CHAPTER 12

DOUBLE-RESONANCE TECHNIQUES

12.1 INTRODUCTION

In this chapter, we briefly introduce several important techniques that represent elaborations of standard cw and pulse EPR spectroscopy. The experimental aspects of these techniques are described, for instance, by Poole [1].

It was noted in Section 3.3 that EPR may at times be used to characterize the nucleus responsible for hyperfine splitting. However, if in the same system there are two or more nuclei of the same spin, there is ambiguity in the assignment of hyperfine multiplets. Indeed, some hyperfine multiplets in spectra reproduced in this book were originally assigned to the wrong nucleus. Furthermore, if the spacings within a set of hyperfine lines do not exceed their individual widths, one fails to detect this splitting, except perhaps for a broadening. For this reason, splittings arising from the more remote nuclei are rarely observed directly. It would seem that in such EPR spectra one must be resigned to the loss of details of hyperfine interaction. This indeed appeared to be the case until 1956, when Feher [2] proposed and demonstrated the technique of electron-nuclear double resonance (ENDOR).\(^1\) His brilliant contribution makes it possible in some cases to obtain otherwise missing details of hyperfine interaction. In many systems, the ENDOR technique completely removes ambiguities. It may provide a wealth of detail about the wavefunction of the unpaired electron. In one favorable case, a distinctive interaction of an unpaired electron with the 23rd nearest-neighbor set of nuclei was established by an ENDOR experiment [4]. The ENDOR technique is applicable whenever any of the spin-bearing nuclides (Table H.4) are present in the paramagnetic sample.

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12.2 A CONTINUOUS-WAVE ENDOR EXPERIMENT

Before undertaking a more detailed description of ENDOR processes, we present a brief phenomenological account of a simple continuous-wave ENDOR experiment on a solid-state system with $S = I = \frac{1}{2}$. Suppose that from the resonant field positions $B_k$ and $B_m$ (Fig. 2.4) of the two hyperfine lines we have established a $g$ factor and have calculated the hyperfine splitting $A/h$ to be, for example, 10 MHz. We now undertake an ENDOR experiment as follows:

1. The sample is placed in a special cavity (one type is shown in Fig. 12.1). At low microwave power, the magnetic field is scanned to find and be set on one transition, say, that at $B_k$. The spectrometer parameters are now optimized to maximize the EPR signal.

2. The microwave power level ($B_{1_e}$) is then increased to several-fold its level set in part 1, to achieve partial saturation.

FIGURE 12.1 Schematic reproduction of a TE$_{011}$ cylindrical cavity designed for ENDOR studies. The sample is placed along the axis of the cavity. The side wall is a helix of spaced turns, with interstices filled by a plastic material of low dielectric loss. This design allows for penetration into the cavity of the radiofrequency field and by a modulating magnetic field. The microwave magnetic-field contours are shown by dashed lines. Since it is the component perpendicular to the static field $B$ of the microwave field or of the rf field that induces the electron-spin and nuclear-spin transitions, one seeks to keep $B$ perpendicular to both. The relative orientation of the microwave and rf fields is in principle arbitrary; that shown here is the most efficient for a set of external coils and involves the least eddy-current loss. In other cavities, the rf field is introduced by a coil (at least partly) inside the cavity. To avoid coupling out microwave energy, the plane of the coil should be parallel to the microwave field. This automatically puts the microwave and the rf magnetic field at right angles to one another. It may be of crucial importance to align the rf field appropriately with respect to a crystal axis (Section 12.4). [After J. S. Hyde, J. Chem. Phys., 43, 1806 (1965).]
3. A radiofrequency (rf) generator of sufficiently wide range and large power output is connected to the side coils of the cavity of Fig. 12.1, so that the sample also experiences an oscillating rf magnetic field $B_{1n}$. The generator is set to scan the region 2–30 MHz, while the oscilloscope or recorder of the spectrometer is operating. The base line, which, apart from noise, is constant and indicates a constant EPR absorption. Although it may be nonlinear, the horizontal axis is a measure of the frequency of the rf generator.

At two frequencies of the rf generator, which we call $v_{n1}$ and $v_{n2}$, the recorder or scope traces out lines such as those shown in Fig. 12.2. This plot of changes in the EPR absorption intensity is called the ENDOR spectrum. If the frequencies of these lines are carefully measured as the peak of each line is traversed, it should be noted that the difference $v_{n2} - v_{n1}$ is numerically just equal to the hyperfine coupling $A/h$ (i.e., 10 MHz), assuming that the higher-order corrections are negligible. This parameter can now be determined with greater accuracy. Furthermore, the mean value of the frequencies $v_{n1}$ and $v_{n2}$ is close to $v_n = g_n \beta_n B_k / h$, the NMR frequency of the bare nucleus in the magnetic field $B_k$. If the nuclide responsible for the hyperfine splitting had previously been uncertain, its identity is now available from the value of $g_n$ (Table H.4). If the experiment is repeated, but with the magnetic field set at $B_m$, the ENDOR spectrum would again consist of two lines, separated in frequency by the hyperfine coupling and symmetrically disposed (in first order) about the NMR frequency of the nucleus in the field $B_m$. However, the relative intensities of the two lines may not be the same in the two ENDOR spectra.

Since the ENDOR lines typically represent a change in EPR line intensity of $\sim 1\%$ of the EPR line under non-saturated conditions, one requires a spectrometer of high sensitivity. There are also various complexities of the ENDOR spectrometer that we have not enumerated. However, the method is well justified for the following cases:

1. Hyperfine lines are not resolved in the EPR spectrum, or the spectrum is complicated, with many lines.

![Figure 12.2](image.png)

**FIGURE 12.2** Change $\Delta Y$ in the EPR signal amplitude, that is, ‘ENDOR lines’ for a system with $S = I = \frac{1}{2}$ as the radiofrequency generator is scanned through the region including the frequencies $v_{n1}$ and $v_{n2}$. These are separated by the hyperfine coupling $|A|$ (to first order), and are symmetrically spaced about the nuclear magnetic resonance frequency $v_n$ of the nucleus for the magnetic field at which the microwave saturation is being carried out.
2. Hyperfine lines are resolved, but more accurate values of the hyperfine couplings are desired.
3. The identity of an interacting nucleus is to be established.
4. Nuclear-quadrupole couplings are to be measured (in a system with $I \geq 1$).

The so-called steady-state ENDOR experiment outlined briefly here is considered in more detail in Section 12.4, after considering the energy levels and possible transitions of this system.

### 12.3 ENERGY LEVELS AND ENDOR TRANSITIONS

In ENDOR experiments there is no attempt to observe directly the absorption of rf power (ordinary NMR) at these frequencies. Rather, one observes the enhancement of the EPR transition intensity resulting from the redistributions of populations of the various states. A description of the ENDOR lines of Fig. 12.2 (or of more complicated ENDOR spectra) requires

1. Use of the complete spin hamiltonian, including the nuclear Zeeman term (and a quadrupole term if $I > 1$).
2. Consideration of the populations of each state at low microwave power, also under microwave saturation conditions, and during (or immediately after) passage through one of the frequencies $\nu_{n1}$ or $\nu_{n2}$ at a high rf power level. The relative populations (and thus the ENDOR line behavior) depend on the dominant relaxation mechanisms in the system. The relaxation aspects are considered in Section 12.4.

