Electron Paramagnetic Resonance Spectroscopy

2.4 – EPR spectrum for a centre which interacts with several nuclei in the isotropic regime

2.4.1 – Hyperfine interactions with several equivalent nuclei

Nuclei are said to be *equivalent* from the point of view of hyperfine interactions when they have the same spin and they are characterised by the same hyperfine constant A_{iso}.

For example, this is the case with an organic radical for which the unpaired electron interacts in the same way with three protons from a CH_3 group, or for a transition ion complex such as $Cu(NH_3)_4{}^{2+}$ where the unpaired electron from the Cu^{2+} ion interacts in the same way with the four ^{14}N nuclei from the ligands.

We will first examine the case of a centre of spin S, its unpaired electrons interact with *two equivalent nuclei* of angular momentum $\mathbf{I}_1$ and $\mathbf{I}_2$, with $I_1 = I_2 = I$. Equation [2.6] then becomes:

$$H = g_{iso} \beta B\, S_Z + A_{iso}\, S_Z I_{1Z} + A_{iso}\, S_Z\, I_{2Z}$$

If we denote M_1 and M_2 the respective values of I_{1Z} and I_{2Z}, the possible energy values are given by:

$$E\,(M_S, M_1, M_2) = g_{iso} \beta B\, M_S + A_{iso} M_S\,(M_1 + M_2)$$

The selection rule becomes:

$$\Delta M_S = \pm 1;\ \Delta M_1 = 0;\ \Delta M_2 = 0$$

The transitions allowed from level $E(M_S, M_1, M_2)$ to levels $E(M_S + 1, M_1, M_2)$ and $E(M_S - 1, M_1, M_2)$ have the same energy:

$$\Delta E(M_1, M_2) = g_{iso} \beta B + A_{iso}(M_1 + M_2) \qquad [2.9]$$

For each value of $\Delta E(M_1, M_2)$ there is a corresponding resonance line for which the position can be determined from $\Delta E(M_1, M_2) = h\nu$. Since M_1 and M_2 can take any of the $(2I + 1)$ values $(-I, -I + 1, \dots, I)$, there exist $(2I + 1)^2$ pairs (M_1, M_2). Among these pairs, some produce the same $(M_1 + M_2)$ value, and their lines are added. To see how this looks, it is convenient to represent equation [2.9] on a diagram (figure 2.8). Starting from $g_{iso} \beta B$, we first add the term $A_{iso} M_1$ considering all possible values of M_1, then we add $A_{iso} M_2$ taking all values of M_2 into consideration.

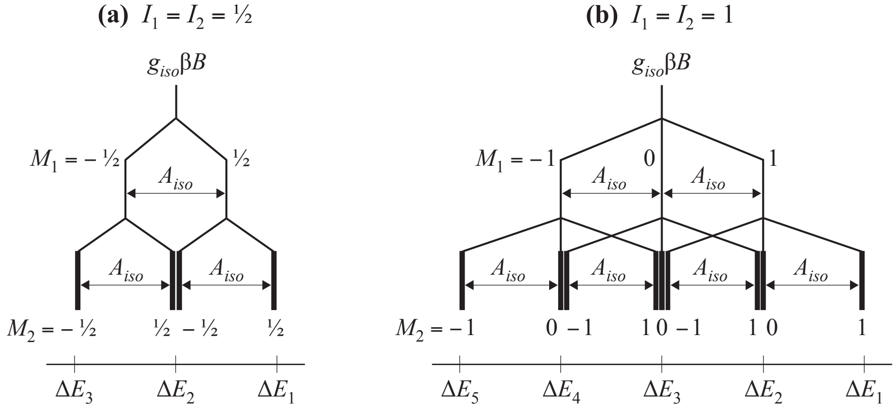

Figure 2.8 – Construction of the quantity $\Delta E(M_1,M_2)$ defined by equation [2.9] for **(a)** $I_1 = I_2 = ½$ and **(b)** $I_1 = I_2 = 1$.

