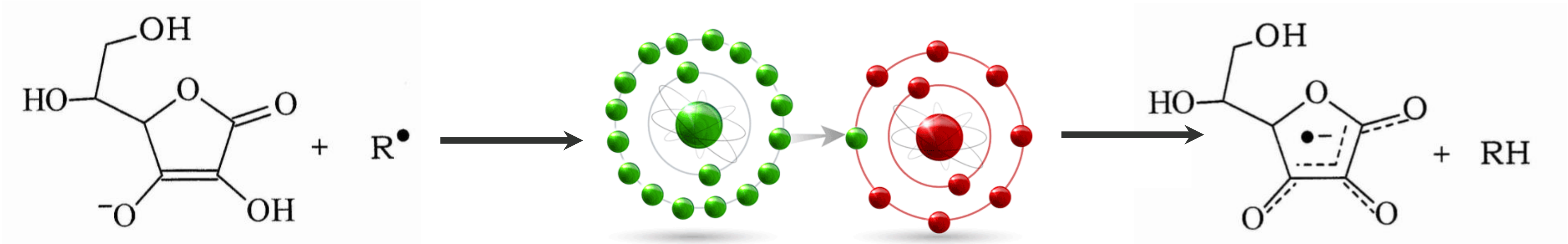
A General Introduction to EPR Simulations

EPR: direct and unambiguous detection of free electrons

- EPR (also called ESR) is a magnetic resonance technique that detects unpaired electrons in paramagnetic substances
- Unpaired electrons occur in free radicals and many transition metals
- EPR is the only technique that unambiguously detects free radicals



Ascorbic acid (vit C)

