10. Magentic Resonance Sectroscopy. The Transition Betweeen Magnetic Dipoles in a Magnetic Field.

Magnetic resonance spectroscopy experiments involve the **radiative transitions** between two magnetic energy levels of a molecule or radical in the presence of an applied laboratory magnetic field. We shall view the theory of magnetic resonance in a relatively primitive manner, but one which should highlight all of the important features of the phenomenon and which should allow a facile transition to an understanding of the features of not only radiative but also radiationless transitions between two magnetic states. The strategy shall be analogous to that employed for the theory of electron spectroscopy, the radiative transitions between electronic states. In order for a radiative transition to be possible between two electronic states, the states must possess an electronic energy difference (ΔE_{el}). In order for a radiative transition to be plausible, the two states must differ in some feature of their orbital structure so that the **oscillating electric field** of the **electro**magnetic field of light can interact with the electrons and drive them into oscillation. For the latter to happen, the frequency of the oscillating electric field, ν, must be such that $\Delta E_{el} = h\nu$. Since the transitions occur only at the frequency ν, we term the phenomenon **electronic resonance** and the technique, electronic (resonance) spectroscopy.

Similarly, in order for a radiative transition to be possible between two magnetic levels or states, the states must possess a magnetic energy difference ΔE_{mag}. In order for a radiative transition between two magnetic states to be plausible, the two states must differ in some feature of their magnetic moments so that the oscillating **magnetic field** of the electro**magnetic** field of light can interact with the magnetic moments and drive them into oscillation. For the latter to happen, the frequency of the oscillating magnetic field, ν, must be such that $\Delta E_{mag} = h\nu$. Since the transitions occur only at the frequency ν, we term the phenomenon magnetic resonance and the technique magnetic resonance spectroscopy. Because of the vector model, we shall move freely between the notion of an light wave oscillating at frequency, ν, and a spin vector precessing at frequency, ω, through the relationships $\Delta E_{mag} = h\nu = \backslash\omega$.

In electronic absorption spectroscopy the light impinges on a sample of randomly reorienting molecules and the light interacts with varying dipole moments to produce electronic transitions, in magnetic resonance spectroscopy, the magnetic moments of electrons and nuclei have definite orientations in space because of the effect of the applied magnetic field. Let us now see how the vector model allow us to visualize radiative transitions between two magnetic states in an applied magnetic field.

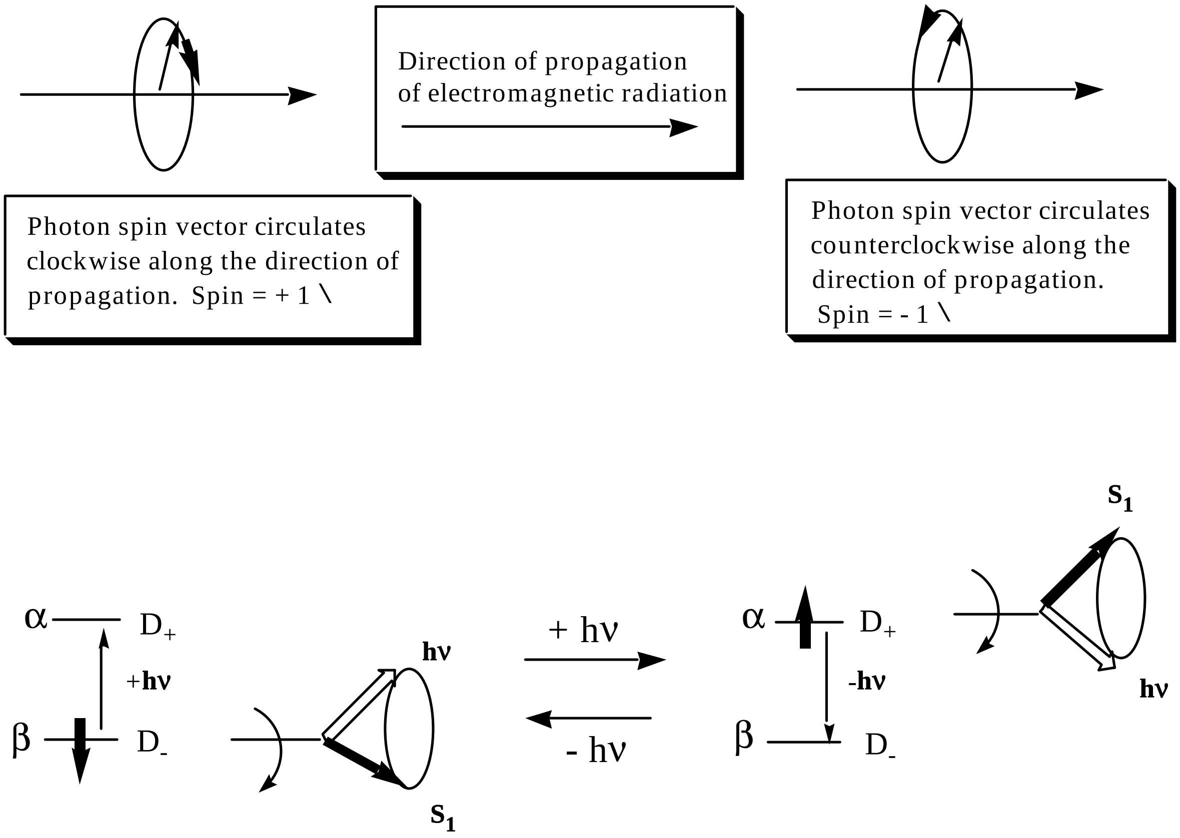
The Vector Model for Magnetic Resonance Spectroscopy

