds to first-order in perturbation theory, and the energies become:

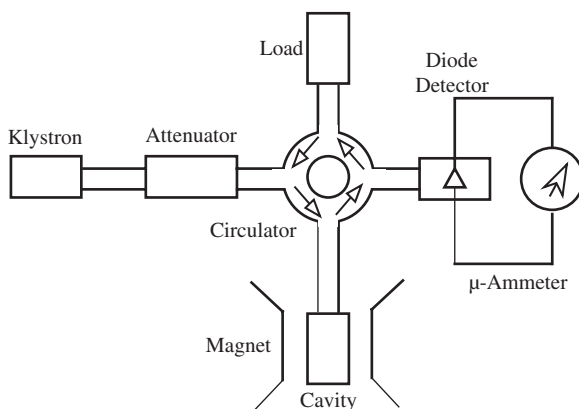
$$E = \pm \frac{1}{2}g\mu_B B \pm \frac{1}{2}A \quad (1.9)$$

These are the energy levels shown in Figure 1.2. The exact energies in eqn. (1.8), which were first derived by Breit and Rabi,<sup>38</sup> are plotted as functions of  $B$  in Figure 1.3 for  $g = 2.00$ ,  $A/hc = 0.1 \text{ cm}^{-1}$ . Notice that, at zero field, there are two levels corresponding to a spin singlet ( $E = -3A/4hc$ ) and a triplet ( $E = +A/4hc$ ). At high field, the four levels divide into two higher levels ( $m_S = +1/2$ ) and two lower levels ( $m_S = -1/2$ ) and approach Figure 1.2, the first-order result, eqn. (1.9) (the first-order solution is called the high-field approximation). To conserve angular momentum, transitions among these levels can involve changes in angular momentum of only one unit. At high fields this corresponds to flipping only one spin at a time; in other words, the selection rules are  $\Delta m_S = \pm 1$ ,  $\Delta m_I = 0$  (ESR transitions) or  $\Delta m_S = 0$ ,  $\Delta m_I = \pm 1$  (NMR transitions). The latter involves much lower energy photons, and, in practice, only the  $\Delta m_S = \pm 1$  transitions are observed in an ESR spectrometer. At lower fields, or when  $A$

<sup>§</sup>An exception to this rule arises in the ESR spectra of radicals with small hyperfine parameters in solids. In that case the interplay between the Zeeman and anisotropic hyperfine interaction may give rise to satellite peaks for some radical orientations (S. M. Blinder, *J. Chem. Phys.*, 1960, **33**, 748; H. Sternlicht, *J. Chem. Phys.*, 1960, **33**, 1128). Such effects have been observed in organic free radicals (H. M. McConnell, C. Heller, T. Cole and R. W. Fessenden, *J. Am. Chem. Soc.*, 1959, **82**, 766) but are assumed to be negligible for the analysis of powder spectra (see Chapter 4) where  $A$  is often large or the resolution is insufficient to reveal subtle spectral features. The nuclear Zeeman interaction does, however, play a central role in electron-nuclear double resonance experiments and related methods [Appendix 2 and Section 2.6 (Chapter 2)].



**Figure 1.3** Energy levels for an electron interacting with a spin-1/2 nucleus with  $A/hc = 0.1 \text{ cm}^{-1}$ . The arrows show the transitions induced by  $0.315 \text{ cm}^{-1}$  radiation.



**Figure 1.4** Block diagram of an ESR spectrometer.

becomes comparable in magnitude to  $g\mu_B B$ , the transitions may involve simultaneous flipping of electron and nuclear spins. This gives rise to second-order shifts in ESR spectra (see Chapters 2 and 3).

### 1.3 Operation of an ESR Spectrometer

Although many spectrometer designs have been produced over the years, the vast majority of laboratory instruments are based on the simplified block diagram shown in Figure 1.4. Plane-polarized microwaves are generated by the klystron tube and the power level adjusted with the Attenuator. The Circulator

behaves like a traffic circle: microwaves entering from the klystron are routed toward the Cavity where the sample is mounted. Microwaves reflected back from the Cavity (which is reduced when power is being absorbed) are routed to the Diode Detector, and any power reflected from the diode is absorbed completely by the Load. The diode is mounted along the  $E$ -vector of the plane-polarized microwaves and thus produces a current proportional to the microwave power reflected from the cavity. Thus, in principle, the absorption of microwaves by the sample could be detected by noting a decrease in current in the Microammeter. In practice, of course, such a measurement would detect noise at all frequencies as well as signal and have a far too low signal-to-noise ratio to be useful.