▹ For $I_1 = I_2 = ½$, the 4 pairs (M_1, M_2) give the following ΔE and resonance fields (figure 2.8a):

$$\begin{array}{rrcll} (½, ½): & \Delta E_1 & = & g_{iso}\beta B + A_{iso}\ ; & B_1 = B_0 - A_{iso}/g_{iso}\beta \\ (½, -½), (-½, ½): & \Delta E_2 & = & g_{iso}\beta B\ ; & B_2 = B_0 \\ (-½, -½): & \Delta E_3 & = & g_{iso}\beta B - A_{iso}\ ; & B_3 = B_0 + A_{iso}/g_{iso}\beta \end{array}$$

As ΔE_2 is obtained twice, the intensity of the central line will be doubled (figure 2.9). The *positions* of the 3 lines are the same as in the case of a single nucleus of spin $I = 1$ (figure 2.5), but their *relative intensities* take the proportions (1 : 2 : 1).

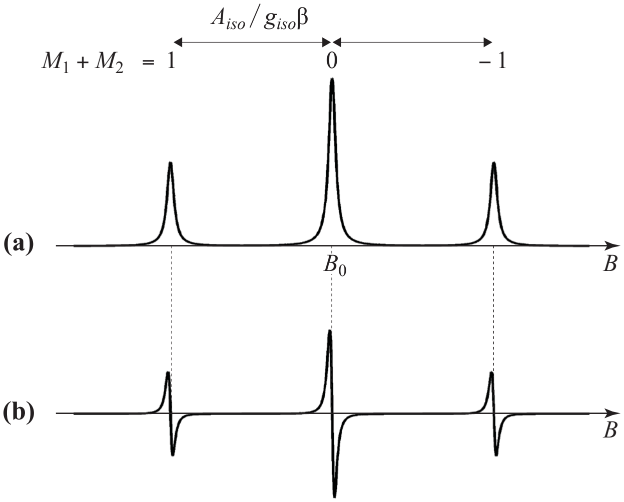

Figure 2.9 – EPR spectrum corresponding to figure 2.8a. **(a)** Absorption signal and **(b)** its derivative.

Figure 2.10 shows the EPR spectrum for a liquid solution of the 2,6-di-*tert*-butyl-4-(4-oxo-4H-chromen-2-yl) phenyloxyl radical, for which the hyperfine structure is produced by interaction with the two meta protons in the phenoxyl group.

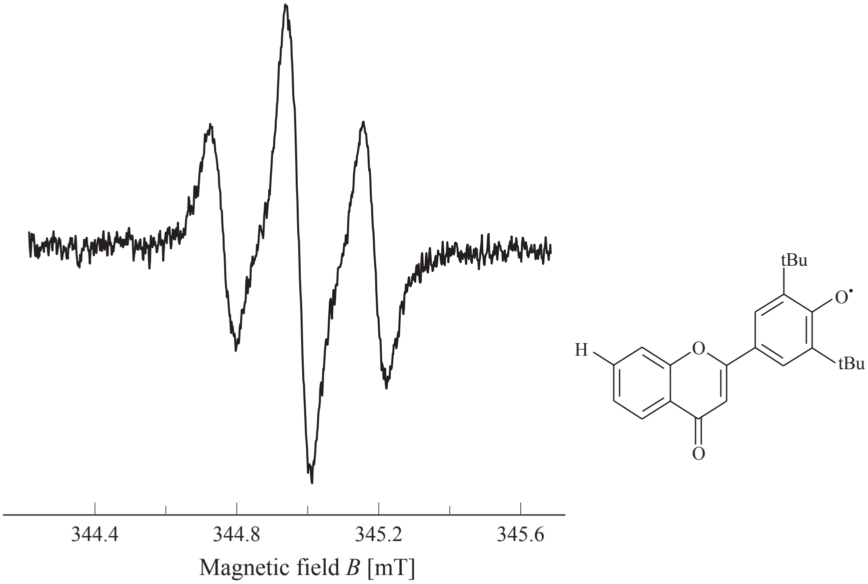

Figure 2.10 – EPR spectrum for the 2,6-di-*tert*-butyl-4-(4-oxo-4H-chromen-2-yl) phenyloxyl radical which has 2 equivalent protons.
Temperature 20 °C. Microwaves: frequency 9.697 GHz, power 4 mW.
Modulation: frequency 100 kHz, peak-to-peak amplitude 0.03 mT.