We initially consider the simplest cases of magnetic resonance, an electron in the absence of any other electrons or nuclei, i.e., a "free" electron and a proton in the absence of any other nuclei or any electrons, i.e., a "bare" proton. All of the principles are the same for ESR and for NMR. For a proton, as a model for a nuclear spin, the ideas of magnetic resonance are quite analogous. One important difference is that the direction of the spin angular momentum vector of a proton (a positivley charged particle) is in the **same** direction as the magnetic moment vector. This contrasts with the situation for the electron (a negatively charged particle) for which the direction of the angular momentum vector is antiparallel to the magnetic moment vector. Thus, in the case of the proton, although we follow the same rules for energy on the magnetic moment in an applied field, the angular momentum vector pointing in the direction of the field is lower in energy for the proton. The reason for this is that it is the energy of the interaction of the magnetic moment with the applied field that dominates the magnetic energy of the system, and the magnetic energy is generally lower when the magnetic moment vector is parallel to the field. This means that for both a proton and an electron the **lower energy state corresponds to the situation for which the magnetic moment vector is parallel to the applied field**. Following this rule, for the electron the lowest level has the angular momentum vector directed antiparallel to the field (β), but for the proton, the lowest level has the angular momentum vector directed parallel to the field (α). A second important difference is the much larger size of the magnetic moment due to electron spin relative to the magnetic moment for nuclear spin. This factor leads to much smaller Zeeman energy splittings for nuclear spins.

Figure 23 describes the vector model of transitions between magnetic states for a free electron. These transitions are induced by a coupled and oscillating magnetic field, $\mathbf{H_i}$. For radiative transitions, we identify this oscillating magnetic field as that of electromagnetic radiation. Clearly, in order to induce transitions from the α to the β orientations, the oscillating field must be such that it oscillates about the x (or y) axis. We consider some important qualities of photons that are important aspects in visualizing the radiative transitions between magentic levels.

A photon may be viewed as a packet of electromagnetic radiation. The photon possesses a spin angular momentum, $\sigma_{h\nu}$, of 1 \. As a relativistic particle, the spin can have only two projections in space along a selected axis. In the case of a photon, the direction of propagation is the obvious and convenient "z axis". The two possible spin states correspond (Figure 23) to the magnetic vector of electromagnetic radiation moving clockwise around the direction of propagation (spin = 1 \) or counterclockwise around the direction of propagation (spin = -1 \).

These two states of a photon are termed "helicity" states becasuse the tip of the spin vectors trace our a helix as the electromagentic wave propagates in space. The two helicity states in turn correspond to left ($\sigma_{h\nu+} = 1\ \backslash$) and right ($\sigma_{h\nu-} = -1\ \backslash$) polarized light.



$$\beta\,(-1/2\ \backslash) \xrightarrow{h\nu\,(+1\ \backslash)} \alpha\,(+1/2\ \backslash)$$ Stimulated Absorption

$$\beta\,(-1/2\ \backslash) + h\nu\,(+1\ \backslash) \xleftarrow[h\nu\,(-1\ \backslash)]{} \alpha\,(+1/2\ \backslash)$$ Stimulated emission

Figure 23. Representation of a photon (top) executing rotation of the magnetic field vecrtor about the direction of propagation of the electromagnetic wave. Representation of the radiative transition (middle) between magnetic energy levels. Equations for the conservation of angular momentum during stimulated radiative transitions (bottom).