The solution to the signal-to-noise problem is to introduce small amplitude field modulation. An oscillating magnetic field is superimposed on the dc field by means of small coils, usually built into the cavity walls. When the field is in the vicinity of a resonance line, it is swept back and forth through part of the line, leading to an a.c. component in the diode current. This a.c. component is amplified using a frequency selective amplifier tuned to the modulation frequency, thus eliminating a great deal of noise. The modulation amplitude is normally less than the line width. Thus the detected a.c. signal is proportional to the *change* in sample absorption as the field is swept. As shown in Figure 1.5, this amounts to detection of the first derivative of the absorption curve.

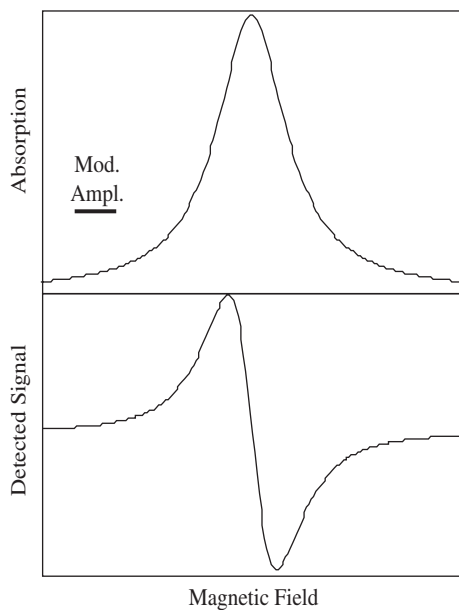
It takes a little practice to get used to looking at first-derivative spectra, but there is a distinct advantage: first-derivative spectra have much better apparent resolution than do absorption spectra. Indeed, second-derivative spectra are even better resolved (though the signal-to-noise ratio decreases on further differentiation). Figure 1.6 shows the effect of higher derivatives on the resolution of a 1:2:1 triplet arising from the interaction of an electron with two equivalent  $I = 1/2$  nuclei.

The microwave-generating klystron tube<sup>†</sup> requires explanation. A schematic drawing of the klystron is shown in Figure 1.7. There are three electrodes: a heated cathode from which electrons are emitted, an anode to collect the electrons, and a highly negative reflector electrode that sends those electrons which pass through a hole in the anode back to the anode. The motion of the charged electrons from the hole in the anode to the reflector and back to the anode generates an oscillating electric field and thus electromagnetic radiation.

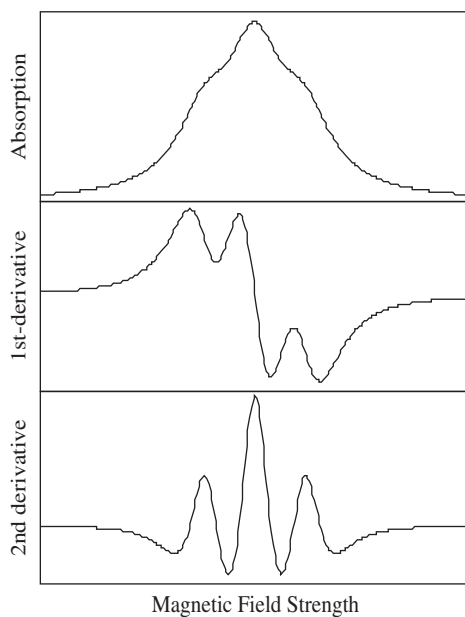
The transit time from the hole to the reflector and back again corresponds to the period of oscillation ( $\nu$ ). Thus the microwave frequency can be tuned (over a small range) by adjusting the physical distance between the anode and

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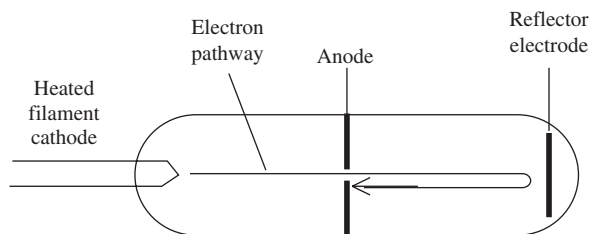
<sup>†</sup>Some modern spectrometers, especially those employing pulsed excitation (see Appendix 2), use a solid-state Gunn diode microwave source. This device makes use of the Gunn Effect, discovered by J. B. Gunn of IBM in 1963, in which electrons become "trapped" in potential wells within a solid and oscillate at a frequency that may be varied by changing the applied voltage. As with a klystron, tuning is done by varying the voltage. Gunn diode oscillators have better frequency stability and longer lifetimes than klystrons and are becoming the preferred microwave source for ESR spectrometers.