Vit C

R•

Ascorbate radical

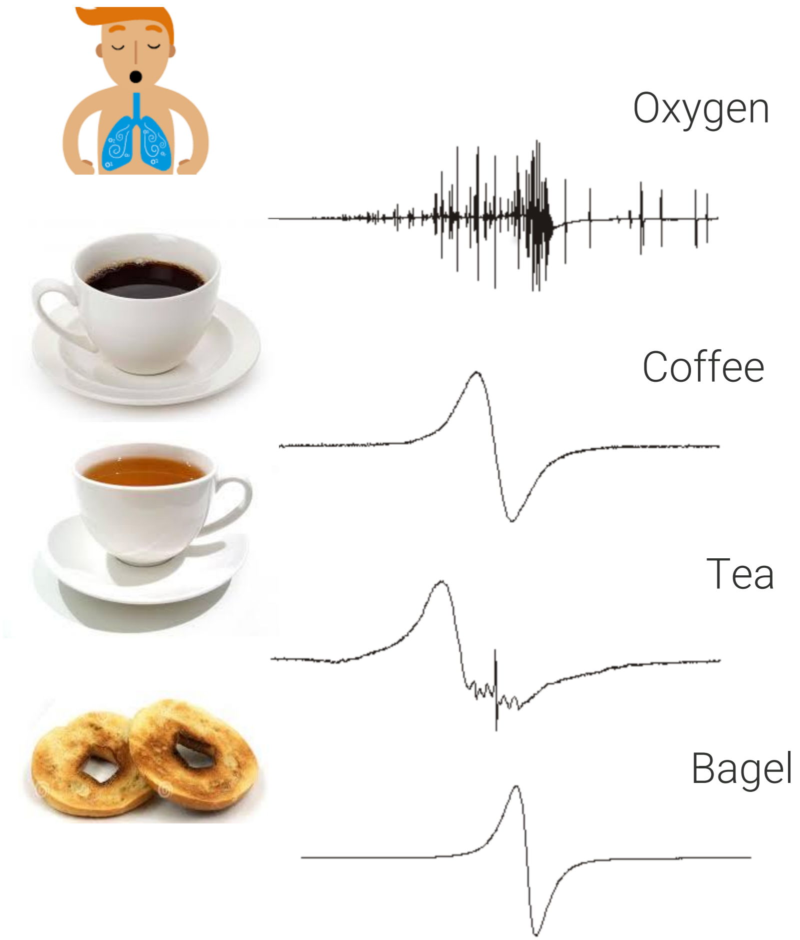
EPR spectrum

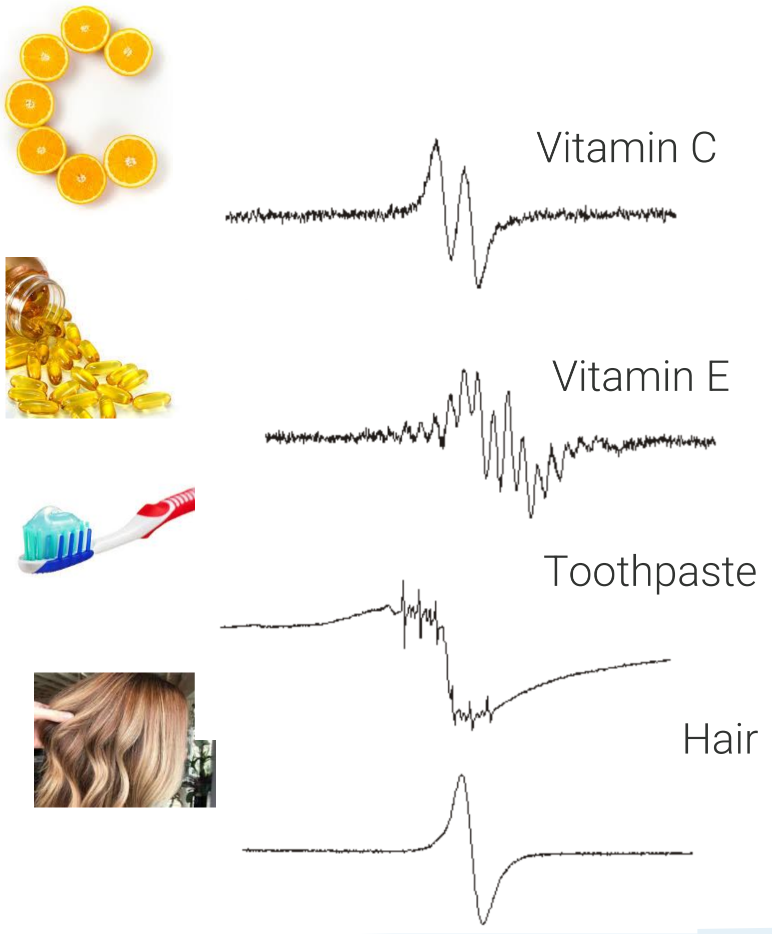
Species that Have Free Electrons

- Transition metal ions and complexes Mn^{2+}, Cu^{2+}, Gd^{3+} etc.
- Simple inorganic compounds: O_2 , NO, NO_2 ….
- Short-lived intermediate radicals OH, H, F etc. in kinetics study
- Defects in crystals
- Electrons trapped in radiation damaged sites
- Stable or long-living organic radicals
- Triplet states
- Ferromagnetic resonance effects