The spin hamiltonian is (Eqs. 5.7 and 5.50)

$$\hat{H} = \beta_e B^T g \hat{S} + \sum_i (\hat{S}^T A_i \hat{I}_i - g_{n_i} \beta_n B^T \hat{I}_i + \hat{I}_i^T P_i \hat{I}_i)$$  \hspace{1cm} (12.1)

where the sum is over all spin-bearing nuclei in the sample. The terms describing interactions with the excitation fields $B_{1e}$ and $B_{1n}$ are not needed, for our purposes.

It is convenient to begin with a fixed magnetic field and a fixed orientation of a single-crystal sample for a single nuclide (assuming that the hyperfine coupling is not too extensive, and temporarily neglecting any nuclear-quadrupole term present) such that the effective values $g$ and $A$ may be used in the simplified spin hamiltonian of Eq. C.1:

$$\hat{H} = \beta_e B^T \hat{S} + A \hat{S}^T \hat{I} - g_n \beta_n B^T \hat{I}$$  \hspace{1cm} (12.2)
The energy levels are (Eqs. C.33)

\[ U_{+\frac{1}{2}, M_I} = +\frac{1}{2} g \beta_e B + \left( \frac{1}{2} A - g_n \beta_n B \right) M_I \]  
(12.3a)

\[ U_{-\frac{1}{2}, M_I} = -\frac{1}{2} g \beta_e B - \left( \frac{1}{2} A + g_n \beta_n B \right) M_I \]  
(12.3b)

These first-order levels for \( I = \frac{1}{2} \) are shown in Figs. 2.4 and 12.3a, b; in the latter figure, the nuclear transitions at frequencies \( v_{n1} \) and \( v_{n2} \) corresponding to the selection rules \( \Delta M_S = 0, \Delta M_I = \pm 1 \), are also shown. Figure 12.3c shows the levels and the transitions at constant microwave frequency. From Eqs. 12.3, one has the rf frequencies

\[ v_{n1} = h^{-1} \left| U_{+\frac{1}{2}, M_I} - U_{+\frac{1}{2}, M_I-1} \right| \]  
(12.4a)

\[ = h^{-1} \left| \frac{1}{2} A - g_n \beta_n B \right| \]  
(12.4b)

Likewise

\[ v_{n2} = h^{-1} \left| U_{-\frac{1}{2}, M_I} - U_{-\frac{1}{2}, M_I-1} \right| \]  
(12.5a)

\[ = h^{-1} \left| \frac{1}{2} A + g_n \beta_n B \right| \]  
(12.5b)

Here \( |g_n| \beta_n B / h = \nu_n \) is the magnetic resonance frequency of nucleus \( n \) in the fixed magnetic field at which the ENDOR spectrum is being observed. The two terms on the right in Eqs. 12.4b and 12.5b represent the two magnetic-field contributions seen by the nucleus: \( A \) arises from the unpaired-electron distribution and \( \nu_n \) arises from the externally applied field. It is important to note that the latter is shiftable, that is, via a change of the EPR frequency (say, from X band to Q band), allowing improvements in resolution. Note that Eqs. 12.4b and 12.5b do not depend on \( I \) or \( M_I \).

The two principal results derivable from the magnitudes \( v_{n1} \) and \( v_{n2} \) are as follows:

1. Determination of the hyperfine coupling parameter \( A \). To first order, one obtains

\[ \left| v_{n1} \pm v_{n2} \right| = h^{-1} |A| \]  
(12.6)

The upper sign applies when \( |A| < 2\nu_n \), and the lower sign applies when \( |A| > 2\nu_n \). However, unless \( A \) is very small, one must use at least a second-order correction. The results cited in Problem 12.2 required fourth-order corrections to match the accuracy of the data. For large hyperfine couplings, one generally resorts to a more general computer solution for the spin-hamiltonian parameters. The greatly increased accuracy of measurement of hyperfine couplings from ENDOR frequencies in
FIGURE 12.3 Energy levels of a system with $S = I = \frac{1}{2}$ in a constant magnetic field. The usual EPR transitions corresponding to the selection rules $\Delta M_S = \pm 1$, $\Delta M_I = 0$ are shown with wide arrows to symbolize the application of higher than usual microwave power. The transitions at the frequencies $\nu_{n1}$ and $\nu_{n2}$ correspond to the selection rules $\Delta M_S = 0$, $\Delta M_I = \pm 1$. The solid lines represent nuclear transitions that give rise to ENDOR lines if there is only one cross-relaxation process, represented by $\tau_0$ (Section 12.4). The dashed transitions also result in ENDOR lines if a second cross-relaxation process is operative. (a) Microwave saturation of the EPR transition $M_I = +\frac{1}{2}$ ($\hbar \nu_{n1}$). (b) Microwave saturation of the EPR transition $M_I = -\frac{1}{2}$ ($\hbar \nu_{n2}$). (c) Energy levels at constant microwave frequency. For the simplest assumptions about relaxation paths in steady-state ENDOR, the partially saturated transition at the field $B_k$ is enhanced by simultaneous irradiation with high rf power at the frequency $\nu_{n1}$. The line at the field $B_m$ is enhanced if the second frequency is $\nu_{n2}$. In some systems, precisely this behavior is observed; however, more typically, enhancement of either line occurs both at $\nu_{n1}$ and at $\nu_{n2}$. Since one observes the enhancement as the rf field is scanned, the recorder traces out ‘ENDOR lines’.
inhomogeneously broadened spectra is possible by virtue of the (usually) relatively much narrower ENDOR lines. The latter often have widths of \( \sim 10 \text{ kHz} \), although they have been observed to range from 3 kHz to \( \geq 1 \text{ MHz} \). EPR lines in solids are considered to be narrow if their width \( \Delta B \) is \( \leq 0.1 \text{ mT} \); for \( g = 2.00 \), this implies a linewidth

\[
\Delta v = h^{-1} g_e \beta_e \Delta B \approx 2.80 \text{ MHz}
\]  

If an NMR line of a proton \((g_n = 5.5857)\) has a width of 0.1 mT, the corresponding frequency width is 4.26 kHz. It is apparent that the smallest observed ENDOR linewidths correspond approximately to typical NMR linewidths. Hence it is not unusual to obtain hyperfine couplings to about \( 10^{-3} \% \) accuracy, from ENDOR frequencies.

2. Determination of an approximate value of \([g_n]\) from the relation

\[
\nu_{n_1} \pm \nu_{n_2} = 2 \nu_n = 2 h^{-1} |g_n| \beta_n B
\]  

The upper sign applies when \(|A| < 2\nu_n\), and the lower sign applies when \(|A| > 2\nu_n\). Even a low-accuracy measurement of the ENDOR frequencies generally permits identification of the nucleus responsible for the hyperfine splitting. In favorable cases, \([g_n]\) may be determined with a precision of 0.1%; however, even with the use of higher-order corrections or computer solution of the spin hamiltonian, one may note a discrepancy between the calculated value of \([g_n]\) and that derived from a table of nuclear moments (Table H.4). The discrepancy may arise from a pseudo-nuclear Zeeman interaction; in some cases (e.g., for ions with low-lying excited states) the contribution to \(g_n\) from this source is appreciable [3, p. 38].

It may occur to the reader to inquire as to why an elaborate ENDOR experimental system is used to detect transitions between nuclear-spin levels, instead of performing an ordinary NMR experiment. The answer is that the concentration of the nuclei present in most EPR or ENDOR experiments is much too low to permit their NMR detection. The far greater ENDOR sensitivity arises from the following reasons:

1. The energy of the EPR quantum is much greater than that of the NMR quantum. Hence one may have much greater population differences for the more widely spaced levels.