Now let us visualize the radiative transition involving the absorption of a photon. Since the photon possess both energy and spin it can couple to en electron spin and supply its spin angular momentum and cause absorption to a higher energy state, i.e., the β∅ α transition (Figure 23). Thus, in this case the photon provides the coupling source, the source of conservation of energy and the source of conservation of angular momentum! Althought spontaneous emission between magnetic states is much too slow to compete with other radiationless mechanism of relaxation, a photon can couple with an electron spin and stimulate emission of a photon. This process is shown in Figure 23.

Thus, the vector model represents radiative processes in the same manner as it does the generalized transitions of Figure 20, i.e., the photon's spin is treated in the same manner as a coupling electron spin, or a coupling nuclear spin or any other general coupling magnetic source, $\mathbf{H_i}$.

The absorptive radiative transition from the β state to the α state is analogous to the absorptive radiative transition from one orbital to another. The cones of possible orientation that can contain the spin vector are the analogues of the orbitals that can contain electrons. There are, however, some important differences between electronic transitions and magnetic transitions.

Comparison of Electronic and Magnetic Spectroscopy

Electronic spectroscopy (in the presence or absence of an applied field) involves the jumps of electrons from one orbital to another accompanied by the absorption or emission of a photon. Magnetic resonance spectroscopy (only in an applied magnetic field) involves the reorientation of the magnetic moment of an electron (or a nucleus) accompanied by the absorption or emission of a photon. For consideration of transitions between energy levels the theoretical concepts are completely analogous and we visualize the absorption and emission processes as radiative jumps between energy levels. The conditions for resonance are precisely the same: the photon carries exactly one unit of angular momentum and possesses the energy $\Delta E = h\nu$ so that energy is conserved, angular momentum is conserved and the perturbing interaction of the electromagnetic field possesses the correct resonance frequency and phase.

At a more detailed structural level a number of important differences between electronic and magnetic spectroscopy emerge:

(1) The **interaction** which induces the transition is Coulombic (electrical) in the case of electronic spectroscopy and magnetic in the case of magnetic resonance spectroscopy. This means that the **electrical part** of the electromagnetic wave is the interaction causing electronic orbital jumps, but that it is the **magnetic part** of the electromagnetic wave that causes the reorientation of the magnetic moment. In further detail, the electronic perturbation is visualized as "pushing" or "pulling" electrons along an axis defined by the

molecular structure, whereas the magnetic perturbation is visualized as "twisting" the magnetic moment about an axis defined by the applied field.

(2) The probability of electronic absorption (or emission) depends on the orbitals involved in the transition and the ability of the molecular structure to possess an axis along which the electrons can be induced to oscillate as a result of the orbital transition, since this feature determines the magnitude of the transition dipole which interacts with the electromagnetic wave. The probability of magnetic absorption (or emision) depends on the magnitude of the magnetic moment, which is essentially fixed for an electron or nucleus. As a result the extinction coefficients for electronic absorption is very dependent on molecular structure and vary over orders of magnitude. On the other hand, the extinction coefficients for magnetic absorption are essentially the same for electrons (or a given nucleus) which possess nearly identical magnetic moments. As a result, the probability of magnetic absorption is proportional to the number of magnetic moments (unpaired spins) and is not dependent on molecular structure.

(3) The difference in magnetic energy between the levels involved in the transition are very small compared to electronic transitions. For example, the absorption of electromagnetic radiation in the visible region of the spectrum corresponds to transitions between energy gaps ranging from ca. 40 kcal/mole (red light) to ca. 80 kcal/mole (violet light). On the other hand, the absorption of magnetic energy in an ESR experiment in an applied field of 10,000 G corresponds to an energy gap of about 10^{-3} kcal/mole, the energy of a microwave photon, whereas the absorption of magnetic energy in a NMR experiment involving protons corresponds to transitions between an energy gap of ca. 10^{-5} kcal/mole. For other nuclei the energy gap is even smaller.

