ESR Line-Shapes

Two general effects that can modify ESR line-shapes:

- g- and/or A-anisotropy in randomly-ordered solids (powders, glasses)

- molecular dynamics (fluxional behavior, electron exchange, slow molecular tumbling, etc)

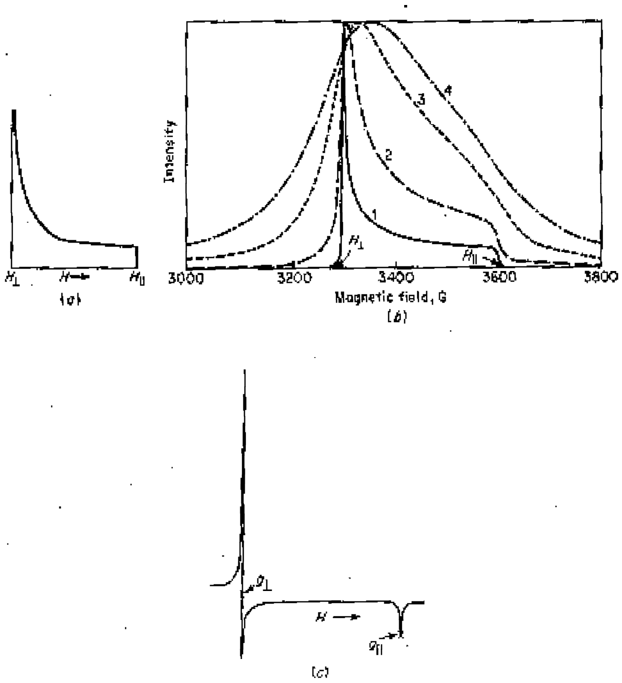
Anisotropy effects

Consider a planar radical which exhibits a single ESR line in solution (no hyperfine splitting).

The ESR spectrum of a single crystal of the radical also shows a single line, the position of which depends upon the orientation of the crystal with respect to the magnetic field. When the molecular axis is aligned parallel to B the line appears at $g_{||}$ and when the molecular axis is aligned perpendicular to B the line appears at $g_\perp$. (Assume, for the sake of argument that $g_\perp > g_{||}$). At intermediate orientations the line appears at intermediate g-values.

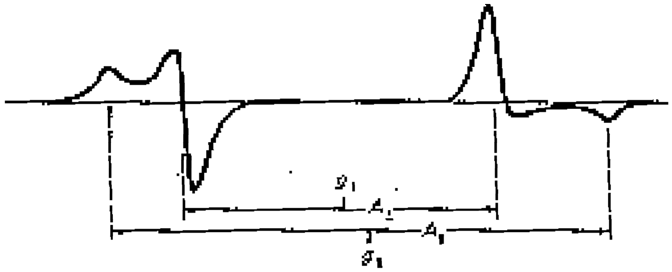
$$g_{solution} = (g_{||} + 2g_\perp)/3 \qquad (g_z = g_{||} \text{ and } g_x = g_y = g_\perp)$$

The ESR spectrum of a polycrystalline powder or a frozen glass contains radicals oriented in all possible directions and yields a composite spectrum of lines ranging from $g_{||}$ to $g_{\perp}$, see Figure.



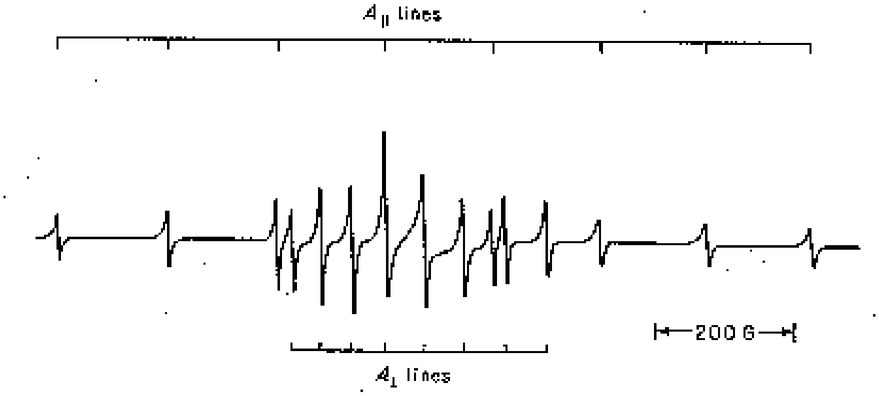
(a) Composite stick spectrum
(b) Computed absorption spectrum with component line-widths of 1, 10, 50, and 100 gauss.
(c) an experimental (first derivative) spectrum of an axial free radical.