2. The rate of energy absorption is far greater at microwave frequencies. (See Section F.3 for a discussion of sensitivity versus frequency.)

3. The effectiveness of a nucleus in altering the intensity of an EPR line during an ENDOR experiment arises from the fact that it is acting not merely in the applied magnetic field but also in the magnetic field of the electron, which is typically of the order of \(10^3 - 10^5\ \text{ mT}\) at a nucleus (Problem 12.4). One may thus generate greater population differences than would be possible if the
12.4 RELAXATION PROCESSES IN STEADY-STATE ENDOR

The phenomenon here referred to as steady-state ENDOR was termed ‘stationary’ ENDOR and was first described in detail by Seidel [5]. The usual EPR experiment involves only the one spin-lattice relaxation time $\tau_1$ (denoted as $\tau_1$ in Section 10.3.3; if this is very short at 300 or 77 K, one is compelled to make EPR observations at 20 K or even at 4 K). However, even in the simplest four-level system on which ENDOR observations are to be made, there are at least three spin-lattice relaxation times that govern the distribution of population in the several levels. These dictate not only the temperature range in which ENDOR experiments may be performed successfully but possibly also other experimental conditions and hence determine the nature of the observed spectrum. This sensitive dependence on temperature is a disadvantage of the ENDOR technique.

Besides $\tau_1$, one is concerned with relaxation times $\tau_{1n}$ and $\tau_{x}$. Here $\tau_{1n}$ is the nuclear spin-lattice relaxation time, associated with the transitions $\Delta M_S = 0$, $\Delta M_I = \pm 1$, and $\tau_{x}$ is a ‘cross-relaxation’ time associated with mutual ‘spin flips’, that is, processes for which $\Delta(M_S + M_I) = 0$. Usually, $\tau_1 \ll \tau_x \ll \tau_{1n}$. In the absence of microwave or radiofrequency fields, the reciprocals of these times represent the rates of transition between the levels that they connect (Fig. 12.4a).

![FIGURE 12.4](image)

(a) $M_S$
(b) $M_I$

$$
\tau_1 \quad \tau_{1n} \quad \tau_x \quad \tau_1 \quad \tau_{1n}
$$

$\frac{1}{2} \quad \frac{1}{2} \quad \frac{1}{2} \quad -\frac{1}{2} \quad -\frac{1}{2} \quad \frac{1}{2} \quad -\frac{1}{2} \quad \frac{1}{2}$

$1 - \epsilon_\theta \quad 1 - \epsilon_\theta \quad 1 + \epsilon_\theta \quad 1 + \epsilon_\theta$

\[1 + \epsilon_\theta \quad 1 - \epsilon_\theta \quad 1 - \epsilon_\theta \quad 1 + \epsilon_\theta\]

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external magnetic field governed these differences. This phenomenon is referred to as ‘enhancement’ of the effective magnetic field.
For most solid-state systems, one requires temperatures of the order of 4 K to do a successful ENDOR experiment. At these temperatures, one may achieve microwave saturation with modest power because $\tau_{1e}$ is relatively long. A lengthened value of $\tau_{1e}$ also makes it possible for the nuclear ($\Delta M_I = \pm 1$) transitions to compete with the $\Delta M_S = \pm 1$ transitions. In extreme cases, for example, phosphorus-doped silicon, $\tau_{1e}$ is of the order of hours; however, more typically, it is a small fraction of a second. Indeed, if the ENDOR linewidths are of the order of 10 kHz, corresponding to $\tau_2 = 10^{-5}$ s, the value of $\tau_{1e}$ can be no shorter if it is not to contribute to broadening from spin-lattice relaxation. With $\tau_{1e}$ and $\tau_2$ of this order of magnitude, and if $\tau_x$ is not too long, one may hope to do a steady-state ENDOR experiment, that is, to observe ENDOR lines that may be traversed at an arbitrarily slow rate and re-traversed an indefinite number of times. (By contrast, in rapid-passage types of ENDOR experiments, one observes an ENDOR signal only during a rapid traverse, and in the process, there is an equalization of populations so that an immediate re-traverse gives no evidence of an ENDOR line.) This designation ‘steady state’ may not be fully accurate, if the relaxation time $\tau_{1n}$ is very long.

It is now profitable to consider in greater detail the steady-state ENDOR experiment outlined in Section 12.1 for a system with $S = I = \frac{1}{2}$. One commences by optimizing the intensity of an inhomogeneously broadened EPR line, after which one sets the field at the center of the EPR absorption line, for example, the line at $B_k$ in Fig. 12.3c. The microwave power is increased somewhat beyond the value at which the intensity of a homogeneously broadened line would be a maximum (Fig. F.8a). The optimum value of the microwave magnetic field $B_{1e}$ for steady-state ENDOR observations should be such that $\gamma_e^2 B_{1e}^2 \tau_1 \tau_2 \approx 3$ [3, p. 244]. Here $g_e$ is the magnetogyric ratio of the electron, and $B_{1e}$ is the amplitude of the microwave magnetic field. The value of $\tau_2$ to be used here is that appropriate to the single spin packet (Section 10.4.2) being saturated [3, p. 264]. Now the power level of the radiofrequency generator (and thus $B_{1n}$) is set sufficiently high so that the rate $(dN/dt)^\dagger$ of induced upward transitions at frequency $\nu_{n1}$ is large in comparison with $\tau_2^{-1}$, that is, $(dN/dt)^\dagger \tau_2 \geq 1$. Stated another way, one requires a large value of $B_{1n}$ because the $\Delta M_S = 0$, $\Delta M_I = \pm 1$ transitions must be able to compete with the $\Delta (M_S + M_I)$ transitions corresponding to the cross-relaxation path measured by $\tau_x$. When the rf frequency passes through the value $\nu_{n1}$, an ENDOR line is observed. In many four-level systems, one also observes a second ENDOR line, when the frequency $\nu_{n2}$ is traversed. If the only effective relaxation paths were those thus far assumed, it would be necessary to saturate the line at the field $B_m$, after traversing the frequency $\nu_{n1}$, before the ENDOR line at $\nu_{n2}$ can be detected.

We now turn to consideration of the population of the levels ($S = I = \frac{1}{2}$) under various conditions. In the absence of a magnetic field, the population of each of the four (almost) degenerate levels would be (almost) $N/4$, where $N$ is the total number of unpaired electrons. In the presence of a magnetic field and ignoring hyperfine effects, the populations of the states are

\[
M_S = \pm \frac{1}{2}; \quad N_{+1/2} = \frac{1}{4} N \exp[-g_e \beta_e B/(2k_B T)] \approx \frac{1}{4} N (1 - v_e) \quad (12.9a)
\]
and

\[ M_S = -\frac{1}{2}; \quad N_{-1/2} = \frac{1}{4} N \exp[+g_e \beta_e B/(2k_B T)] \approx \frac{1}{4} N(1 + e_e) \quad (12.9b) \]

Here \( e_e = g_e \beta_e B/(2k_B T) \). If the \( M_I = +\frac{1}{2} \) EPR transition (Fig. 12.4) is activated by the microwave field, the only effective relaxation path is that indicated by \( \tau_{1e} \); the path via \( \tau_x \) is ineffective, since the much longer \( \tau_{1n} \) is in series with it.