(4) The tiny energy gap between magnetic states, even in a strong applied magnetic field leads to an important practical difference between electronic and magnetic spectroscopy. Whereas in electronic spectroscopy the higher energy state is not significantly populated at room temperature, in magnetic spectroscopy the higher energy state is nearly as populated as the lower energy state. Even in a strong magnetic field, there is only a very small difference between the populations of the two states, with the lower state possessing a small excess of population. For example, in an applied field of 10,000 G the populations of the two electronic spin states differ by only 1 part per 100 and the population of the two proton spin states differ by only ca. 1 part per 10,000. This means that in the more favorable case of the electron spin, if one is dealing with an ensemble of 20,001 spins, 10,001 will be in the lower level and 10,000 will be in the upper level!

(5) There are several important consequences of the small energy gap between magnetic levels. The first has to do with the effect on a small energy gap on the rate of spontaneous emission. According to classical theory of spontaneous emission, the rate of such emission is proportional to ν^3. Now, since the rate of spontaneous emission is of the order ot 10^8 s^{-1} for electronic transitions occurring for energies of the order of 20,000 cm^{-1}, the rate of spontaneous radiation is expected to be ca. $(20,000)^3$ or 8×10^{12} times less than emission in the microwave region! In other words the rate of spontaneous emission is of the order of 10^{-4} s^{-1} from one magnetic level to another. This rate is much slower than that for radiationless interconversion of the magnetic states, so that no spontaneous emission is generally observable for transitions between magnetic states. **This means that practically speaking, magnetic spectroscopy has no analog to electronic emission spectroscopy.**

The second important consequence of the small energy gap is indirect and is associated with the nearly equal populations of the two magnetic states and the very slow rate of relaxation of the upper level by radiative or radiationless mechanisms. This consequence is the tendency of the populations of the upper and lower levels to balance exactly after a certain amount of absorption has occurred, i.e., the small excess population of the lower lever is transferred to the upper level by the absorbed photons. When the population of the upper and lower levels are equal, the magnetic system is said to be "saturated" with respect to the absorption of photons. The term means that no **net** absorption of photons will occur because the probability of a photon converting an α spin to a β spin is just as probable as the conversion of a β spin to an α spin. As a result, for each photon that is absorbed to cause a β to α transition, an equally probable stimulated α to β transition occurs so that there is no net absorption of photons. **This means that magnetic absorption spectroscopy is an inherently insensitive technique for measurements at room temperature, because the "effective" transitions leading to the net absorption of photons is proportional to the excess population of spins, which is very small.**

(6) In contrast to electronic spectroscopy, for which the separation of the energy levels do not depend on the strength of the applied field, in magnetic spectroscopy the separation of the energy levels depends directly on the strength of the magnetic field.

Information Avalailable from Magnetic Resonance Spectra

NMR and ESR spectroscopy both provide analogous structural and dynamic information which can be extracted by analysis of the following experimentally observable parameters:

(1) The frequency, ω_i, of the magnetic resonance signal;
(2) The structure of the signal due to an individual spin (or group of equivalent spins);
(3) The shape of the signals;
(4) The intensity of the signals.

We now consider each of these briefly.

The Frequency of an Observed ESR or NMR Signal

Each ESR or NMR signal corresponds to a radiative transition between two magnetic energy levels when the resonance condition is achieved. Thus, for the simplest case of a two level system (Figure 23) each transition can be considered in terms of eq. 23:

$$\Delta E = h\nu = \backslash\omega = E_\alpha - E_\beta \qquad (23)$$

The energies E_α and E_β are directly related to the total magnetic field the spins experience and the magnetic moment of the spin. The electron spin being observed in an ESR experiment is always part of a molecule or radical so that it experiences not only the applied field, H_0, but also any other fields arising from magnetic moments that are nearby and interact with the electron spin. Thus, the actual magnetic field at the spin, H_Z, is always a composite of the **exteranl** applied laboratory magnetic field, H_0, and the sum of **internal** fields, $\Sigma\mathbf{H_i}$. The important internal fields are commonly of two types: (1) those due electronic orbital circulations induced by the applied field, H_i and (2) those due to internal field due to the magnetic moments of other spins. In more familiar NMR spectroscopy the first internal field is termed the shielding constant, σ, and leads to the chemical shift, δ, which causes nuclear spins in different chemical environments to undergo resonance at different frequencies (in the presence of a fixed value of an applied laboratory field). In NMR spectroscopy, the second internal field is associated with a spin-spin coupling constant. It is assumed that the reader is familiar with these NMR parameters, so that an analogy can be made with the corresponding ESR parameters.

