

12. The Molecular Intersystem Crossing Step $S_1 \rightarrow T_1$. Zero Field Splitting of the Triplet Levels and Spin Polarization of the Triplet State.

In Section 7 it was pointed out that under certain circumstances the three triplet sublevels may not be degenerate at zero field. This will happen when the dipolar interaction between the two electron spins is significant (strong orbital overlap) and does not average to zero (slow molecular motions). Let us now consider how the dipolar interaction modifies the energy diagram for a molecular triplet at zero field and how this modified diagram transforms in high field.

The ESR of Molecular Triplets. The Dipolar Interaction and Zero Field Splitting of the Triplet

We noted numerous times in this chapter that in the absence of magnetic interactions, the magnetic sublevels of a given state of spin angular momentum will be degenerate. We might conclude, therefore, that the three triplet sublevels of a molecular triplet, T_1 , of an organic molecule such as a ketone, ACOB, will be degenerate in the absence of an applied field. This conclusion, however, is incorrect because the molecular triplets of organic molecules experience magnetic interactions that cause the triplet sublevels to possess different energies, even in the absence of an applied field. These energy splittings are due to anisotropic dipolar magnetic **interactions** of the unpaired electrons due to the overlap of the orbitals containing the odd electrons and is termed the zero field splitting (ZFS) of triplet states. The source of the dipolar interactions are typically due to one of two types of couplings, either spin orbit coupling or spin spin coupling.

What is the effect of dipolar interactions on the energy level diagram of the triplet? We have seen in section 7 that dipolar interactions between spins average out to zero when the spins undergo rapid isotropic molecular motion about all possible axes. This does not happen for molecular triplets due to the overlap of the orbitals containing the unpaired spins. Because the overlap causes a strong electron exchange, there is a very strong tendency for the two triplet spins to be quantized or fixed relative to each other as a result of the Pauli Principle (requiring the electrons and therefore their spins to be correlated). This correlation can be represented by an axis, which in turn can be related to a molecular axis as shown in Figure 19. We say that the axis tracking the triplet spin follows the molecular axes as the molecule tumbles in solution. This coupling of the molecular axis and the spin axis opposes averaging of the dipolar interaction, which remains finite in the absence of an applied field.

A second important feature of the coupling of the spin to the molecular axes appears when a magnetic field is applied. For technical reasons, ESR spectra are obtained with magnetic fields of the order of 10,000 G or less. The dipolar coupling of many organic triplets is of the order of this field strength, so that the "strong field" limit is not met and the mutual interaction of the two electron spins is of the same order as the interaction of the applied field, H_z . The result is that the ESR spectrum of molecular triplets requires a higher level of theory for interpretation. For example, since the spins interact with each other and the external applied field, the magnetic moment due to the spins does not have a fixed value along the H_z direction. This means that the description of the three triplet sublevels in terms of a "good quantum number" $M_s = +1, 0$ and -1 is not valid in general, but depends on the specific orientation of a molecule with respect to H_z . There are, however, three limiting cases for which the quantization in terms of M_s is still valid or a reasonable approximation: (1) in the case of a triplet molecule possessing a cylindrical axis of symmetry in the vicinity of orbital overlap of the two spins when the direction of H_z is along the cylindrical axis; (2) in the case of a triplet for which there is a large separation of the spins or a small orbital overlap; and (3) in the case of a triplet in an applied field that is much larger than the dipolar interaction.

In summary, in considering experimental ESR spectra of molecular triplets, we must always keep in mind the interaction of the magnetic moment of the molecule as a whole with the field, H_0 and the dipolar interactions of the two spins. The magnetic interaction energy between two electron spins is given the symbol D and is termed the zero field splitting parameter. The reason for this term is that at zero field the dipolar interactions between electron spins still persists, so there are three magnetic energy levels even in the absence of any applied field. We now present a qualitative discussion of how D is extracted from ESR spectra.

Extraction of the Dipolar Interaction from Zero Field Splittings.