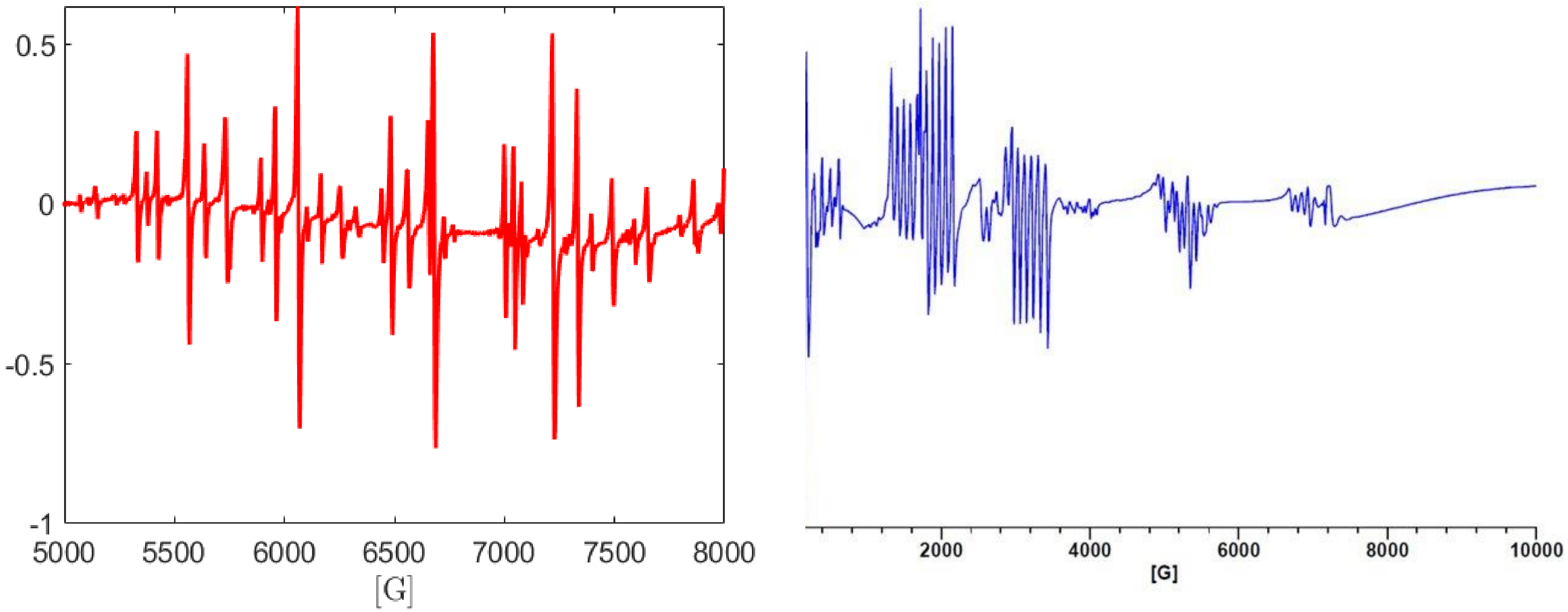
Free electrons around us

- Free radicals and transition metals are very common in everyday life





EPR spectrum can be very complicated



Fortunately, we can describe even complicated EPR spectra with very few parameters!

The Spin Hamiltonian

$$\mathcal{H} = \beta_e \underline{B}_0^T \cdot \underline{\underline{g}} \cdot \underline{S} + \underline{S}^T \cdot \underline{\underline{D}} \cdot \underline{S} + \underline{S} \cdot \underline{\underline{A}} \cdot \underline{I} + \underline{I}^T \cdot \underline{\underline{Q}} \cdot \underline{I} - \gamma_N \beta_N \underline{B}_0^T \cdot \underline{I}$$

Electron Zeeman Interaction

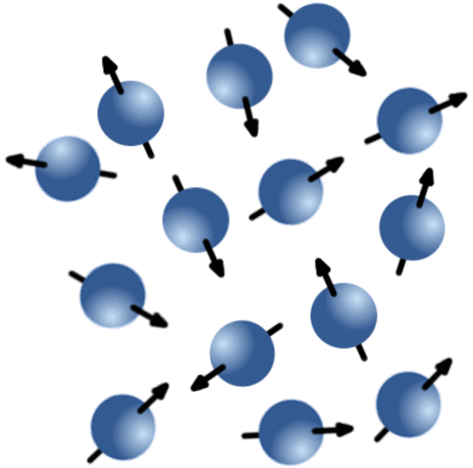
Electron Dipole-Dipolar Interaction

Nuclear Hyperfine Interaction

Abragam, A.; Pryce, M.H.L. Theory of the Nuclear Hyperfine Structure of Paramagnetic Resonance Spectra in Crystals. *Proceedings of the Royal Society of London Series A* **1951**, *205(1080)*, 135-153.