The basic principles of ESR are as follows. An electron has a magnetic moment $\boldsymbol{\mu}_S = g_e\gamma_e\mathbf{S}$; and in a magnetic field along the z axis (the direction of the magnetic field form south to north pole) the energies of the moment are restricted to two values, of $g_e\boldsymbol{\mu}_e\mathbf{H}S_z$ where $S_z = 1/2$ and $-1/2$. Thus, the gap between the two energy levels is exactly \, the angular momentum carried by a photon. If the photon possesses the correct energy and frequency, all of the conditions for a transition are in effect. Since $\Delta E = \backslash\omega$, when ω is the same as the Larmor frequency, absorption can occur if the photon provides the correct torque to twist it from an α spin to a β spin or *vice versa*, as shown in Figure 23. Experimentally, either the frequency, ν or the magnetic field strength, H_0 is varied until the resonance condition is met (eq. 24). We shall consider the variation of ν because of the close analogy with electronic spectroscopy and because the relationship between the energy gap for the transition and the frequency is direct.

$$\Delta E = h\nu = E_\alpha - E_\beta = g_e\boldsymbol{\mu}\mathbf{H}_0 = \backslash\omega \qquad (24)$$

This is the situation for the ESr of a "free electron". In actual experimental systems invovling triplets and radicals, the magnetic currents resulting form orbital circulations induced by the applied field lead to an internal field H_i at an electron spin, just as is the case for a nuclear spin, so that the eq. 24 must be modified to take H_i into account. By convetion, this effect is incorporated in the g-factor as a term that causes a deviation from the g-factor of the free electron (eq. 25), i.e., in the same way that the chemical shift in NMR is defined as the field corresponding to a term σH_0, in ESR, the deviation is considered to be due to a term g_iH_0.

$$\Delta E = h\nu = \backslash\omega = E_\alpha - E_\beta = g\mu_eH_0 = (g_e + g_i)\mu_eH_0 \qquad (25)$$

Experimentally, since both ν and H_0 can be measured precisely and μ_e is known with precision, g can be extracted with high precision from experimental data.

The Relationship of the g Factor to Molecular Structure: the Spin Orbit Connection

As mentioned above, the g-value in ESR serves a role analogous to the shielding constant, σ, in NMR. Both measure the magnitude of electric currents induced in the electron coulds of a molecule by an applied magnetic field and the extent of the coupling of these currents to a spin magnetic moment. Since the chemical shift provides information about the chemical environment in the vicinity of nuclear spins, we expect the g factor to provide information about the chemical environment of electron spins.

What is the relationship between the g factor for electron spin and molecular structure? The experimental value of the g factor for an electron spin embedded in a molecule is slightly different from that for a free electron (g_e = 2.003). The reason for the difference is that the spin in the molecule experiences magnetic fields due to its environment which effectively add or subtract from the magnetic moment due to the electron spin. For example, an electron, in executing an orbital motion, generates a magnetic moment that can couple with the magnetic moment due to the electron spin, a process termed spin-orbit coupling. We can imagine that the electron "picks up" or "loses" some spin angular momentum as a result of spin-orbit coupling. Thus, the experimental value of g will deviate from the value for the free electron.

The value of g_i (Eq. 25) in a molecular environment is related to the ease with which the applied field, H_0, can "stir up" electric currents that generate magnetic fields which interact with the electron spin. The most important source of such currents is due to the orbital motion of the electron whose spin is being affected. This is reasonable because the "stirring" is related to the ability of the orbital motion to generate angular momentum and therefore a magnetic moment. This is easiest for an electron when it is in an atom, since in an atom the circular motion required for the generation of angular momentum can be readily achieved.

As an example, consider a hydrogen atom (Figure 24) possessing an electron in a 2 p orbital (an electron in a 1s orbital does not possess any angular momentum). We imagine that the 2 p electron can readily move in a circular manner about the nucleus by jumping from a 2 p_x to a 2 p_y orbital. This motion generates angular momentum along the z axis. Application of an external field along the z axis will cause the electron to "jump" from the p_y orbital to the p_x orbital and this motion will produce an induced angular momentum (Figure 13) which, in turn, can couple to the spin through the inherent spin orbit coupling of the system and cause the observed value of g to deviate from the value of g_e.