At zero field the difference in triplet levels depends on the parameter D , which may be considered as being analogous to a coupling constant such as the exchange interaction, which splits the energy of S and T states, but does not mix them. We can relate D to the vector model by noting that at zero field, the total magnetic moment due to the spin is quantized and therefore may lie in any one of three possible axes of a molecular structure. The three triplet sublevels in the molecular frame are labeled by the axis (or plane) on which they lie, i.e., T_x , T_y and T_z . For the case in which the molecular system has approximate cylindrical symmetry, the energies of the T_x and T_y states are equal. The z axis at zero field is defined as the molecular axis which has zero magnetic energy, i.e., when the

molecule is placed in a magnetic field there would be no magnetic energy along this axis. For ketones, which will be discussed in the following sections, spin orbit coupling dominates the internal magnetic field on the molecular frame and it is experimentally found that for ketones T_z possesses a higher magnetic energy than T_x or T_y as shown in Figure 28. The energy gap between T_z and T_x (or T_y) is effectively equal to the zero field splitting, D .

Thus, at zero field it is possible to measure D by simply observing the transition between the T_x (or T_y) state and the T_z state. Experimentally this is done by measuring some non-magnetic property of the triplet (typically optical absorption or emission) and then applying electromagnetic radiation of varying frequency, ν . When the correct resonance frequency for which $\Delta E = D = h\nu$ occurs, transitions between the triplet sublevels occurs and detected by a change in the non-magnetic property. From the definition of the T_z axis in the molecular frame, it is expected that the application of a magnetic field will not change the energy of the T_z state. Thus, at very high fields, we expect that T_z will transform into T_0 , as shown in Figure 28.

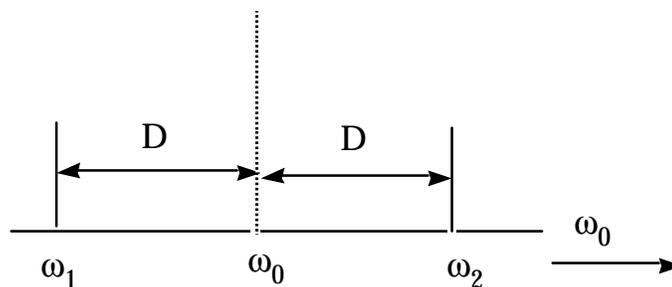
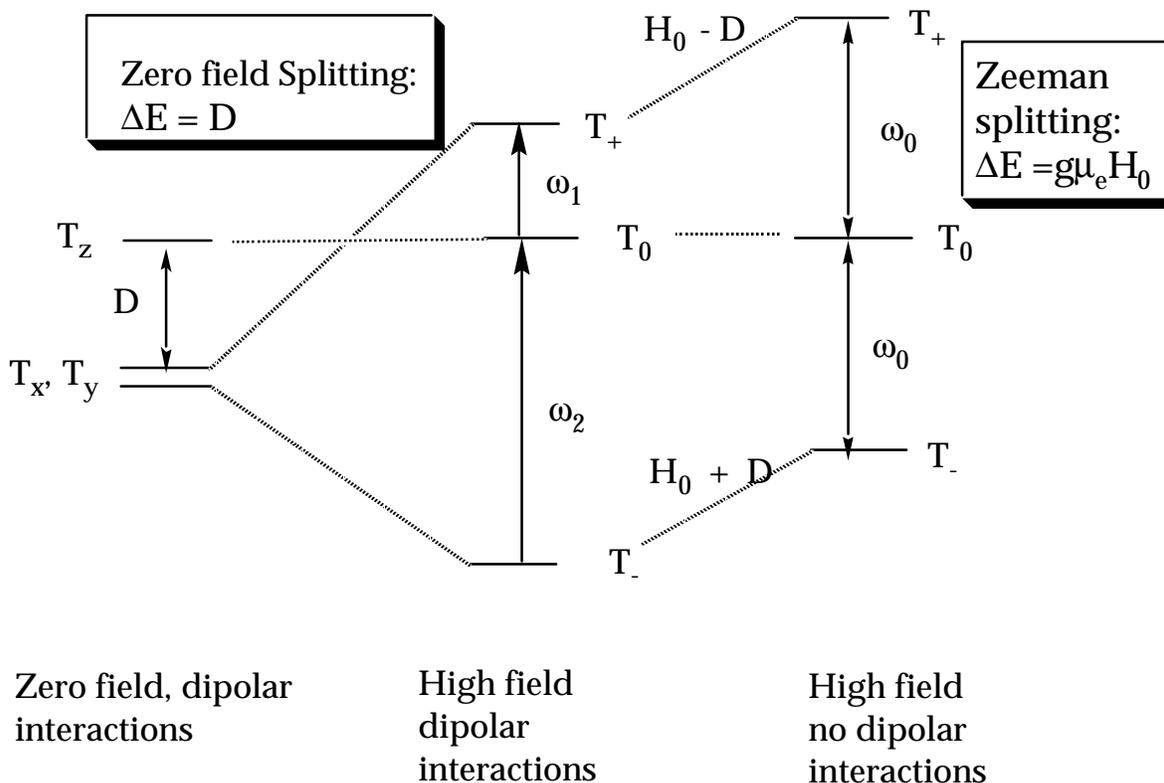