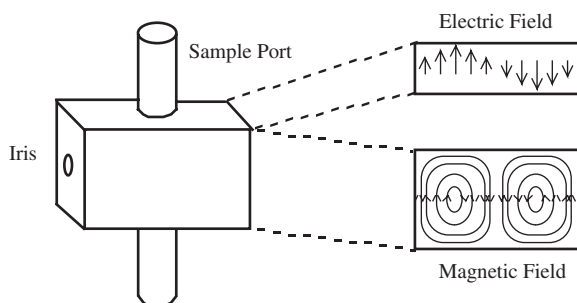
**Figure 1.5** Small-amplitude field modulation converts the absorption curve into a first-derivative.



**Figure 1.6** First-derivative curves show better apparent resolution than do absorption curves – and second-derivatives curves are still better.



**Figure 1.7** Schematic drawing of a microwave-generating klystron tube.

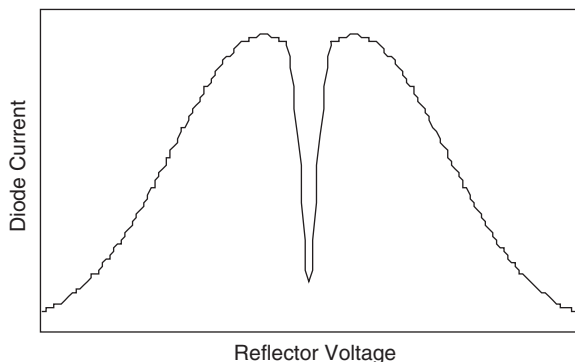


**Figure 1.8** Microwave cavity.

the reflector or by adjusting the reflector voltage. In practice, both methods are used: the metal tube is distorted mechanically to adjust the distance (a coarse frequency adjustment) and the reflector voltage is adjusted as a fine control.

The sample is mounted in the microwave cavity (Figure 1.8). The cavity is a rectangular metal box, exactly one wavelength long. An X-band cavity has dimensions of about  $1 \times 2 \times 3$  cm. The electric and magnetic fields of the standing wave are shown in the figure. Note that the sample is mounted in the electric field nodal plane, but at a maximum in the magnetic field. The static field,  $B$ , is perpendicular to the sample port.

The cavity length is not adjustable, but it must be exactly one wavelength. Thus the spectrometer must be tuned such that the klystron frequency is equal to the cavity resonant frequency. The tune-up procedure usually includes observing the klystron power mode. That is, the frequency is swept across a range that includes the cavity resonance by sweeping the klystron reflector voltage, and the diode detector current is plotted on an oscilloscope or other device. When the klystron frequency is close to the cavity resonance, microwave energy is absorbed by the cavity and the power reflected from the cavity to the diode is minimized, resulting in a dip in the power mode (Figure 1.9). The “cavity dip” is centered on the power mode using the coarse mechanical frequency adjustment, while the reflector voltage is used to fine tune the frequency.



**Figure 1.9** Klystron mode and cavity dip.

**Table 1.2** Parameters involved in the recording of an ESR spectrum

Microwave frequency	Center field	Modulation frequency	Modulation phase
Microwave power	Sweep width	1st or 2nd harmonic	Signal gain
Sweep time	Field offset	Modulation amplitude	Filter time constant

## 1.4 Optimization of Operating Parameters<sup>||</sup>

Determining the ESR spectrum of a sample using a typical CW spectrometer of the sort outlined in Figure 1.4, which is still the most common commercially available type of instrument, involves adjustment of the set of operating parameters described below. In the early days of ESR these adjustments would be carried out using control knobs on a console. Nowadays, of course, the settings are carried out under control of a computer interface. The purpose of these parameters and typical values, however, has remained unchanged. Such spectrometers are quite adequate for studying relatively stable samples. Characterizing transient species by ESR, however, requires substantial modification of commercial instruments or the use of a pulsed spectrometer.

