Anisotropic spectra of s = ½ paramagnets

In Part I we assumed that the EPR spectra were isotropic. "Isotropic" means that there is no orientation dependence (a sphere is an isotropic object). In general, the interactions that determine the form of an EPR spectrum (for example, the Zeeman and hyperfine interactions) are anisotropic – they depend on the orientation of the paramagnet with respect to the magnetic field. Mathematically, they are described by 3×3 matrices, but we can define principal values associated with specific orientations of the molecule (often referred to as $g_{x,y,z}$ and $A_{x,y,z}$). In fluid solution, the magnetic field "sees" an average orientation of the molecule, assuming rapid tumbling, and the spectra appear isotropic (this is also true of NMR), giving $g_{iso} = (g_x+g_y+g_z)/3$ and $A_{iso} = (A_x+A_y+A_z)/3$.
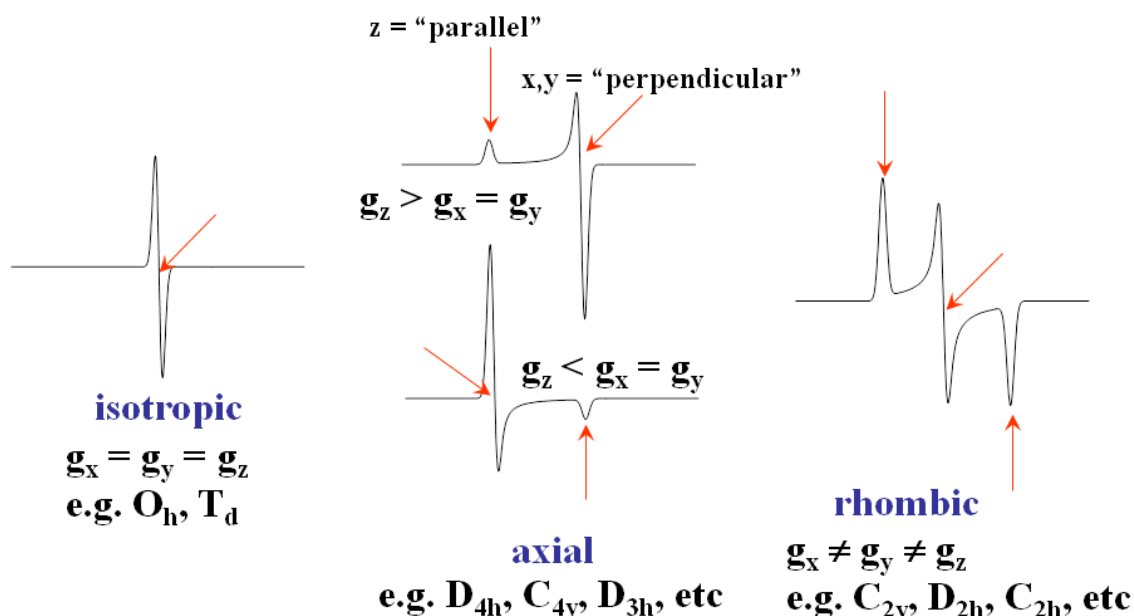
What happens if the sample is immobilised?

(i)   Powders, glasses and "sum over all orientations": g-values

EPR spectra of a powder or of a frozen solution are an addition over all orientations with respect to the applied magnetic field. The form of the spectrum depends on the symmetry of the paramagnet.

- Isotropic molecular shapes (e.g. octahedron, tetrahedron, i.e. $g_z = g_x = g_y$) will give isotropic spectra.
- Axially symmetric species will give two distinct g-values ($g_z \neq g_x = g_y$); this includes e.g. trigonal bipyramid, square-based pyramid, square plane, elongated octahedral geometries. The two g-values are sometimes called $g_{||}$ and $g_{\perp}$.
- In lower, rhombic, symmetry there are three distinct g-values ($g_z \neq g_x \neq g_y$).

These different symmetries give characteristic powder or frozen solution spectra. The "in-between" orientations cancel out due to the derivative nature of the spectra. This effect also gives rise to the different lineshapes observed.

z = "parallel"

x,y = "perpendicular"

$g_z > g_x = g_y$

$g_z < g_x = g_y$

isotropic
$g_x = g_y = g_z$
e.g. O_h, T_d

axial
e.g. D_{4h}, C_{4v}, D_{3h}, etc

rhombic
$g_x \neq g_y \neq g_z$
e.g. C_{2v}, D_{2h}, C_{2h}, etc

The actual locations of the principal axes might be dictated by symmetry (e.g. in axially symmetric species). They can be located experimentally by single crystal spectroscopy. Although this is a time consuming experiment it can give a great deal of information.