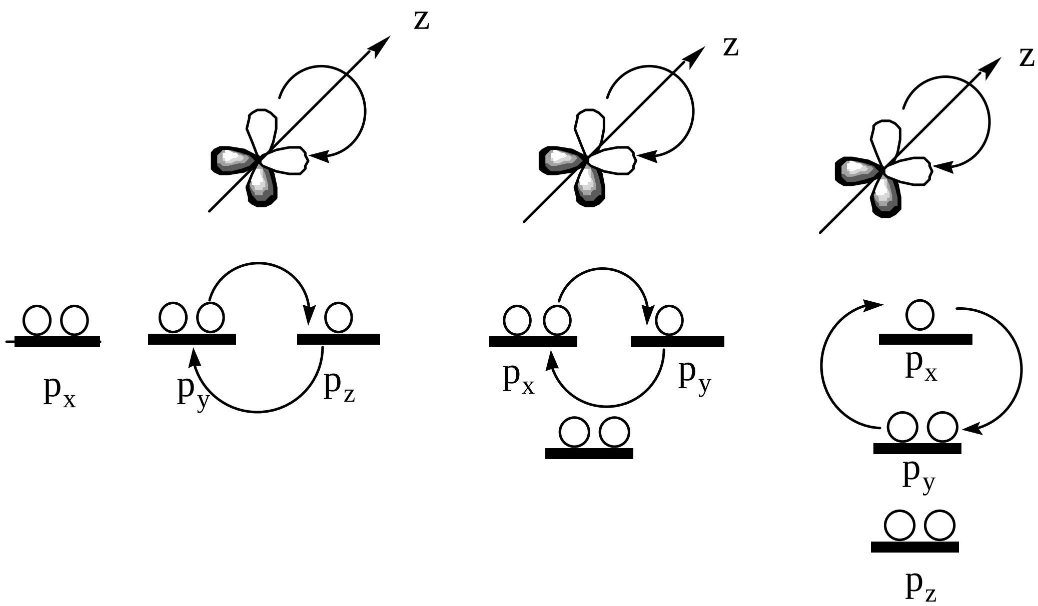


Figure 24. Spin orbit coupling is strongest in organic molecules when jumps between p orbitals can occur on a single atomic center and between a degenerate p orbital. Of the situations shown, the one on the right has poor spin orbit coupling and the ones on the left have good spin orbit coupling.

The strength of the magnetic fields generated by orbital motion is proportional to the magnitude of the spin-orbit coupling constant ζ (see discussion in Chapter XX), which is related to the nuclear charge. In addition, the ability of the electron to make circular orbits is inversely proportional to the energy gap, Δ, between the orbitals involved in the process. Hence the g factor is expected to differ from the value of g_e by an amount proportional to ζ/Δ (eq. 26).

$$g\,(\text{measured}) = g_e\,(\text{free electron}) - \alpha\zeta/\Delta E \tag{26}$$

The extent of the deviation of the g factor from g_e can be understood readily in terms of eq. 26. The energy term in the denominator is typical of the results of perturbation theory and reflects the extent to which an applied field can mix in excited states to provide pathways through the molecule for electrons to acquire orbital angular momentum. This induced momentum is then transmitted to the electron spin as an effective magnetic field via the spin orbit coupling, which is proportional to ζ. As the energy separation decreases, the ability of a given field strength to induce currents increases and so the measured g deviates more strongly from g_e. On the other hand, as the spin orbit coupling constant increases, the spin is subjected to a more effective field and the ability to induce fields is also enhanced by the stronger coupling of the spin to the induced fields through the spin orbit interactions.

For organic molecules possessing only H, C, O and N atoms, the value of ζ is generally small. Furthermore, most organic molecules possess a large value of Δ, so that the value of g_i is expected to be small in general for organic molecules possessing an odd electron. For carbon centered radicals, the value of g is close to that for a free electron.

Whether the deviation is to larger values of g or smaller values of g depends on factors such as the sign of the spin orbit coupling constant, but for most organic radicals the measured value of g is in the range 2.010 to 1.990, compared to the value for g_e which is 2.003. Although these differences are small, they can be measured with high accuracy and are excellent experimental parameters for the structure of molecules and radicals possessing an ESR spectrum.

Fine Structure and Hyperfine Structure of Magentic Resonance Spectra.