At this point, although our steady-state ENDOR experiment involves only partial saturation of the electron-spin transition, the discussion is simplified by assuming equalization of the populations of the states \( M_I = +\frac{1}{2} \), as indicated in Fig. 12.5a. For complete saturation of the transition between the states with \( M_I = -\frac{1}{2} \), the populations are those given in Fig. 12.5b. It is still true that for \( \tau_{1e} \ll \tau_x \), very little cross-relaxation occurs. For saturation of the \( M_I = +\frac{1}{2} \) transition, it is to be noted that the \( |+\frac{1}{2}, +\frac{1}{2} \rangle \) and \( |+\frac{1}{2}, -\frac{1}{2} \rangle \) states differ in population by \( e_e \), whereas in the absence of microwave saturation they would have differed by \( e_n = g_n \beta_n B/(2k_B T) \). Thus, if a short-circuiting path is provided between these two states, there can be a significant reduction in the population of the \( |+\frac{1}{2}, +\frac{1}{2} \rangle \) state as compared with that of the \( |-\frac{1}{2}, +\frac{1}{2} \rangle \) state. The intense rf field at the frequency \( \nu_{n1} \) provides such a path. The rate of transition between the \( |+\frac{1}{2}, +\frac{1}{2} \rangle \) and \( |+\frac{1}{2}, -\frac{1}{2} \rangle \) states must at least equal \( \tau_x^{-1} \). If the \( M_I = -\frac{1}{2} \) transition is saturated, it is the \( |-\frac{1}{2}, -\frac{1}{2} \rangle \) and \( |-\frac{1}{2}, +\frac{1}{2} \rangle \) states that have the large population difference \( e_e \), and hence an intense rf field at frequency \( \nu_{n2} \) gives rise to an ENDOR line. The equality in population of the other pair of levels, if only these relaxation processes are operative, would not result in an ENDOR line at the frequency \( \nu_{n1} \). The same applies to saturation of the \( M_I = +\frac{1}{2} \) states, for which no ENDOR line at \( \nu_{n2} \) should be expected. It is apparent that in many systems there must be at least one additional path of relaxation if both ENDOR lines are to be observed on saturating either microwave transition.

**FIGURE 12.5** Relative populations of levels in an \( S = I = \frac{1}{2} \) system in which the ENDOR behavior is governed by the combined effects of \( \tau_{1e} \) and \( \tau_x \). (a) On saturation of the low-field EPR line, only the lower-frequency ENDOR line is observed. (b) On saturation of the high-field EPR line, only the higher-frequency ENDOR line is observed.
We note that the operators $\hat{S}_z \hat{I}_+ + \hat{S}_- \hat{I}_+$ in the hyperfine term (expansion of the second term on the right of Eq. 12.2; see Eq. C.32) admix the states $|M_S - 1, M_I + 1\rangle$ or $|M_S + 1, M_I - 1\rangle$ with the state $|M_S, M_I\rangle$. It is such mixing that makes partially allowed the $\Delta (M_S + M_I) = 0$ transitions associated with the relaxation path $\tau_s$. The alternative path labeled $\tau_{sx}$ in Fig. 12.4 could be described as involving $\Delta (M_S + M_I) = \pm 2$ transitions. For the latter transitions, one requires mixing induced by the term $\hat{S}_z \hat{I}_+ + \hat{S}_- \hat{I}_-$ of the states $|M_S + 1, M_I + 1\rangle$ or $|M_S - 1, M_I - 1\rangle$ with the state $|M_S, M_I\rangle$. The mixing coefficient has the form $(A_X - A_Y)/4\hbar\nu_c$, where $A_X$ and $A_Y$ are two of the principal components of the hyperfine matrix [3, p. 247]. It is thus apparent that this mixing is non-zero and $\tau_{sx}$ is finite only if the hyperfine interaction is not isotropic. There are now two alternative relaxation pathways (other than $\tau_{1e}$) to reach the lowest-lying state $| - \frac{1}{2}, \frac{1}{2}\rangle$ from the uppermost state $| + \frac{1}{2}, \frac{1}{2}\rangle$; one involves $\tau_{sx} + \tau_{1n}$, and the other $\tau_{1n} + \tau_s$ (Fig. 12.5). In either case, the relaxation rate is controlled by $\tau_{1n}$ (since $\tau_{sx}$ is generally much shorter than $\tau_{1n}$). Application of saturating rf power at either nuclear frequency sufficiently enhances the rate of the transitions $\Delta M_S = 0, \Delta M_I = \pm 1$ that the effective value of $\tau_{1e}$ is reduced because of the competing relaxation path, independent of which microwave transition is saturated. This is indeed the essential characteristic of steady-state ENDOR.

If one or more cross-relaxation times and nuclear spin-lattice relaxation times are of favorable magnitude, the application of saturating rf power reduces the effective value of the electron spin-lattice relaxation time sufficiently so that ENDOR lines may be observed continuously, as long as the exciting frequency is within the ENDOR linewidth. In many cases the intensities of pairs of ENDOR lines are similar; in others, they may be so unequal that one line is not even detected. This phenomenon is particularly marked when the nuclear Zeeman and the hyperfine interactions are comparable in magnitude [3, p. 221; 6, 7]. For systems with uniaxial symmetry, one can calculate the differences in intensity arising from differences in enhancement (see end of Section 12.2) of the effective rf field by the hyperfine field of the electron at the nucleus, in good agreement with observation. The orientation of the rf field relative to the axis of symmetry can be extremely important in determining the intensity of a particular ENDOR line, even though the rf field is always maintained perpendicular to the static field $B$.

Our discussion has thus far been limited to the response of a four-level system. In the case in which one has a system of general spin $S$ and general nuclear spin $I$, the maximum possible number of ENDOR lines is $16SI$. This allows for occurrence of all EPR transitions that are forbidden in first order. Thus for $S = I = \frac{1}{2}$, there will be 4 ENDOR lines (see Fig. 5.4). If any nucleus has spin $I > 1$, it may be essential to consider the term for the nuclear quadrupole interaction (fourth term on the right in Eq. 12.1). Here there are additional relaxation paths, so that it is even more difficult to predict the intensity of the ENDOR lines or to specify in detail the ENDOR (relaxation) mechanism.

We now consider very briefly two other types of ENDOR mechanisms. The first of these, ‘packet-shifting’ ENDOR, can be discussed by considering the
phosphorus-doped silicon system [4,8]. Here the electron wavefunction of the donor extends over a large number of nuclei, some of which are $^{29}$Si ($I = \frac{1}{2}$) and, of course, $^{31}$P. Since all relaxation times $\tau_{1e}, \tau_{1n}$ and $\tau_s$ are all of the order of hours for this system, one can easily ‘burn a hole’ in one of the inhomogeneously broadened EPR lines by saturating those spin packets that experience a particular local field. Since the ‘hole’ recovers with characteristic time $\tau_{1e}$, the redistribution of population of nuclear states associated with this microwave-saturated transition is achieved in leisurely fashion. The most effective means of providing a favorable population redistribution in the nuclear levels is the ‘rapid-passage’ technique, which allows the populations of a pair of levels to be inverted by the use of an appropriately intense rf pulse. It is expedient to observe the signal in dispersion (rather than absorption) for observation of the transient signals that arise.

A particular spin packet of the inhomogeneously broadened line, which is the envelope of all such packets, represents one particular value of the local field, to which many nuclei contribute. The redistribution of populations by the rapid-passage inversion changes the local field at neighboring nuclei, which in turn may have as neighbors electrons not involved in the microwave saturation. The changed local field means that some spin packets are shifted to other regions of the inhomogeneously broadened line, while other packets now find themselves in just the local field defining the region of the line that was saturated. The net changes of nuclear populations allow transient ENDOR signals to be observed both for $^{29}$Si and for $^{31}$P nuclear transitions. Thus the term ‘packet-shifting’ is very appropriate for this type of ENDOR.