▹ For $I_1 = I_2 = 1$, we obtain (figure 2.8b):

$$\begin{array}{rcll} \Delta E_1 & = & g_{iso}\beta B + 2A_{iso}\,; & B_1 = B_0 - 2A_{iso}/g_{iso}\beta \\ \Delta E_2 & = & g_{iso}\beta B + A_{iso}\,; & B_2 = B_0 - A_{iso}/g_{iso}\beta \\ \Delta E_3 & = & g_{iso}\beta B\,; & B_3 = B_0 \\ \Delta E_4 & = & g_{iso}\beta B - A_{iso}\,; & B_4 = B_0 + A_{iso}/g_{iso}\beta \\ \Delta E_5 & = & g_{iso}\beta B - 2A_{iso}\,; & B_5 = B_0 + 2A_{iso}/g_{iso}\beta \end{array}$$

The positions of the 5 lines are the same as in the case of a single nucleus of spin $I = 2$, but their relative intensities vary in the proportions (1:2:3:2:1) (figure 2.11).

4.3 – Shape of the spectrum produced by an ensemble of paramagnetic centres in the absence of hyperfine interaction

In this section we consider a sample containing identical molecules characterised by their spin S and their $\tilde{\mathbf{g}}$ matrix, without hyperfine interaction, and we wish to determine the shape of the EPR spectrum for different modes of organisation of the molecules in the sample.

4.3.1 – Variation in g' values with the direction of $\mathbf{B}$

We saw in section 3.3.2 that the interaction between the magnetic moment given by equation [4.1] and a magnetic field **B** produces a pattern of $(2S + 1)$ equidistant energy levels, with splitting:

$$\Delta E = g'\beta B$$

where:

$$g' = [g_x^2\, u_x^2 + g_y^2\, u_y^2 + g_z^2\, u_z^2]^{1/2} \qquad [4.3]$$

The numbers (g_x, g_y, g_z) are the principal values of the $\tilde{\mathbf{g}}$ matrix and (u_x, u_y, u_z) are the components of the unit vector **u** in the direction of **B**, in the system of magnetic axes $\{x, y, z\}$ of the molecule. The “prime” suffix of g' indicates that this number depends on the *direction* of **B** relative to the molecule. Resonance occurs when $\Delta E = h\nu$, where ν is the frequency of the spectrometer. The resonance field is therefore given by:

$$B = h\nu / g'\beta \qquad [4.4]$$

The sample is fixed in the cavity of the spectrometer, but the orientation of the molecules relative to **B** can vary in the sample. Since the EPR spectrum results from superposition of the resonance lines produced by all the molecules, the following questions arise:

- If the sample is such that all the molecules are oriented in the same way, how does the spectrum vary when the sample is rotated in the field?
- If the molecules in the sample are oriented differently relative to the magnetic field, what is the shape of the spectrum?

To answer these questions, we must examine how the resonance field B (equation [4.4]), and consequently the g' value (equation [4.3]), vary as a function of the direction of **B**.