Figure 28. Energy diagram for a molecular triplet at zero and high fields: (a) Zero field in the presence of dipolar interaction; (b) high field in the absence of dipolar interactions; (c) high field in the presence of dipolar interactions.

It is also possible to measure D through magnetic resonance spectroscopy at high field. As mentioned above, in the special case for which the applied field is along the axis of T_z , the interaction energy between the two spins is exactly equal to D . Thus, if we could measure the interaction energy in this special case, we can experimentally determine the value of D from magnetic resonance spectroscopy. (A second quantity, E , is employed to measure the magnetic distinction in the x,y planes. For most organic molecules this quantity is small relative to D and is therefore not considered in this qualitative discussion.)

To obtain an understanding of how D related to an experimental ESR spectrum, let us consider the influence of D on the magnetic energy diagram at zero field and in the presence of an applied field. Figure 28 shows the three triplet sublevels (a) at zero field in the presence of dipolar interaction, D ; (b) at high field in the absence of dipolar interactions; and (c) at high field in the presence of a dipolar interactions of strength, D . The parameter D , as for many magnetic parameters, may be positive or negative (which must usually be determined by experiment). The sign of D determines whether the T_0 or the T_{\pm} level are raised or lowered in energy in the presence of a high magnetic field. In Figure 28, it is assumed that the sign of D is negative, causing (relative to the case for no dipolar spin-spin interactions) a lowering of the energy of both T_- and T_+ , while the T_0 level is unaffected. The corresponding ESR spectrum for this special case consists of two allowed transitions: (T_-/T_0 and T_0/T_+), and the ESR consists of two lines separated by $2D$. Thus, from measurement of the ESR of molecules oriented along the H_z axis, the value of D may be obtained from the ESR of the triplet. In the absence of dipolar interactions, the energy gaps for the T_-/T_0 and T_0/T_+ transitions are identical so that the ESR would consist of a single line (of twice the intensity, due to two overlapping transitions).

Experimental Complications in the Measurement of D

The ESR of triplet states is complicated by the enormous magnetic field that the two unpaired electrons exert on each other due to magnetic dipole-dipole interactions. This field varies widely throughout the population of triplet molecules because it is highly orientation dependent, i.e., it is anisotropic (Figure 19). The situation is further complicated because the strength of the anisotropic magnetic field is often comparable to the magnetic field at which ESR measurements are commonly made, so that the external field does not completely govern the direction of the spins. The net result is that the spectrum over all of the population of triplets is broad and the sensitivity of the measurement is low.