There are twelve parameters that must be set or known in recording an ESR spectrum (Table 1.2). Briefly, below, each parameter is discussed and the means used to optimize or measure the parameter described.

### 1.4.1 Microwave Frequency

The resonant microwave frequency reaching the sample is determined by the effective length of the microwave cavity. The actual length is somewhat

<sup>||</sup> A comprehensive discussion and illustrations of the effects of spectrometer operating parameters on ESR spectra are given by the author in Electron spin resonance, in *Physical Methods of Chemistry*, ed. A. Weissberger and B. W. Rossiter, John Wiley and Sons, Inc., New York, 1972, part IIIA, ch. VI.

modified by the influence of the sample tube and the Dewar insert (if controlled temperature operation is required) so that the microwave frequency varies by a few percent even for the same cavity. Since the klystron frequency is locked to the cavity resonant frequency by a suitable feedback circuit, this is not an adjustable parameter. However, to compute a  $g$ -value from a spectrum, the frequency must be known quite accurately. This is normally done using a microwave frequency counter installed somewhere in the waveguide circuit.

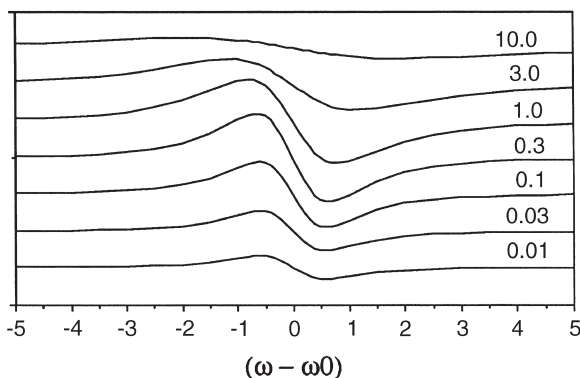
## 1.4.2 Microwave Power

According to the solution of the Bloch equations (Chapter 5), the magnetic resonance absorption, sometimes called the “ $v$ -mode signal”,  $v$ , is given by eqn (1.10).

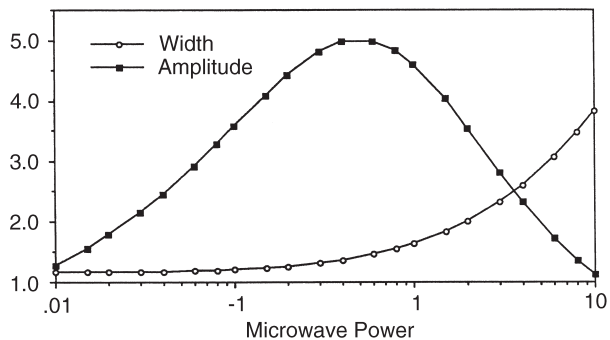
$$v = \frac{\gamma B_1 M_0 T_2}{1 + T_2^2 (\omega_0 - \omega)^2 + \gamma^2 B_1^2 T_1 T_2} \quad (1.10)$$

where  $T_1$  and  $T_2$  are the spin–lattice and transverse relaxation times, respectively,  $M_0$  is the bulk magnetization,  $\gamma$  is the magnetogyric ratio ( $g\mu_B$  in ESR terms),  $\omega_0$  is the resonant frequency (proportional to  $B_0$ ),  $\omega$  is the angular microwave frequency ( $\nu$ ), and  $B_1$  is the amplitude of the oscillating field. The microwave power is proportional to  $B_1^2$ . For small  $B_1$ , the absorption signal increases linearly with increasing  $B_1$ . However, when the third term in the denominator becomes important,  $v$  goes through a maximum when  $\gamma^2 B_1^2 T_1 T_2 = 1$ , and begins to decrease with increasing  $B_1$  – the resonance begins to “saturate”. At maximum  $v$ , however, the saturation term leads to an increase in apparent line width by a factor of  $\sqrt{2}$ . This effect is illustrated in Figure 1.10.

To simultaneously maximize signal-to-noise ratio (S/N) and minimize distortion, it is best to adjust the microwave power, as measured by the power



**Figure 1.10** Effect of increasing microwave power on intensity and shape of an ESR line. Power increases from top to bottom of the figure. Units are relative values of  $B_1^2$ .