Hyperfine splitting in powder spectra.
Example of hypothetical case where I = ½ and both g and A are anisotropic

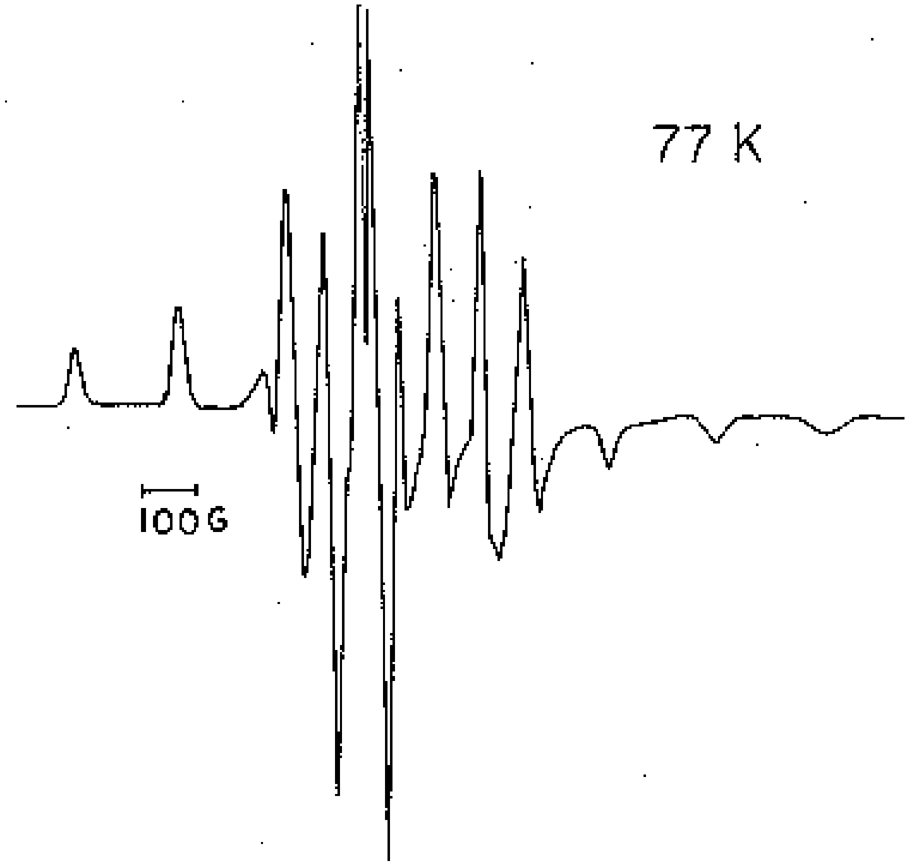


(C)