Although the internal magnetic fields due to orbital circulations modify the frequency at which an electron spin undergoes resonance in a given magnetic field, this factor does not increase the number of magnetic enegy levels, i.e., the g factor modifies the energy gaps between levels and therefore the frequencies of the transitions (eq. 23), but does not change the number of levels. As we have seen in section 7, the interaction of an electron spin with another electron spin or with a nuclear spin does increase the number of energy levels. These new levels lead to new transitions that are said to cause a "splitting" relative to the uncoupled situation. In the case of electron-electron spin couplings, the splittings are termed "fine structure" of the spectrum and in the case of electron-nuclear spin couplind, the splittings are termed "hyperfine structure". Both fine and hyperfine couplings are characterized by parameters, the fine coupling constant and the hyperfine coupling constant, which can be related to molecular structure. These relationships will be discussed in more detail below when examples of ESR spectra are given for a case history example.

The Shape of the ESR Signal.

As in NMR spectroscopy, the shape of the signal due to a single transition provides information on the rate of the radiationless transitions involving the levels undergoing the transition. The shorter the lifetime of the level, the broader the signal. If the total spin remains the same during the radiationless transition, we are dealing with a magnetic **internal conversion**. These conversions are characterized by relaxation of the spin system along the z axis (with a characteristic time, T_1) and relaxation of the spin in the x, y plane (with a characteristic time, T_2). If the total spin changes during the radiationless transition, we are dealing with a magnetic **intersystem crossing**, which can also be characterized by characteristic times, T_1 and T_2 .

The Intensity of the Magnetic Resonance Signal. Boltzmann Factors and Spin Polarization.

The intensity of a mangnetic resonance signal due to a certain electron spin might be expected to depend on the number of these spins in the sample and the number of photons bathing the spins. This would be true if all of the spins were in one level and none in the other. However, consider the situation for a sample containing "free electrons" for which there are an equal number of spins in the α state and in the β state. According to Einstein's principle of stimulated absorption and emission, a beam of photons (which is not circularly polarized) has an equal probabililty of striking an α spin and stimulting it to emit a photon and form a β spin as it does of striking a β spin and stimulating it to absorb the photon and form the α state. In this extreme case, there would be **no absorption not matter how many spins were in the system!** In order to obtain measurable absorption, there must be an excess of spins in one of the levels.

Thus, in an an actual magnetic resonance experiment, we must consider the fact that we are dealing with a net absorption from only a tiny fraction of the total number of spins in the system. At any temperature, there exists an equilibrium distribution of spins in the upper and lower magnetic states. The specific equilibrium distribution is call the Boltzmann population and its value depends on the temperature and the energy gap according to eq. 27.

$$N_\alpha / N_\beta = \exp(\Delta E / kT) \qquad (27\ )$$

We now view the experimental form of an ESR spectrum in terms of the Boltzmann distribution. When photons corresponding to the frequency for which $\Delta E = h\nu$ interact with the Boltzmann population of spins, some α ∅ β and some β ∅ α transitions will occur. However, since there are more β spins present when the system is at the Boltzmann distribution, there will be a net absorption at the magnetic field which causes the resonance condition to be achieved, i.e., the value of H_0 for which $\Delta E = g\mu_e H_0 = h\nu$. The same ideas pertain for a proton NMR spectrum, except that the energy gap is much smaller and that the α state is lower in energy than the β state.

In certain cases the rate of relaxation between spin levels is relatively slow and the Boltzmann distribution is not achieved during the time scale of the experiment. In such cases non-Boltzmann or **polarized distribution** of spin levels occur. When spin polarization occurs (we'll discuss mechanisms by which it may occur in later sections), the intensity of the observed ESR or NMR spectra bear no relationship to the spectrum produced by a Boltzmann distribution. Figure 25 displays schematically a comparison of a Boltzmann distribution and two extreme cases of polarization. Near ambient temperatures, there will be a very slight excess of spins in the lower level for a Boltzmann (Figure 24, left). Since the probability of transitions is related to the difference in populations, the magnetic resonance signe will be relatively weak. If, by some mechanism, a large excess of spins are in the lower level during the time of measurement, the observed signal will be a much stronger absorption than expected based on the Boltzmann distribution. If, by some mechanism, a large excess of spins are in the upper level during the time of measurment, the observed signal will be a **net emission**!