- ▹ We will start with a centre with *cubic symmetry* for which $g_x = g_y = g_z = g$. Equation [4.3] shows that $g' = g$ whatever the direction of **B**. The resonance lines of all the molecules add together to produce a single line at $B = h\nu/g\beta$. The spectrum is therefore reduced to this unique line and it is independent of how the molecules are organised in the sample, and of the orientation of the sample relative to **B**.
- ▹ We then consider a centre with *axial symmetry*. If z is the axis of symmetry, the two principal values g_x and g_y are equal, and are generally written:

$$g_x = g_y = g_\perp\,,\ g_z = g_{//}$$

Equation [4.3] can then be written:

$$g' = [g_\perp^2\,(u_x^2 + u_y^2) + g_{//}^2\,u_z^2]^{1/2}$$

If θ is the angle between the axis z and the vector **u** (figure 4.3a), we have $u_z^2 = \cos^2\theta$ and $u_x^2 + u_y^2 = \sin^2\theta$, and g' can be written:

$$g' = [g_\perp^2 \sin^2\theta + g_{//}^2 \cos^2\theta]^{1/2} \qquad [4.5]$$

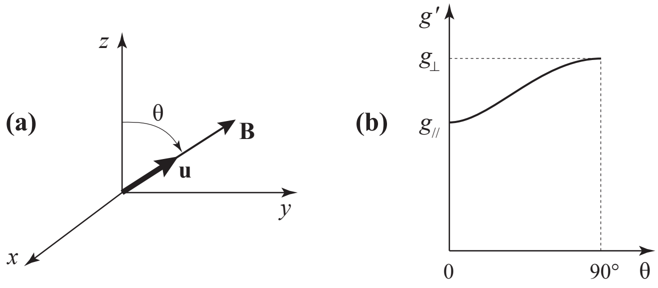

Figure 4.3 – Centre with axial symmetry: **(a)** definition of the angle θ, **(b)** variation of g' as a function of θ for $g_\perp > g_{//}$.

In this case, g' only depends on the angle θ between the molecular axis z and the field **B**. The number g' varies monotonically from $g_{//}$ for $\theta = 0$ (**u** parallel to z) to $g_\perp$ for $\theta = 90°$ (**u** perpendicular to z), which explains the notations $g_{//}$ and $g_\perp$ (figure 4.3b).

- ▹ In the general case where the three numbers (g_x, g_y, g_z) are distinct, g' depends on two parameters, and its variations as a function of the direction of **B** are more difficult to visualise. An idea can be obtained by seeking the directions of **u** which satisfy equation [4.3] for a given value of g'. This problem is dealt with in complement 2 with the help of a simple geometric representation. The principal axes can always be labelled such that:

$$g_x \leq g_y \leq g_z$$

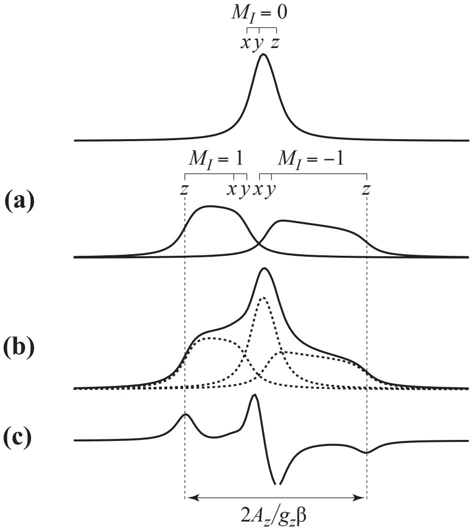

Figure 4.13 – Interpretation of the shape of the X-band spectrum for a frozen solution of a nitroxide radical characterised by $g_x = 2.0089$, $g_y = 2.0064$, $g_z = 2.0027$, $A_x = A_y = 14$ MHz, $A_z = 98$ MHz. **(a)** Shape of the three components from figure 4.12a. For each value of M_I, "stick diagrams" identify the position of the lines for the canonical directions of the field. **(b)** Sum of the three components. **(c)** The spectrum. The lines are assumed to be Lorentzian.

4.5 – How molecular movements affect the spectrum: isotropic and very slow motion regimes

Up to now, we have assumed that the paramagnetic molecules were *frozen* in the sample placed in the field **B**. However, in a crystal, a frozen solution and even more so in a liquid solution, the molecules are in motion. This motion causes their orientation relative to the field to vary, which can alter the shape of the spectrum. Indeed, we have already indicated that the effects of anisotropy *disappear* from the EPR spectrum in the *isotropic regime* when these movements allow the molecules to rapidly explore all the possible orientations relative to the field with an equal probability (section 2.2.3).