Case where I = 7/2.
$[VO(CN)_5]^{3-}$ in oriented single crystal of KBr

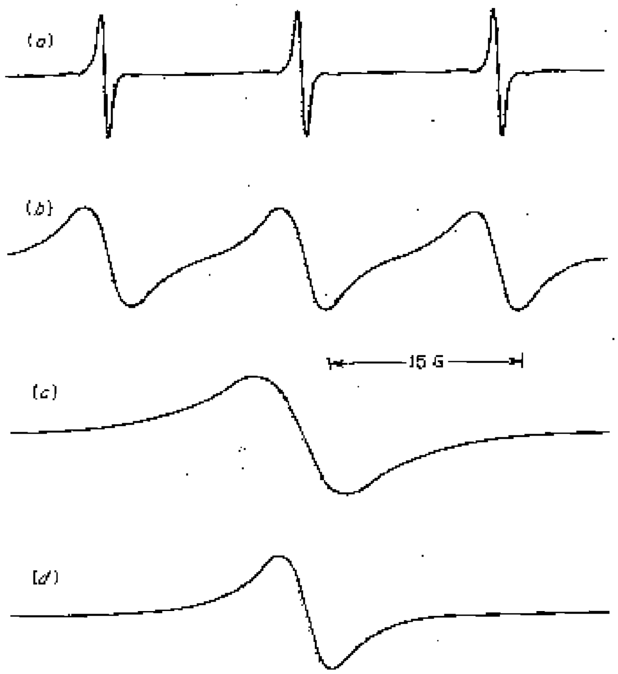


Powder spectrum of a VO^{2+} complex



Dynamic Effects

Exchange Narrowing



10^{-4} M

10^{-2} M

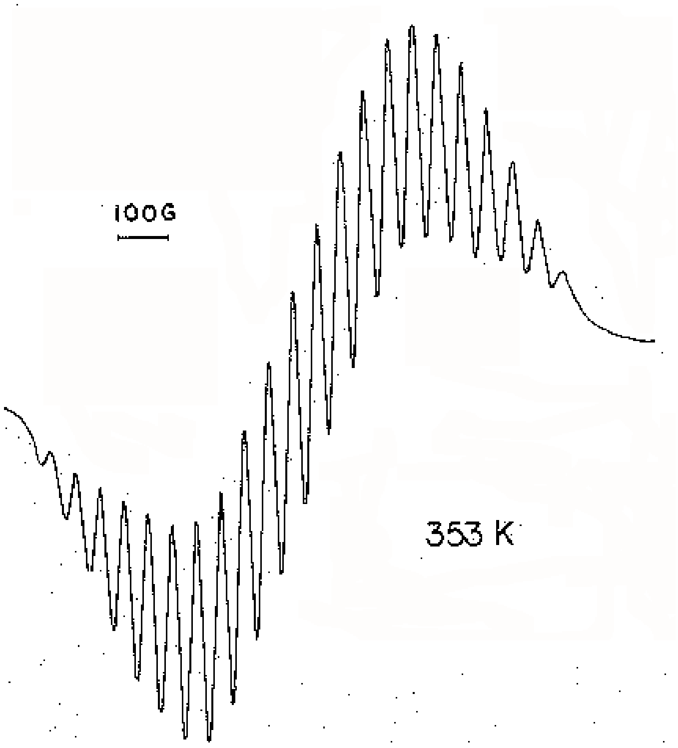
10^{-1} M

Neat liquid

ESR spectrum of di-*t*-butyl nitroxide radical (DTBN, $(Me_3C)_2NO^\bullet$) in ethanol at room temperature Shows effect of increasing rate of electron exchange as concentration increases.

[Note that the g-marker, diphenyldipicrylhydrazyl (DPPH), is used for this purpose as a neat solid, and gives a sharp single line. In dilute solution, the spectrum shows hyperfine coupling to 2 nitrogens (I=1) and multiple protons.]

Intramolecular electron transfer, e.g. in the mixed-valence complex $[P_2W_{15}V_3O_{62}]^{10-}$ (one V^{IV} and two V^{V} centers). Electron exchange between the three V atoms is fast on the ESR time-scale, and gives 2×3×7/2 + 1 = 22 hyperfine lines.



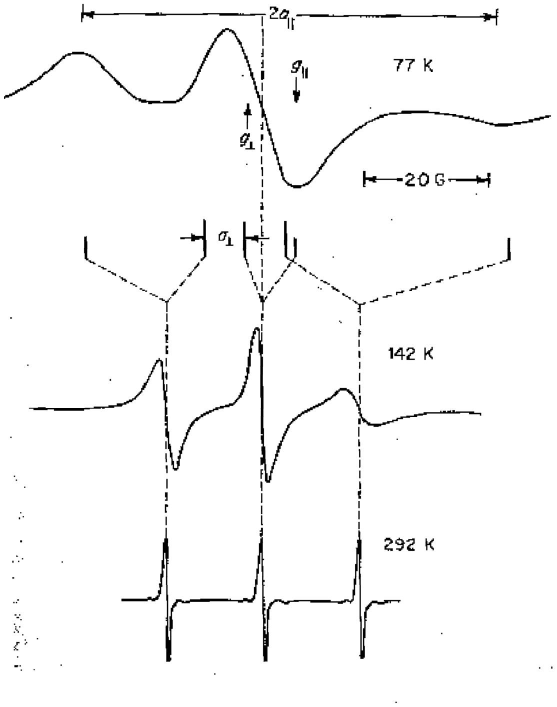
Note that A is ~⅓ that of A for a mononuclear V^{IV} complex.

What is the expected intensity pattern for this spectrum?

In principle, electron exchange/transfer rates can be evaluated from ESR spectral changes

Solution dynamics – rates of molecular tumbling

Example of DTBN



solid

viscous solution

non-viscous solution

(g’s and A’s are taken from single crystal measurements.)

It’s possible to simulate these spectra and determine the rate of molecular tumbling.

Similar effects can be produced if the nitroxide is attached to a large biomolecule (“spin-labelling”) which undergoes slow tumbling rearrangements in solution. Examples: large proteins, membranes).

Species with more than one unpaired electron ($S \geq 1$).

The energy levels of complexes with $S = 1$ or greater are subject to a splitting of the M_S states in the absence of a magnetic field ("Zero Field Splitting", ZFS) The splitting arises from a distortion of the molecule, or via spin-orbit coupling, or both. Although ZFS is very small (usually a few cm^{-1} at most) it can have a profound effect on the ESR spectrum.

If S = an even number, ZFS splits states into $M_S = 0, \pm 1, \pm 2$, etc

S = an odd number, ZFS splits states into $M_S = \pm ½, \pm 3/2$, etc

$S = 1$ case:

In the absence of ZFS, the two allowed ESR transitions ($\Delta M_S = 1$) occur at the same magnetic field, but in the presence of ZFS these transitions are no longer degenerate and may be observed separately ("fine structure"). The separation depends upon the magnitude of the ZFS parameter (D).