Another of the important ENDOR mechanisms is that of ‘distant’ ENDOR. In the course of investigations on ruby ($\text{Cr}^{3+}$ in $\text{Al}_2\text{O}_3$), ENDOR lines were observed from $^{27}$Al transitions (not surprisingly), but the NMR frequency of the Al nuclei that were involved was not affected by the $\text{Cr}^{3+}$ ions [10]. Hence these Al nuclei must have been located so far away from the unpaired electrons that the dipolar interaction was negligible. It can be shown [3, p. 74; 11] that there is marked polarization of nuclei in the vicinity of a paramagnetic ion in a magnetic field, if high microwave power is applied at a frequency on the shoulder of a resonance line. The term ‘polarization’ implies preferential population of spin levels. Instead of being confined to the vicinity of the paramagnetic ion, these population differences are transmitted throughout the sample by mutual spin flips of the nuclei, at the eventual expense of the energy of the microwave field. This ‘spin diffusion’ is thus the mode of communication of the paramagnetic ion with distant nuclei. When rf power corresponding to Al nuclear transitions is applied, the change in spin orientation of the distant nuclei is transmitted back to the $\text{Cr}^{3+}$ ions; the change in their EPR signal level indicates that energy is absorbed. In consonance with this mechanism, it was noted that when the rf power was removed, the EPR signal recovered with a characteristic time of about 10 s, the $^{27}$Al nuclear spin-lattice relaxation time $\tau_{1n}$. For both packet-shifting and for steady-state ENDOR, the recovery rate is of the order of $\tau_{1e}$, which here is about $10^{-1}$ s.
12.5 CW ENDOR: SINGLE-CRYSTAL EXAMPLES

12.5.1 The F Centers in the Alkali Halides

Perhaps the most spectacular successes of the ENDOR method have been in its application to systems that give inhomogeneously broadened lines that are the envelope of large numbers (in some cases, literally hundreds) of overlapping hyperfine components. An example is the electron in an anion vacancy ($F$ center) in KBr, for which the width of the (gaussian) EPR line is about 12.5 mT. The six first-shell neighbors in the face-centered structure are either $^{39}$K (relative abundance 93.26%) or $^{41}$K (relative abundance 6.73%). These nuclides also comprise all other odd-numbered shells. The even-numbered (second, fourth, etc.) shells are composed of $^{79}$Br (abundance 50.69%) and $^{81}$Br (abundance 49.31%). All four of these nuclides have $I = \frac{3}{2}$. Taking, for a moment, all these nuclides to be equivalent, one may compute (Section 3.5) the maximum number $P_j(2n_j I + 1) = 19 \times 37 = 703$ of hyperfine lines arising just from the six first-shell and the 12 second-shell neighbors. To be sure, many of these lines have low relative intensities. For example, the outermost line of a set of 19 has an intensity only $\frac{1}{580}$ that of the central line (Problem 3.2). Considering the extra lines arising from interaction with additional shells of nuclei, as well as the non-identity of nuclear moments, anisotropic interactions and the effects of the nuclear-quadrupole moments, it is understandable that ordinarily the EPR line of the $F$ centers in KBr gives no indication of any structure.

From Eqs. 12.4 and 12.5 one expects that the very wide range of hyperfine interactions of the unpaired electron with nuclei in the various shells ensures that the ENDOR spectrum is spread over a considerable range of frequency.

Both the isotropic and anisotropic parts of the hyperfine interactions fall off with distance from the anion vacancy, in accordance with the ideas discussed in Chapter 5. Thus valuable information about the unpaired-electron distribution of the $F$ center becomes available by measuring these effects.

Looking now at the ENDOR spectrum of crystalline KBr in Fig. 12.6, one sees that the frequencies at which the lines are observed vary from roughly 0.5 to 26 MHz. Clearly, there is also a considerable variation in linewidths, the narrowest lines being of the order of 10 kHz. Especially in the 3–4 MHz region, such a small width makes it possible to resolve the pairs expected from Eqs. 12.4 and 12.5, separated by $2\nu_{\text{Br}}$, for each of the bromine nuclides. Various line pairs from $^{39}$K, $^{41}$K, $^{79}$Br and $^{81}$Br are identified with brackets above the lines (Fig. 12.6).

Identification of the shell numbers (indicated as a subscript to a symbol or bracketed below it) is accomplished by a study of the angular dependence of the lines. In Fig. 12.6, the field $\mathbf{B}$ is oriented along a (100) axis of KBr. When the hyperfine interaction has uniaxial symmetry (shells I, III and IV), the angular dependence of a line is similar to that shown in Fig. 12.7a for the first-shell nuclei of the $F$ center in LiF. For nuclei in this and other shells, one can measure and also predict the angular dependence of the dipolar hyperfine interaction. These angular dependences are given in Fig. 12.7 out to the eighth shell [12]. Where the angular dependence of
two shells is similar, the magnitudes of the hyperfine coupling are usually very different, and the line pairs are usually assignable without ambiguity. If the hyperfine couplings are large, the higher-order terms (Sections 3.6 and 5.3.1) must be taken into account.

In KBr, an additional complication arises from the quadrupolar contributions (Section 5.6) from the nuclides present \[ Q = 0.054 \ ({}^{39}\text{K}), \ 0.060 \ ({}^{41}\text{K}), \ 0.29 \ ({}^{79}\text{Br}), \ 0.27 \ ({}^{81}\text{Br}), \ \text{in units of} \ 10^{-28} \ \text{m}^2 \]. For example, for shell I, there are actually three \(^{39}\text{K}\) lines that show the angular dependence corresponding to Fig. 12.7a. These, which also show the effects of second-order hyperfine coupling,
are clearly seen in the range 10–12 MHz (Fig. 12.6). These triplets can be understood by consideration of the spin hamiltonian (Eq. 12.1) containing the quadrupole interaction term (Eq. 5.51b). For nuclei in which the quadrupole interaction matrix \( P \) has uniaxial symmetry (\( \eta = 0 \)), this reduces to

\[
\hat{H}_Q = P[3\hat{I}_z^2 - \hat{I}^2]
\]

where \( P \) is given by Eq. 5.50. At sufficiently high field \( B \) and when \( g \) and \( A \) are close to isotropic, the additive transition-energy term can be obtained by using first-order

**FIGURE 12.7** Angular dependence of the \((^7\text{Li}, ^{19}\text{F})\) ENDOR frequencies for shells 1–8 of nuclei about the trapped electron from the \( F \) center in LiF: (a–g) the rotation axis is \((100)\); (h) for nuclei of shell 2, with \((110)\) as the rotation axis. The frequency scale has its zero at \( a_0/2 \) and is divided into units of \( b_0/2 \), that is, relative to the appropriate hyperfine parameters. Labels \( A, B, C, \ldots \) refer to lines from sets of ions at positions equivalent in the absence of the external magnetic field. [After W. C. Holton, H. Blum, Phys. Rev., 125, 89 (1962).]
perturbation theory [3, pp. 225–228; 13] and is given by

\[ h \nu_Q = 3P [3 \cos^2 \theta - 1] (M_I - \frac{1}{2}) \]

(12.11)

where \( \theta \) is the angle between \( B \) and \( Z \), and \( \Delta M_I = \pm 1 \). Here \( M_I \) is the greater of the two such quantum numbers. Including the nuclear Zeeman term and the hyperfine

**FIGURE 12.8**  
(a) First-order energy-level splitting arising from nuclei with \( I = \frac{1}{2} \), showing the coinciding ENDOR transitions when \( A > |g_n|B, B \) and \( P = 0 \) (upper set for \( M_S = +\frac{1}{2} \), lower set for \( M_S = -\frac{1}{2} \)) as well as the effect of \( P > 0 \).  
(b) First-order ENDOR spectrum showing quadrupole splitting, when \( P > 0 \) and \( \theta = 0 \).