4.5.1 – A hypothetical experiment

Consider a paramagnetic molecule of spin S characterised by its $\tilde{\mathbf{g}}$ matrix. This molecule is placed in a magnetic field **B** of variable magnitude, but with a fixed direction perpendicular to the principal axis z. Its Hamiltonian can be written:

5.2.4 – Intensity of the resonance lines and of the spectrum in the presence of hyperfine interactions

When a hyperfine interaction with a nucleus of spin I exists, each of the energy levels E_a and E_b in figure 5.2 splits to give $(2I + 1)$ equidistant levels separated by $A'/2$, the value of which depends on the orientation of the molecule relative to $\mathbf{B}$ (equation [4.11]). Each value of M_I has a corresponding transition of energy (figure 5.5)

$$\Delta E(M_I) \ = \ g'\beta B + A'M_I$$

which gives a line centred at $B_0'(M_I) = B_0' - (A'/g'\beta)M_I$, where $B_0' = h\nu/g'\beta$ (equation [4.12]). To determine the intensity of this line, we will return to the calculation performed in section 5.2.1. Based on the note following equation [5.11], expression [5.12] can be used to determine the transition probability, on the condition that we replace $h\nu$ by $(h\nu - A'M_I)$, i.e., replace B_0' by the field $B_0'(M_I)$. In addition, we saw in section 3.5.2 that the matrix element involved in the transition probability is not modified in the presence of hyperfine interaction. The intensity of the line (M_I) is therefore given by an expression similar to equation [5.16]:

$$I(M_I, \theta, \varphi) = \frac{\pi\beta}{2\hbar}\, g_P(\theta,\varphi) B_1\, n(M_I) \tanh\left(\frac{h\nu}{2k_\mathrm{B}T}\right) \qquad [5.20]$$

where $n(M_I) = n_a(M_I) + n_b(M_I)$ is the sum of the populations of energy levels between which transitions take place (figure 5.5). When the intensities of the $(2I + 1)$ lines for the hyperfine structure are added, the sum $\sum_{M_I=-I}^{I} n(M_I)$ emerges, which is equal to $n = n_a + n_b$ and we find the intensity of the line in the absence of interaction.

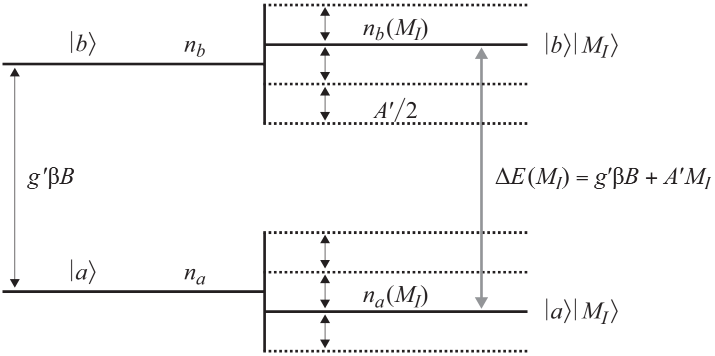

Figure 5.5 – Definition of the $n_a(M_I)$ and $n_b(M_I)$ populations of the energy levels involved in the transition with energy $\Delta E(M_I)$.