In principle, one way to remove these difficulties is to take the ESR of the triplet state of a crystal. In a crystal all of the triplet molecules can be oriented in the same way in the magnetic field so that the angles between the molecular axes and the external magnetic field directions will be the same for all of the molecules. This will eliminate the line broadening due to anisotropy. In this interesting case the ESR spectrum depends on the orientation of the crystal in the magnetic field! For example, the rotation of a naphthalene crystal in a magnetic field causes a variation of a given transition as much as 2000 G. The entire ESR spectrum of a typical organic radical spans only ca. 100 G or less. Therefore, in a

random sample of naphthalene triplets, the spectrum would be distributed over ca. 2000 G and the intensity at any given field strength would be quite weak.

Since a typical sample in an ESR spectrometer consists of molecules in a wide range of orientations relative to the applied field, special considerations must be taken to extract D from experimental spectra. Furthermore, rapid rotation of molecules in solution adds a further complication of line broadening due to rotational relaxation. As a result, the D parameters are extracted from samples that are rigidly trapped in a solid, typically in a solid solution or glass at low temperature.

The Distance of Separation of Electron Spins From the Dipolar Interactions.

Because the dipolar interaction depends on orbital overlap, which in turn represents the average distance separating electrons, the zero field splitting parameter, D, (which provides a measure of the dipolar interaction) also provides a means of determining electron distributions and assigning orbital configurations of the triplet state. The effective internal magnetic field, \mathbf{H}_i , that one electron expresses on the second electron is given approximately by Eq. 28 (which should be compared to Eq. 19), where R_{12}^3 is the average separation of the electron spins and μ_e is the magnetic moment of an electron spin.

$$\mathbf{H}_i = (\mu_e/R^3)(3\cos^2 - 1) \quad (28)$$

Since the magnitude of D is directly related to \mathbf{H}_i , it is expected that the magnitude of D is proportional to R_{12}^3 . However, the value of \mathbf{H}_i depends on the orientation of the spins relative to the applied field because of the $3\cos^2 - 1$ term. For the limiting cases of cylindrical symmetry with the applied field direction parallel to the z direction in the molecular frame, the distance of separation along the magnetic field axis is given by eq. 29. For a separation of spin of 1 Å, the value of D is 1 cm⁻¹, which corresponds to a magnetic field of ca 10,000 G.

$$D (\text{cm}^{-1}) \sim 10^{-24}R_{12}^3 (\text{Å}) \quad (29)$$

For the specific example of a ketone triplet (spectrum taken along the z-axis), the ESR will consist of two lines with separation of 2D. For n, π^* triplets the value of D is typically 0.3 cm⁻¹, which corresponds to a dipolar magnetic field of ca. 3000 G. Indeed, this is the value of the magnetic field of typical ESR spectrometers.

Intersystem Crossing Step at Zero Field.

At zero field, the spin of a triplet state must be quantized in one of the three molecular axis of a molecular structure. Since spin orbit coupling is typically the dominant mechanism for ISC of ketones, it stands to reason that the $S_1 \rightarrow T_1$ ISC will be specific for the molecular axis possessing the highest degree of spin orbit coupling. In other words, there will be spin orbit forces operating on each of the orbitally unpaired electrons of S_1 and these forces will have a certain symmetry with respect to the molecular axes corresponding to the three molecular planes. Thus, the $S_1 \rightarrow T_1$ ISC will produce a triplet which is **polarized**, i.e., the ISC process is expected to produce predominantly in one of the three triplet sublevels, T_x , T_y or T_z .

As mentioned above, in the case of ketones, the energetic ordering of the typical zero field levels, determined by dipolar interaction and spin orbit coupling, is typically $T_z > T_x \sim T_y$, i.e., the T_z state, whose axis is along the C=O bond. Since the T_z level is strongly coupled to S_1 by spin orbit coupling, the ISC occurs via a selective $S_1 \rightarrow T_z$ process. At temperatures near 4° K (liquid helium temperature), interconversion of the triplet sublevels is relatively slow, so that the T_z level may be examined with little interference from the unpopulated T_x and T_y states. For example, the phosphorescence of the T_z level will be different from that of the T_x and T_y levels because phosphorescence depends on spin orbit coupling and as we have seen above, the effectiveness of spin orbit coupling depends on the coupling of the spin to the molecular axis!