The pattern of anisotropic g-values gives information not only on symmetry, but also on the nature of the electronic ground and excited states (e.g. which d-orbital contains the unpaired electron in transition metal complexes). They can also be very sensitive to environmental effects, e.g. nitroxyl spin probes are used to probe the H-bonding and site polarity in biological systems via their anisotropic g-values.

(ii)   Anisotropic hyperfine coupling

The hyperfine interaction can also be anisotropic and the form of the spectrum follows directly from that of the glass spectra for an anisotropic Zeeman interaction. For example, an s = ½ coupled to a single I = ½ could give the spectra below.

$A_x = A_y$

A_z

isotropic

axial

rhombic
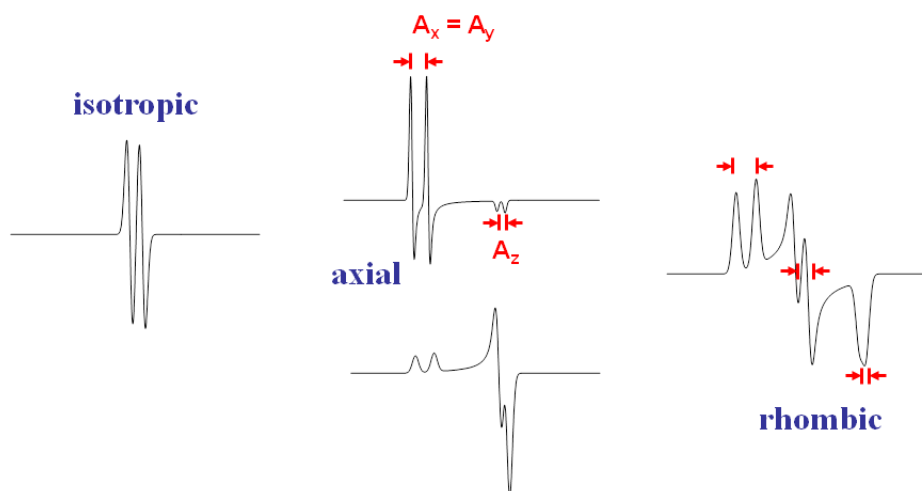
When the sample is immobilised, the dipolar interaction (as well as the Fermi contact) contribute to the observed hyperfine splitting. Analysis of this gives a wealth of electronic and structural information. Hyperfine couplings to remote nuclei (i.e. when the interaction is entirely dipolar) can be used to determine electron-nuclear distances.

Hyperfine couplings are independent of frequency/field of measurement, but the field resolution of g-anisotropy is enhanced at higher fields. This is one advantage of measurement at higher frequency (hence field). The example below shows spectra for a typical nitroxide with parameters gx = 2.002, gy = 2.006, gz = 2.008, and 14N hyperfine parameters Ax = 32 G, Ay = 1 G, Az = 1 G, at different experimental frequencies. At low frequency (L-, S- and X-bands) the spectrum is dominated by the hyperfine effects of the 14N nucleus, but at K- and Q-band frequency the g-value anisotropy is becoming apparent, and at W-band frequency all three g-values and the three hyperfine lines from Ax are resolved.
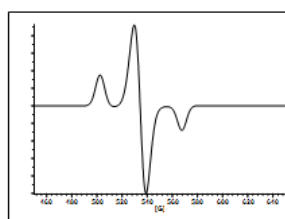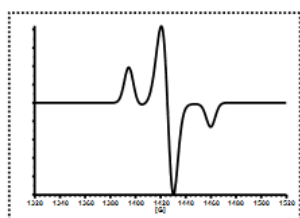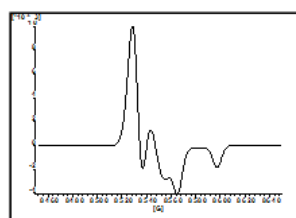

L-band, 200/1420 G, 1.5 GHz
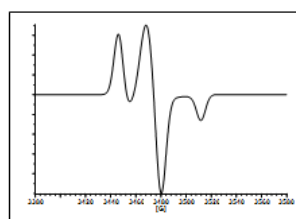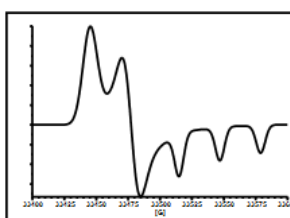

X-band, 200/3480 G, 9.75 GHz
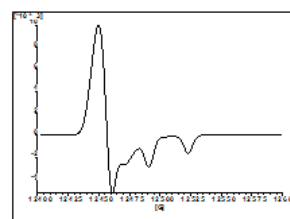
Q-band, 200/12500 G, 35.0 GHz

S-band, 200/1420 G, 4.0 GHz

K-band, 200/8550 G, 24.0 GHz

W-band, 200/33500 G, 94.0 GHz