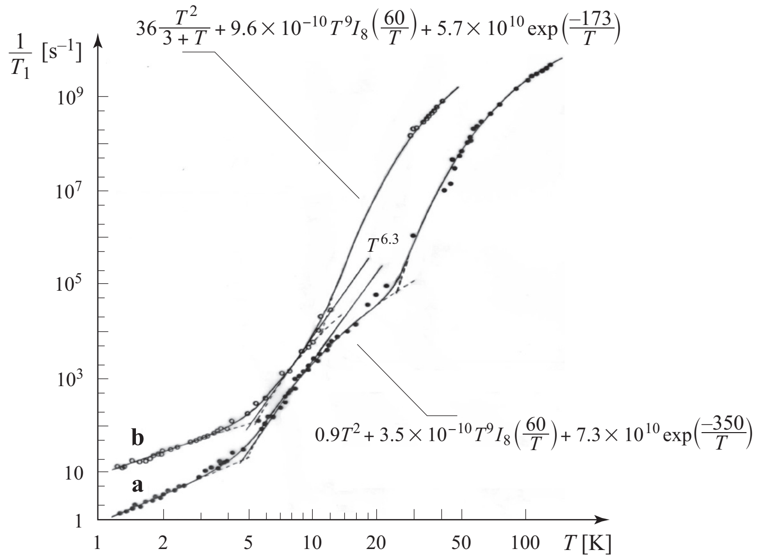

Figure 5.11 – Temperature-dependence of $1/T_1$ for iron-sulfur centres:
(a) $[2Fe-2S]^+$ centre for a protein from the cyanobacterium *Spirulina maxima*.
(b) $[4Fe-4S]^+$ centre for a protein from the bacterium *Bacillus stearothermophilus*.
The $T^{6.3}$ temperature-dependence is that predicted by a "fractal" model [Stapleton *et al.*, 1980].

[Reproduced with permission from: Bertrand P. *et al.*, *Journal of Chemical Physics*, **76**, 4715–4719 © 1969, American Institute of Physics]

5.4.3 – Relaxation phenomena and EPR spectroscopy in practice

In any spectroscopic technique, the molecules are brought to thermal equilibrium by "thermalisation" processes. In optical or vibrational spectroscopies, we are interested in transitions between states which are strongly coupled to the lattice due to molecular collisions (in liquid solution) or deformations (in solid medium). Thermalisation processes are very efficient, and thermal equilibrium is continuously maintained. In addition, these processes contribute little to the linewidth which is determined by other causes. Apart from in exceptional cases, thermalisation processes therefore do not alter the spectrum.

The situation is very different in EPR, and more generally in magnetic spectroscopies, where paramagnetic centres are brought to thermal equilibrium by the very specific processes of spin-lattice relaxation.

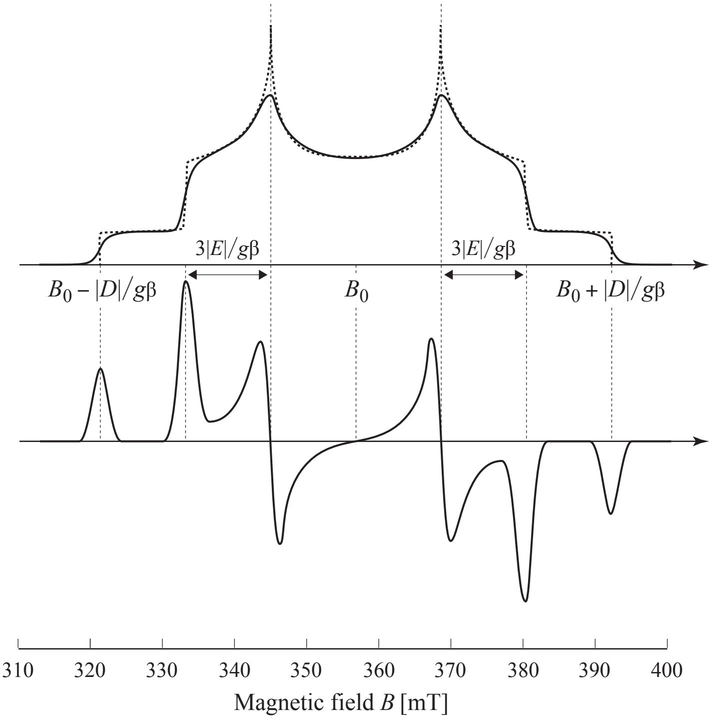

Figure 6.9 – Density (dashed line) and shape (continuous line) of the spectrum given by a centre of spin $S = 1$ with rhombic symmetry in the high-field situation. The spectrum is calculated for: $\nu = 10$ GHz, $g = 2.00$, $|D| = 0.033$ cm^{-1} (1000 MHz), $|E/D| = 0.1$.