We shall see later on that in many photochemical reactions the primary radical intermediates and the molecules formed from reactions with these radicals are formed with electron spins and nuclear spins that are not at the Boltzmann distribution. This means that there may be more spins in the lower level than there are for the Boltzmann distribution at the temperature of the reactions or **even that there are more spins in the upper level than there are for the Boltzmann distribution at the temperature of the reaction.** The phenomena of generating electron spin polarized radicals is termed CIDEP (chemically induced dynamic electron polarization) and the phenomena of generating nuclear spin polarized molecules is termed CIDNP (chemically induced dynamic nuclear polarization).

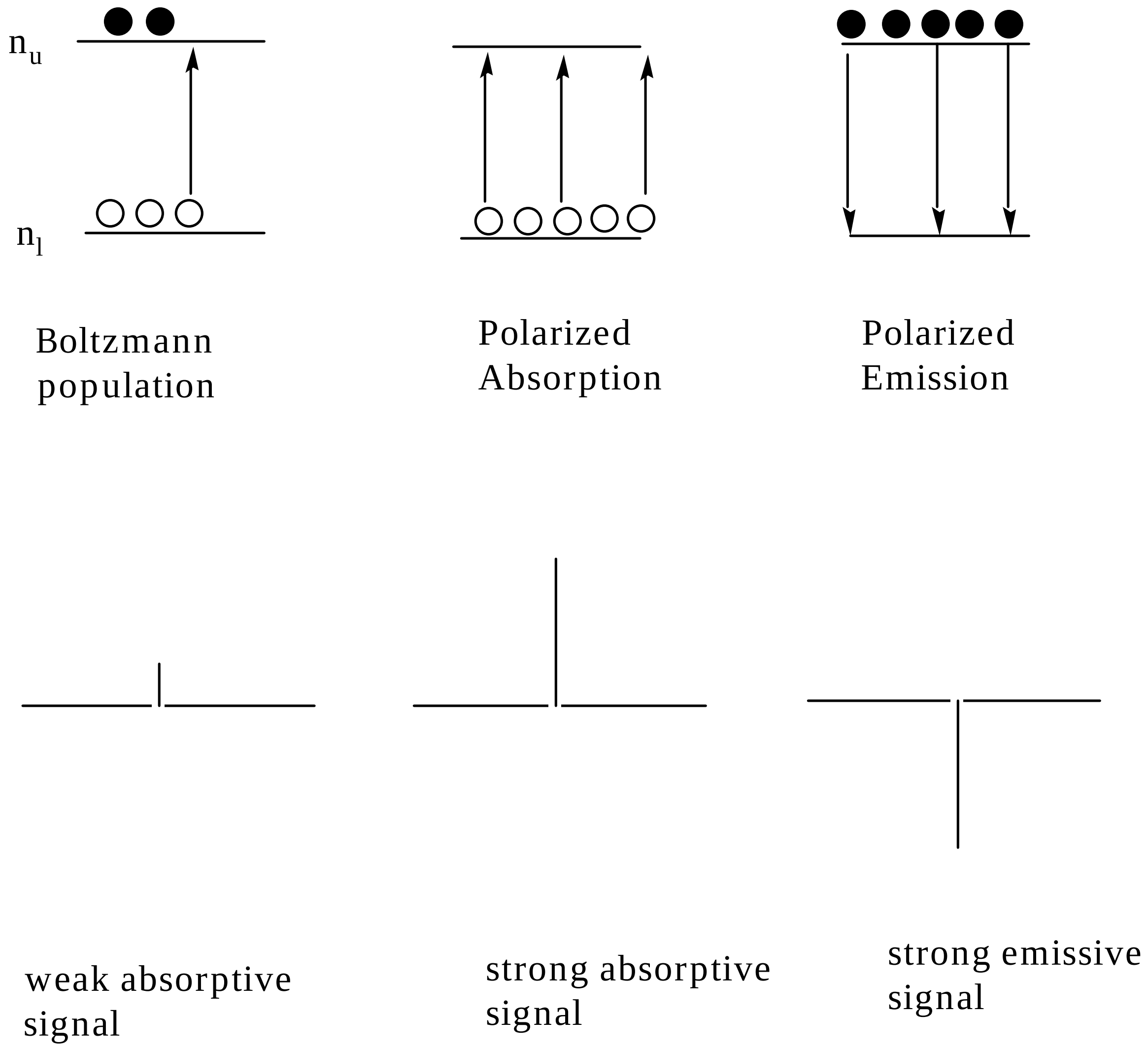


Figure 25. Schematic representation of spin polarization in terms of an energy diagram and in terms of an experimental signal