**TABLE 12.1**  
Hyperfine and Quadrupole Couplings (in MHz)  
in KBr at 90 K, from ENDOR Spectra

| Shell | Nuclide | \( A_{||}/h \) | \( A_\perp/h \) | \( P/h \) |
|-------|---------|----------------|----------------|---------|
| 1     | \(^{39}\text{K} \) | 18.33          | 0.77           | 0.067   |
| 2     | \(^{81}\text{Br} \) | 42.85\(^b\)    | 2.81\(^b\)     | 0.077   |
| 3     | \(^{39}\text{K} \) | 0.27           | 0.022          | —       |
| 4     | \(^{81}\text{Br} \) | 5.70           | 0.41           | 0.035   |
| 5     | \(^{39}\text{K} \) | 0.16\(^b\)     | 0.021\(^b\)   | —       |
| 6     | \(^{81}\text{Br} \) | 0.84\(^b\)     | 0.086\(^b\)   | —       |
| 7     | \(^{81}\text{Br} \) | 0.54           | 0.07           | —       |

\(^b\) Detectable departures from uniaxial symmetry.
term, the ENDOR frequencies are given by

$$v_{n1} = \frac{1}{2}[A_\parallel + A_\perp (3 \cos^2 \theta - 1)] - g_n\beta_n B + 3P(3 \cos^2 \theta - 1)(M_I - \frac{1}{2})/\hbar$$  \hspace{1cm} (12.12a)

$$v_{n2} = -\frac{1}{2}[A_\parallel + A_\perp (3 \cos^2 \theta - 1)] - g_n\beta_n B + 3P(3 \cos^2 \theta - 1)(M_I - \frac{1}{2})/\hbar$$  \hspace{1cm} (12.12b)

Here A and P have been taken to be coaxial. The energy levels and the ENDOR spectrum for a nucleus with $I = \frac{3}{2}$ are given in Fig. 12.8. The hyperfine and some quadrupole couplings in successive shells for KBr are given in Table 12.1.

### 12.5.2 Metal-Ion Tetraphenylporphyrins

Detailed studies of ENDOR of $^{63}$Cu$^{2+}$ and $^{107,109}$Ag$^{2+}$, of $^{14}$N and of $^1$H in magnetically dilute single-crystal complexes M(II)TPP have been reported and discussed in detail [14]. The various hyperfine matrices (and nuclear quadrupole matrices for nitrogen) were obtained, and used to obtain a picture of the electronic distribution ($d$ character on M, spin populations on the ligand atoms in specific orbitals, etc.).

### 12.6 CW ENDOR IN POWDERS AND NON-CRYSTALLINE SOLIDS

For many systems consisting of a paramagnetic guest in a host matrix, it is extremely difficult or impractical to grow a single crystal of a size sufficient for EPR studies. This is especially the case for biologically important systems, for example, metalloenzymes [15–17].

We have noted earlier that for crystalline powders and glassy solid solutions one may see distinct EPR lines, especially from those molecules that have an axis of dominant interaction at right angles to the static magnetic field $B$. For example, with the $V^-$ center in powdered MgO (Fig. 4.7) where the predominant effect is $g$ anisotropy, the most intense feature corresponds to those defect centers whose tetragonal electric field axis lie perpendicular to $B$; that is, the position of this line corresponds to $g_\perp$. Figure 5.12 illustrates the case in which there is a marked anisotropy of $g$ and also of a hyperfine coupling $A$, where the matrices $g$ and $A$ have the same principal axes. By contrast, consider systems in which electron spin-spin interaction is dominant (e.g., triplet states), with the $g$ anisotropy small (and $A = 0$), as illustrated in Figs. 6.5 and 6.7. Here the line pairs arise from molecules having magnetic field $B$ directions parallel to principal axes of the matrix $D$.

In general, every ENDOR spectrum of a paramagnetic species in a powder or glass arises from molecules occurring in a very limited range of orientations, selected by fixing the EPR absorption at a chosen location within the envelope. Here too, especially informative ENDOR spectra occur when $B$ is along one of
the above-mentioned canonical directions. Provided that the signal-to-noise ratio at the EPR powder spectral setting is adequate, one may obtain ENDOR spectra and gather much information about the paramagnetic species, including geometric detail. Thus relative orientations of the principal axes of matrices $g$, $D$ and $A$ may be obtainable. By suitable analysis, one may be able to extract a number of parameters otherwise obtainable only from single-crystal measurements [18,19].

The hyperfine couplings arising from each type of nuclide (e.g., $^1H$) give distinctive contributions that can be related to (in simple cases, centered on) the nuclear resonance frequency $v_n$ of that nuclide at the magnetic field value $B$ where the ENDOR spectrum is taken. We note (Eqs. 12.4b and 12.5b) that for nuclei with $I = \frac{1}{2}$, each hyperfine coupling, to first order, gives a line pair at radiofrequencies $|v_n \pm K/2h|$, centered about $v_n$, when hyperfine parameter $K(\theta, \phi)$ in Eq. 6.55 is sufficiently small compared to $hv_n$. Similarly, for nuclei with $I \geq 1$ (e.g., $^{14}N$; see Ref. 19), both lines of such a hyperfine pair may split into $2I$ lines, the set occurring at radiofrequencies $|v_n \pm K/2h \pm (3p/2h)(2M_I - 1)|$, where parameter $p \equiv (n^T g T A T P A g n)/g^2K^2$ wherein $P$ is the nuclear quadrupole coupling matrix (Eq. 5.51a), $n(\theta, \phi) = B/B$, and where $-I + 1 \leq M_I \leq I$.

We see then that powder ENDOR spectra can yield information about quadrupole couplings, which is never available from first-order EPR spectra, and that the complications due to the presence of sums, differences and combinations of hyperfine lines in EPR and ESEEM are absent in ENDOR. A brief review of the structural information available from powder ENDOR spectroscopy has been published [20].

As an interesting example of ENDOR in glassy media, we can cite trapped electrons in $\gamma$-irradiated aqueous NaOH, methanol and 2-methyltetrahydrofuran at 77 K [21]. Here the EPR line is broadened as a result of dipolar interactions with surrounding matrix protons. Analysis of the $^1H$ ENDOR lineshape gives information about the extent of delocalization of the unpaired electron.

As a second example, we cite proton ENDOR powder work done on nitrosyl horse-heart myoglobin [22]. Here, detailed analysis using computer simulation, led to identification of the protons in the heme pocket.

### 12.7 CW ENDOR IN LIQUID SOLUTIONS

The possibility of detecting ENDOR of substances in liquid solution was first demonstrated by Hyde and Maki [23]. Subsequent experimental and theoretical works have shown this to be a very valuable technique [24–27].