6.6 – EPR spectrum for complexes of half-integer spin in the low-field situation. Kramers doublet

The low-field situation is achieved at X-band when $|D|$ exceeds a few cm^{-1}. It is therefore not observed with organic molecules in a triplet state, but it is frequent with transition ion complexes. For complexes with half-integer spin, we will see that calculation of the spectrum comes down to that for a centre of spin ½. It is therefore possible to use the results obtained in chapters 4 and 5. We will deal with the case of complexes with axial symmetry and generalise the results for any symmetry.

6.6.1 – Case of a complex with axial symmetry

Consider a complex characterised by the Hamiltonian [6.9], in which the principal term is the zero-field splitting term and the Zeeman term is a perturbation.

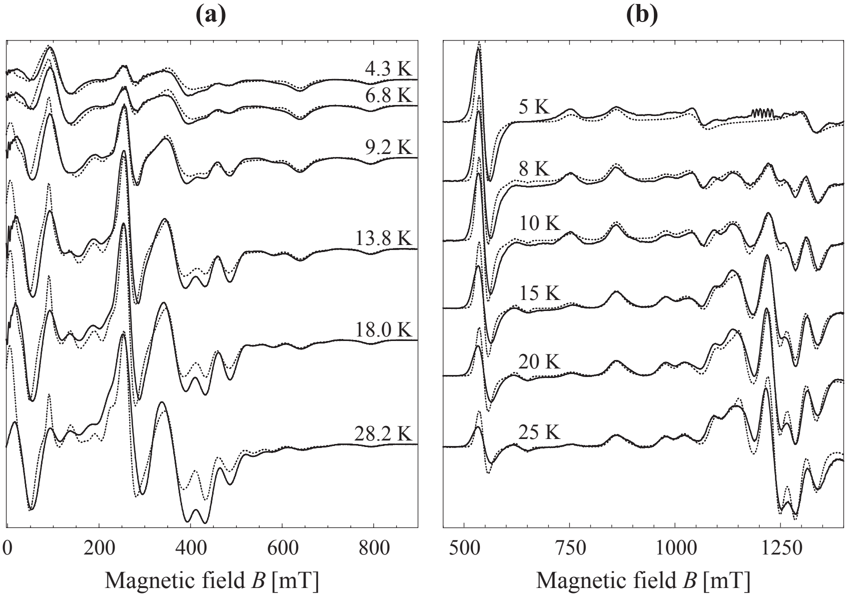

Figure 7.14 – **(a)** X-band (ν = 9.40 GHz) and **(b)** Q-band (ν = 34 GHz) spectra for the $[(Bpmp)Mn_2(\mu\text{-}OAc)_2](ClO_4)$ complex recorded at different temperatures. Power: X-band 0.5 or 2 mW, Q-band: 0.58 or 2.3 mW. Modulation: frequency 100 kHz, peak-to-peak amplitude 0.5 mT. Numerical simulations are represented by the dashed lines. [Reproduced with permission from Blanchard S. *et al.*, *Inorganic Chemistry*, **42**, 4568–4578 © 2003, American Chemical Society]

7.5 – How intercentre interactions affect the intensity of the spectrum and the relaxation properties

7.5.1 – EPR spectrum intensity

The intensity of the spectrum produced by two interacting paramagnetic centres is simply expressed in the two limit situations studied in sections 7.3 and 7.4.

◇ Situation with weak intercentre interactions

Within this limit, the intensity of the spectrum for each centre is unmodified. If the sample contains N (A, B) pairs, the total intensity is equal to the sum of the intensities of the spectra produced by N centres A and N centres B (equations [5.17] and [5.19]). When the experimental spectrum is integrated, a large enough field range must be chosen to include any lateral lines due to exchange interaction (section 7.3.2).