**Figure 1.11** Effect of microwave power on relative width and amplitude of a line.

meter, down by a factor of 4 or 5 (6–7 db) from the maximum amplitude power. This will result in a decrease of less than 2 in signal amplitude. In practice, following this procedure would require finding the maximum amplitude by trial and error and then turning the power level down by 6–7 db. This effect is illustrated in Figure 1.11.

In general it is unnecessary to spend much time adjusting the power level. The general rule is to adjust the power to about 10 db attenuation for organic radicals and to use full power for transition metal complexes and those organometallics where the unpaired electron is primarily located on the metal.

### 1.4.3 Center Field, Sweep Width and Field Offset

Once you know, or can guess, the field limits of your spectrum, setting the center field and sweep width values is not very difficult. The center field corresponds to the middle of the spectrum and a sufficiently large sweep width chosen so that all of the spectrum is recorded.

If you do not know the field range occupied by your spectrum in advance, the center field must be chosen by educated guess; set the sweep width 2–4 $\times$  greater than the expected width. Hopefully, you will see at least a piece of your spectrum and can make appropriate adjustments to zero in on the correct settings.

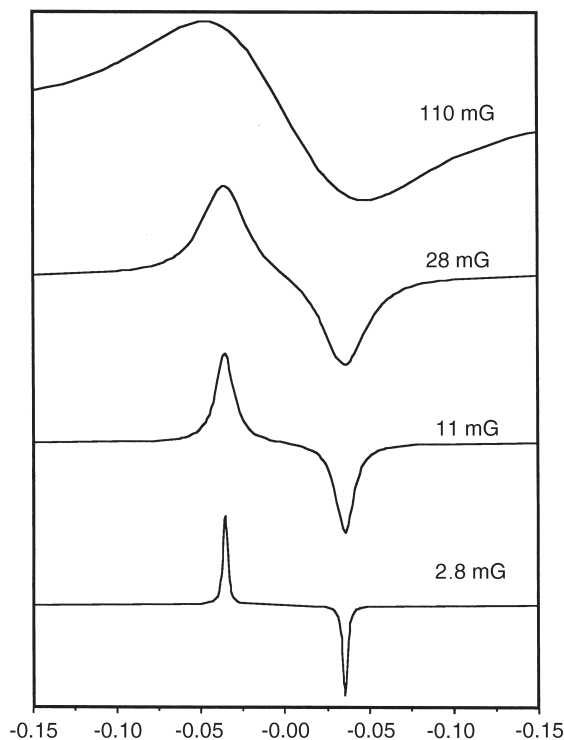
Most spectrometers measure the magnetic field by a Hall effect probe consisting of a sensor mounted on one of the pole faces of the magnet. However, such estimates of the value of  $B$  inside the cavity are not sufficiently accurate to be used for  $g$ -factor determinations. There are two ways around this problem: (i) measure the spectrum of a solid free radical such as diphenylpicrylhydrazyl (DPPH), which has a well-known  $g$ -value (2.0028), at least once during acquisition of the desired spectrum; or (ii) use of an NMR gaussmeter probe inserted in or near the cavity several times during the collection of the spectrum.

### 1.4.4 Sweep Time

In general, the longer the sweep time the better the sensitivity since the filter time constant parameter can be set longer with consequent improvement in signal-to-noise ratio. In practice, however, sweep times are usually set in accordance with the expected lifetime of the radical species, the stability of the instrument, and the patience of the operator. Decay of the radical or drift of the spectrometer during a scan is clearly undesirable. The sweep time is most commonly set in the range 4–10 min.

### 1.4.5 Modulation Frequency

With most spectrometers, you have a choice of either 100 kHz or a lower frequency of field modulation. The higher frequency generally gives better S/N, but if the lines are unusually sharp ( $<0.08$  Gauss), 100 kHz modulation leads to “side bands”, lumps in the line shape that confuse the interpretation of the spectrum. This effect is illustrated in Figure 1.12. Under such circumstances, use the lower frequency for which the sidebands are closer together and thus less likely to be a problem.



**Figure 1.12** Effect of 100 kHz modulation on an ESR line of decreasing width. The  $x$ -axis is magnetic field, in Gauss, relative to the center of the line.

### 1.4.6 Second Harmonic Detection

In most cases, you will use the first harmonic and the normal first-derivative of the absorption spectrum will be presented. If your spectrum has *very* good S/N and has some regions where you would like better resolution, a second-derivative presentation may help. However, second derivatives from second harmonic detection are very costly in terms of S/N ratio and so you really do have to have a *strong* signal!