Intersystem Crossing Step at High Field.

An interesting issue is how the polarized T_z level produced in the molecular frame at zero field might be transformed into one of the T_+ , T_0 or T_- level in the presence of a strong applied field. In Figure 29 we note that there is a surface crossing between T_z and T_x as the magnetic field strength is increased. Thus, there are two pathways for the representative point starting from T_z : (1) T_z possesses a "natural" correlation with T_0 at low field and in the absence of mixing or rapid passage through the crossing region, the **diabatic** process $T_z \rightarrow T_0$ will occur; (2) if mixing is strong or passage through the mixing region is slow, the **adiabatic** process $T_z \rightarrow T_0$ will occur. Whether the adiabatic correlation will occur and how such a correlation can be established experimentally by direct magnetic resonance measurements (by measuring the temperature dependence of the ESR signal) or by monitoring the polarization of the radicals produced by primary photochemical process will be seen. We shall consider below the more photochemically interesting method of determining the adiabatic or diabatic pathway for ISC by observing the spin polarization of the radicals produced in a

primary photochemical step. To do this we must move from the "spectroscopic region of the energy surface" corresponding to vertical electronic transitions of the representative point to the "chemical regions of the energy surface" corresponding to bond breaking. Moving from the spectroscopic region to the chemical regions of the energy surface will be the topic of the following sections.

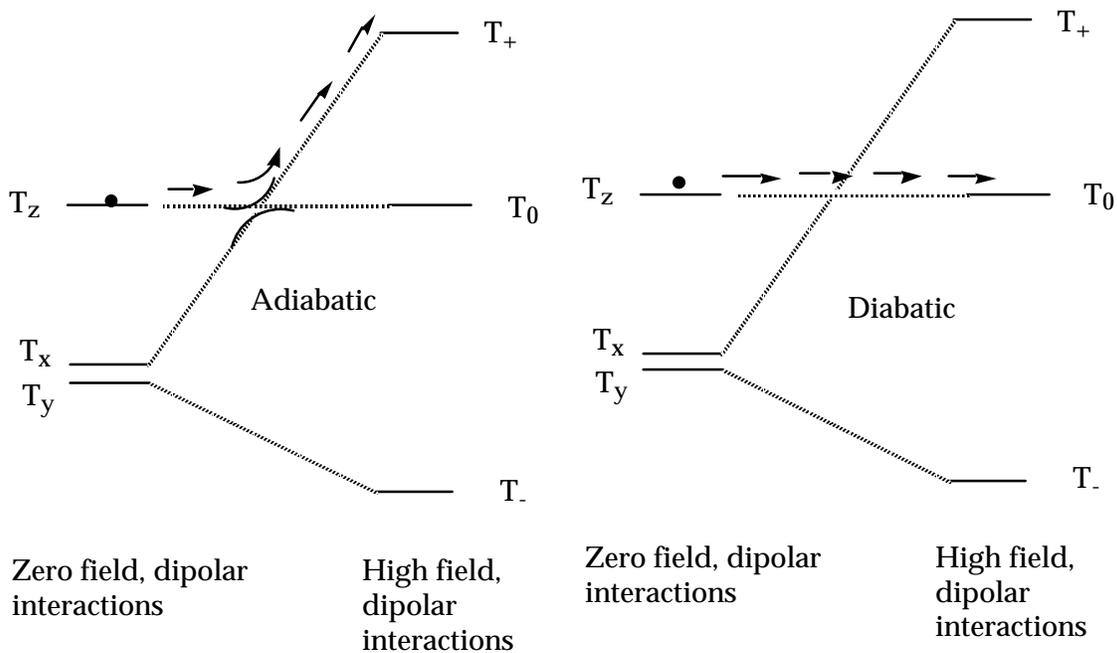


Figure 29. Adiabatic (left) and diabatic (right) trajectories of a representative point starting from the T_z state.