The discussion of Section 12.5 has emphasized that for solids one often is able to resolve far more lines in the ENDOR than in the EPR spectrum. For free radicals in liquid solution, this may still be true if inhomogeneous broadening limits the resolution. However, even in these cases, the number of possible lines in the ENDOR spectrum is less than that for the EPR spectrum. Consider a radical with one set of four equivalent protons, which gives the familiar $1:4:6:4:1$ EPR
The full spin hamiltonian is given by Eq. 12.2, where now $\hat{I} = \Sigma_i \hat{I}_i$, yielding $\hat{I}' = 2$. That the number of lines in the ENDOR spectrum is less than that for the EPR spectrum may readily be shown by application of Eq. 12.2 to the four-proton system. If the hyperfine coupling constant is small enough so that second-order effects (Section 3.6) are negligible, then the full spin hamiltonian gives a set of five equally spaced levels with $M_S = -\frac{1}{2}$ (Fig. 12.9) and also with $M_S = +\frac{1}{2}$. The five levels corresponding to $M_S = -\frac{1}{2}$ have a uniform spacing greater than that of the $M_S = +\frac{1}{2}$ levels. Hence only two ENDOR transitions are observed; these occur at $\nu_{\text{ENDOR}} = \nu_p + A/2h$. Here $\nu_p$ is the proton NMR frequency at the constant magnetic field used for the ENDOR experiment. For radicals in which there are $n$ sets of $m$ non-equivalent protons, there are only $2n$ lines in the ENDOR spectrum, irrespective of the number of protons in any set. In the EPR spectrum there are $(m + 1)^n$ lines.

There are special problems in constructing equipment for studies of ENDOR spectra of liquids. The difficulties in this case arise from the necessity of using an intense rf field, which causes heating if applied continuously. Hence pulse rf ENDOR systems have been developed. The requirement of a large rf field arises because the nuclear transitions must be saturated. Relaxation times $\tau_{\text{re}}$ are of the order of $10^{-5} - 10^{-6}$ s for free radicals at room temperature, whereas the relaxation times $\tau_{\text{in}}$ of protons in these are typically several orders of magnitude longer than this. The application of an intense rf field $B_{1n}$ at the nuclear-resonance frequency

![Figure 12.9](image.png)
greatly reduces the lifetime of a nuclear-spin orientation in an excited state because of emission stimulated by this field.

12.8 PULSE DOUBLE-RESONANCE EXPERIMENTS

With the advent of pulse ENDOR spectrometers, all the benefits of time-resolved spectroscopy, as outlined in Chapters 1, 10 and 11, have become available. Various sequences of pulse microwave and RF excitations can be used, with much scope for imaginative research. At present, Mims ENDOR (Fig. 12.10) [29] and Davies ENDOR [30] have a favorite ranking.

The various techniques include ENDOR with circularly polarized $B_{1n}$, polarization-modulated ENDOR, double and triple ENDOR, stochastic ENDOR, multiple-quantum ENDOR and ENDOR-induced EPR. For example, we can cite a spectrometer operating at 140 GHz, demonstrating orientation-selective Davies ENDOR [31]. These techniques are yielding new levels of understanding of the structural and relaxation properties of unpaired-electron species. Unfortunately, it is not possible to give the details in this book; happily, various excellent descriptions have become available [32–37].

12.9 ELECTRON-ELECTRON DOUBLE RESONANCE (ELDOR)

In an ENDOR experiment one observes a change in intensity of a partially saturated EPR signal when one establishes a connection to an energy level belonging to a
different hyperfine transition. A very different experiment, termed electron–electron double resonance (ELDOR), consists of the observation of a reduction in the intensity of one hyperfine transition when a second hyperfine transition is simultaneously being saturated [38]. Simultaneous electron-spin resonance in one magnetic field for two different transitions requires irradiation simultaneously at two microwave frequencies; that is, one requires a bimodal resonator tunable to two frequencies separated by a multiple of the hyperfine coupling. In principle, the simplest case is that of a single nucleus of spin $\frac{1}{2}$, illustrated in Fig. 12.11. Although the two transitions have no level in common, they may be coupled by two mechanisms:

1. Rapid nuclear relaxation that may be induced by dipolar coupling of electrons and nuclei. The flipping of an electron spin under appropriate conditions can cause a simultaneous flip of a coupled nuclear spin. This mechanism is predominant at low concentrations and at low temperatures.

2. At high concentrations or at sufficiently high temperatures, spin exchange or chemical exchange (Section 10.5.3) tend to equalize the populations of all spin levels.

The ELDOR technique is very sensitive to the various relaxation mechanisms involved. For example, it was used (as an alternative to ENDOR measurements)

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**FIGURE 12.11** Electron-electron double-resonance experiment. The intensity of the EPR line observed in a spectrometer operating at a low microwave power level at frequency $\nu_2$ is recorded as a function of the (high) microwave power applied to the same bimodal cavity by a separate source operating at a frequency $\nu_1$. 

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to distinguish between the two nearly identical large nitrogen hyperfine splittings in DPPH, making use of the differences in the relaxation times of the various nuclei present. This study produced accurate values of the $^{14}$N hyperfine coupling constants [39]. A careful ELDOR study of the effect of the Heisenberg spin exchange between pairs of paramagnets (see Section 6.2.1) on their saturation behavior was studied for peroxylamine disulfonate (PADS) radical anions in de-oxygenated water, and agreed with the existing theory [40].

Pulse ELDOR, as applied to a CH fragment ($S = I = \frac{1}{2}$) [i.e., CH(COOH)$_2$ in irradiated malonic acid], yielded both spin-relaxation and cross-relaxation times, the latter between the $M_I = \pm \frac{1}{2}$ manifolds [41].

Another example is the now-familiar $V^-$ center in MgO (Sections 4.2, 4.8 and 12.6). Here, pulse ELDOR has revealed that the tetragonally distorted hole centers jump between the three possible orientations [42]. One can sit at fixed magnetic field with the pumping microwave excitation (frequency $\nu_1$) on the line from one such site, and the observed signal (frequency $\nu_2$) at another site. Power saturating the first manifests itself on the second, due to the pumping. This saturation transfer probably proceeds, at least at 4.2 K, via tunneling of the hole, taking place without reorientation.

Special 2D ELDOR experiments have given valuable information about magnetization-transfer rates between spin-label nitroxide radicals in disordered solid polymers [43], as well as about local motional effects extending right down to the rigid-limit region in such systems [44]. The pulse sequences are shown explicitly [43]. A review of these techniques is available [45].

Multi-quantum jumps excited in ELDOR spectroscopy, observed initially in pyrrol black powder (oxypyrrol free radical), have been known for some decades now [46].

### 12.10 OPTICALLY DETECTED MAGNETIC RESONANCE

The intensity of every EPR transition is proportional to the difference $\Delta N$ in the populations of the two $|M_S\rangle$ states spanned, that is, to the net spin polarization (Section 4.6). It follows that any other process affecting $\Delta N$ influences the EPR intensity, and vice versa, unless the spin-lattice relaxation is too efficient. The above-mentioned concepts are the essence of how ENDOR works. Under the right circumstances, optical transitions induced by polarized light have intensities proportional to $\Delta N$, so that electronic transitions and EPR transitions are linked. Detection of such effects is not easy, generally requiring very low temperatures to maximize $\Delta N$. Such optically detected magnetic resonance (ODMR) experiments make it possible to characterize those portions of broad optical bands that arise from a specific unpaired-electron species. References 47–52 cite applicable reviews of ODMR.