### 1.4.7 Modulation Amplitude

Since the absorption signal is usually detected by imposing a 100 kHz field modulation on the static field, the signal disappears when the modulation amplitude is turned to zero. In general, the signal increases more or less in proportion to the modulation amplitude, but eventually the detected lines begin to broaden and then the signal amplitude decays as well. This is illustrated in Figure 1.13.

Depending on what you want to optimize, here are some rules:

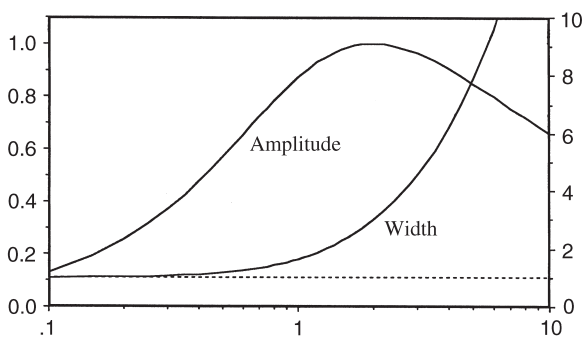
For optimum S/N ratio, but decreased resolution: Modulation amplitude =  $2 \times$  line-width.

For accurate line width measurements: Modulation amplitude = line-width/10.

For most practical work: Modulation amplitude = line-width/3.

### 1.4.8 Modulation Phase

To improve the S/N ratio, the modulation signal is processed by amplification with a tuned amplifier using phase-sensitive detection. This means that the detected signal must not only be at the modulation frequency, but must also be in phase with the modulation. Since the amplifier itself can introduce a bit of phase shift, there is a phase control which, in principle, should be adjusted to maximize the signal amplitude. In practice, this control needs to be adjusted only rarely and in most cases the best approach is to leave it alone.



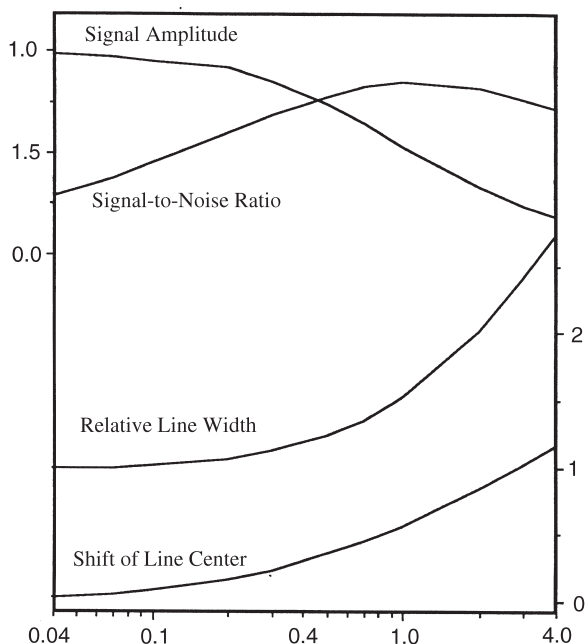
**Figure 1.13** Effect of field changing (modulation/line width) on relative amplitude (left-hand axis) and observed width (right-hand axis) of an ESR line.

### 1.4.9 Signal Gain

Adjustment of the signal gain is straightforward. Set the gain sufficiently high that the recorded spectrum is nearly full-scale on the computer displays or recorder. If you have no idea of the strength of your expected signal, a good starting point would be  $1 \times 10^4$ . Too high a gain can result in amplifier overload.

### 1.4.10 Filter Time Constant

The output of the signal amplifier is filtered using a circuit designed to pass low-frequency, but not high frequency, signals. The cut-off frequency is the reciprocal of the time constant setting. Thus, a time constant of 0.1 s would lead to signals with frequencies greater than about 10 Hz being attenuated. The best time constant setting thus depends critically on the sweep time. If you sweep through a line rapidly using a long time constant, you may filter out the signal altogether! With a shorter, but still too long, time constant, the line shape will be distorted, the apparent line center will shift, and the apparent line width will increase. These effects are illustrated in Figure 1.14. The best rule-of-thumb is to set the time constant to 10% of the time required to pass through the narrowest line of your spectrum.