ODMR of the [AlO$_4$]$^0$ ‘point’ defect (one unpaired electron, primarily on an oxygen anion positioned between the Al and a Si cation) in irradiated crystalline quartz has disclosed which of several optical absorption peaks (1–5 eV) is linked to the paramagnetic center [53].
As second example, we point to crystals of luminescent gold(I) complexes, with halo (triphenyl)phosphine and arsine ligands, which exhibit phosphorescences from phenyl-localized triplet states. These have yielded zero-field ODMR data allowing determination of the electronic quadrupole parameters $|D|$ and $|E|$ (see Section 6.3.1) [54]. An elegant method for measuring relative populating rates of photoexcited triplet-state sublevels during optical pumping, using ODMR in an indole chromophore, has been developed quite recently [55], and points to the potential of ODMR in the future.

12.11 FLUORESCENCE-DETECTED MAGNETIC RESONANCE

A newly developed optical technique enables far better sensitivity and time resolution than does ordinary (cw) EPR, in some circumstances. It uses detection of fluorescence from the recombination product of short-lived free radicals in liquid or solid solution to display the EPR spectrum of one or both of these. For instance, the fluorescence-detected magnetic resonance (FDMR) can be utilized to observe primary radical cations created by ionizing or photoionizing radiation (e.g., pulses

![Fluorescence-Detected Magnetic Resonance](image)

**FIGURE 12.12** (a) FDMR spectrum observed at 190 K in cyclopentane containing $10^{-3}$ M cubane and $10^{-4}$ M perdeuterated anthracene. The asterisks indicate signals from the cyclopentane solvent. The insertion is the enlargement of the left outermost three peaks. (b) First-derivative FDMR spectrum of part (a). [After X.-Z. Qin, A. D. Trifunac, P. E. Eaton, Y. Xiong, *J. Am. Chem. Soc.*, 113, 669 (1991).]
of 5–15 ns duration) [56]. A microwave pulse applied immediately thereafter alters the fluorescence intensity, by an amount sensitive to the EPR intensity appropriate to the field $B$ present. The ‘EPR’ spectrum, including hyperfine structure, can be obtained by varying $B$ step-wise.

Thus, for example, the spin-correlated radical pair cubane$^+$ and perdeuteroanthracene$^-$ recombine, within picoseconds after an ionizing 3 MeV electron beam pulse, to yield an excited singlet-state anthracene scintillator molecule [57]. The X-band FDMR spectrum observed at 190 K is shown in Fig. 12.12 and displays the proton hyperfine septet (1:6:15:20:15:6:1 with spacing 1.61 mT) expected for cubane$^+$.

As another example of FDMR, we select the creation of naphthalene$^+$/naphthalene$^-$ in dilute solution (>0.01 M) at room temperature [58]. The detection of field($B$)-dependent fluorescence from such radical pairs, created by electron irradiation, provides a very sensitive technique, using triplet-state EPR at (say) X-band, for observing such short-lived species.

REFERENCES

410 DOUBLE-RESONANCE TECHNIQUES


NOTES

1. A detailed account of ENDOR theory, including applications, is given by Abragam and Bleaney [3, Section 1.3 and Chapter 4].
2. Generally, special rf modulation coils or loops are installed, often inside the resonator.
3. In some systems, only the ENDOR line at \( v_{e1} \) would be observed when the magnetic field is set at \( B_{k} \); furthermore, only the ENDOR line at \( v_{e2} \) would be observed when the magnetic field is set at \( B_{m} \). We shall consider these cases in Section 12.4.
4. The reader is reminded that the sign of \( A \) may be negative. In the normal experiment in which an oscillating radiofrequency field is used, one is unable to establish the order of energy levels; hence it is appropriate to indicate absolute magnitudes (‘moduli’) where differences are involved. The use of a rotating radiofrequency field allows the order of the energy levels to be determined.
5. In some types of ENDOR experiments, in which one monitors the dispersion (Section F.3.4) instead of the absorption signal, the field is set on one side of the EPR absorption maximum.
6. To avoid repetitious use of the factor \( N/4 \), we shall divide all population numbers by it; hence the relative populations in Eqs. 12.9 are taken as \( 1 - \varepsilon \) and \( 1 + \varepsilon \), in the absence of a microwave field or in the presence of a very weak one. These populations are shown in Fig. 12.4b.
7. An alternative mechanism that may give rise to the cross-relaxation path \( \tau_{xx} \) and that may affect the values of the other relaxation times as well, even with isotropic hyperfine interaction, is thermal modulation of this interaction [3, p. 248].
8. This is to be contrasted with either ‘packet-shifting’ or ‘distant’ ENDOR, which constitute two other important mechanisms; these are discussed briefly at the end of this section.

9. However, saturation of the forbidden lines of Fig. 5.4 would give rise to ENDOR lines of the same frequency as saturation of the allowed lines. These would be difficult to detect, especially since one would require a very intense rf field to compete with the very fast relaxation rate $\tau_{1e}$.

10. It is not to be inferred that these ENDOR mechanisms are mutually exclusive. The order of magnitude of $\tau_{1e}$, for systems in which packet shifting predominates, is typically much longer than those for steady-state ENDOR; a typical value for the latter case may be taken as $\tau_{1e} < 1 \text{ ms}$.

11. Rapid passage represents a traverse of the resonant absorption line in a time short compared with $\tau_1$ and $\tau_2$, with a radiofrequency field $B_{1n}$ large enough so that $\tau_2 \gg |g_n B_{1n}|^{-1}$ and $|g_n B_{1n} \tau_1| \gg 1$, where $g_n$ is the nuclear magnetogyric ratio [9].

12. In the discussion of energy levels of free radicals in Chapter 3, the nuclear Zeeman term was omitted since, just as for the hydrogen atom (Appendix C), the energies of the EPR transitions are hardly affected by its inclusion.

13. This is true provided that terms of the order of magnitude of $A^2/g_e \beta_e B$ can be neglected [28].

FURTHER READING


PROBLEMS

12.1 The second-derivative EPR spectrum of Cu-$\alpha$-picolinate in Zn-$\alpha$-picolinate powder (Cu$^{2+}$, 3$d^9$ in covalent system) is shown in Fig. 12.13a. The
corresponding ENDOR spectrum is shown in Fig. 12.13b. Determine $A_\perp$, $v_n$ and the quadrupole splitting for $^{14}$N.

12.2 The ENDOR spectrum of Co$^{2+}$ (3d$^7$) in MgO (Fig. 12.14) is observed when the transition $\Delta M_S = \pm 1$, $M_J = +\frac{1}{2}$ is partially saturated at a frequency $v = 9.563$ GHz, for $B = 156.1$ mT. From an EPR experiment, one knows that $g = 4.2785$ (Fig. 1.11).
(a) Why are four lines observed? Assign each transition.

(b) Assuming that only second-order hyperfine corrections are necessary, estimate the hyperfine coupling $A_\text{o}$. (Anisotropic effects are here very small.) (The value obtained by using corrections to fourth order is 290.55 MHz.)

(c) From the data, estimate the nuclear $g$ factor of $^{59}\text{Co}$.

12.3 (a) Justify the number of separate curves in Figs. 12.7a–g. (b) Explain the angular variation for each curve for shells 1–4.

12.4 At the nucleus, the magnitude $B_{hf}$ of the magnetic field caused by the unpaired electron is (Eq. 5.14a) derivable from the relation

$$AM_S = -g_n \beta_n B_{hf} \quad (12.12)$$

(a) Calculate $B_{hf}$ at a proton for which the coupling $A/h$ is 142 MHz (one-tenth that of the free hydrogen atom).

(b) Calculate $B_{hf}$ at a $^{55}\text{Mn}$ ion ($M_S = +\frac{1}{2}$) for which the coupling $A/hc = -9.10 \times 10^{-3}$ cm$^{-1}$. The values of $g_n$ can be found in Table H.4.