**Figure 1.14** Effect of time constant/time to sweep through the line (*x*-axis) on the relative amplitude and signal-to-noise ratio (left-hand axis) and relative width and shift (right-hand axis) of an ESR line.

For example, suppose that the line width is 0.25 G, that you are scanning through 10 G in 4 min. The scan rate then is  $10 \text{ G}/4 \text{ min} = 2.5 \text{ G min}^{-1}$ . The time required to pass through a line is  $0.25 \text{ G}/2.5 \text{ G min}^{-1} = 0.1 \text{ min}$  or 6 s. The time constant should be set close to 0.6 s.

## 1.5 Applications of ESR Spectroscopy

### 1.5.1 Electronic Structure Determination

Most commonly, ESR spectroscopy is used to obtain information pertaining to the electronic structure of the species being studied. We will explore these kinds of applications extensively in subsequent chapters.

The magnetic field values at which microwaves are absorbed to produce the ESR spectrum of an isotropic sample, *e.g.*, the spectrum of a freely tumbling radical in liquid solution, can contain two principal types of chemically useful information: (i) The hyperfine coupling pattern provides information on the numbers and kinds of magnetic nuclei with which the unpaired electron interacts. (ii) The spacing of the lines and the center of gravity of the spectrum yield the hyperfine coupling constants,  $A_i$ , and  $g$ -value,  $g$ , which are related to the way in which the unpaired electron spin density is distributed in the molecule. In isotropic spectra the observed parameters are averaged over rotation of the molecules. In solids the parameters may also depend on molecular orientation relative to the magnetic field,  $B$ .

Structural applications range from organic, inorganic and organometallic radicals to coordination complexes and biological macromolecules containing a paramagnetic center.

Even more information is available from the spectrum of a solid-state sample, either a dilute single crystal or a frozen solution. We will discuss solid state samples later, beginning in Chapter 4.

### 1.5.2 Analytical Applications

Like all forms of spectroscopy, ESR intensities, through the dependence on the number of spins,  $N$ , can be used analytically to determine the concentration of a paramagnetic species. Such analytical applications usually require a standard solution to establish a calibrated intensity scale. Computer software is required in most cases to doubly integrate the spectrum (two integrations are required to convert the derivative spectrum into absorption and then to a number representing the total concentration of the species being studied). The interested reader is referred to Wertz and Bolton,<sup>12a</sup> who discuss the technique, point out the variables that must be controlled, and suggest intensity standards. The degree to which ESR intensities have been exploited varies widely. Experimentalists often make qualitative observations relating “strong” or “weak” spectra to chemical circumstances, but quantitative applications of integrated intensities are rare in ESR studies.

“Spin traps” which scavenge a reactive radical to give a more persistent radical may be used to detect the intermediacy of such transient radicals in sorting out a reaction mechanism.<sup>39</sup>

### 1.5.3 Determination of Rates

In some cases, ESR spectra can be used to determine the rate of a chemical reaction or the rate of a conformation change. Such applications are discussed in more detail in Chapter 5.

The spectral line widths are related to the rate of the rotational motions, which average anisotropies in the  $g$ - and hyperfine matrices (Chapter 5), and to the rates of fluxional processes, which average nuclear positions in a radical.

The saturation behavior of a spectrum – the variation of integrated intensity with microwave power – is related to the spin–lattice relaxation time, a measure of the rate of energy transfer between the electron spin and its surroundings. Saturation often depends on the same structural and dynamic properties as line widths.

Largely because spin–orbit coupling results in spin state admixture, electronic spin–lattice relaxation times are normally short for species containing heavy atoms such as transition metals. This has three consequences. Short relaxation times mean that saturation problems, which plague ESR spectroscopists studying organic radicals and NMR spectroscopists in general, are largely absent in organometallic ESR studies. Thus, spectra ordinarily can be recorded at full microwave power with salutary consequences for sensitivity. However, relaxation times are most easily determined by measuring spectral intensity as a function of microwave power in the saturation region. If relaxation times are short, very high power is required, which is out of the range of operation of most continuous wave spectrometers. Similarly, short relaxation times imply broad lines and reduced sensitivity. The advent of modern high power pulsed spectrometers<sup>32,34,36</sup> has made it possible to overcome some of the restrictions arising from relaxation behavior.

Some workers have used “spin labels” attached to a membrane or biological macromolecule to study the motion of these components of living cells (Chapter 5).

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