The Zeeman Interaction

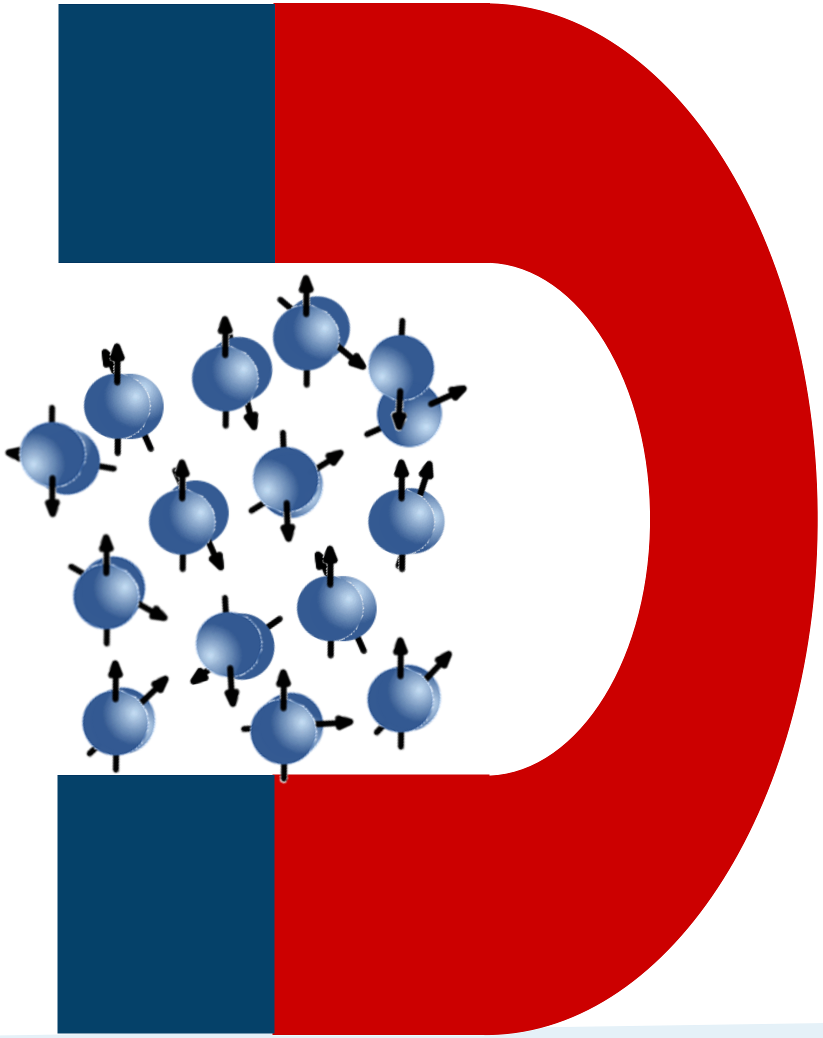
Without an external magnetic field spins are randomly oriented



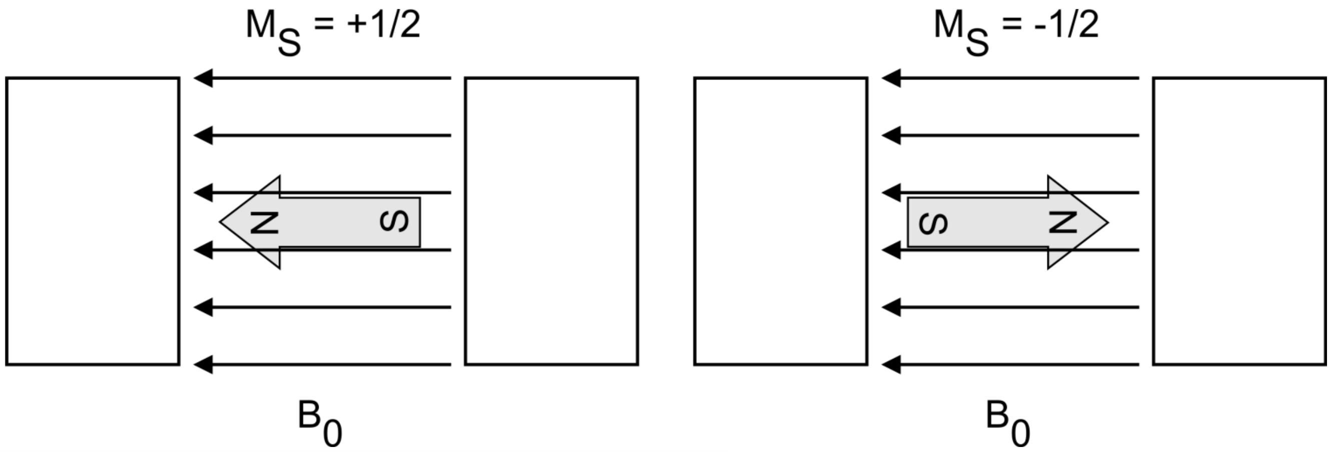
The Zeeman Interaction

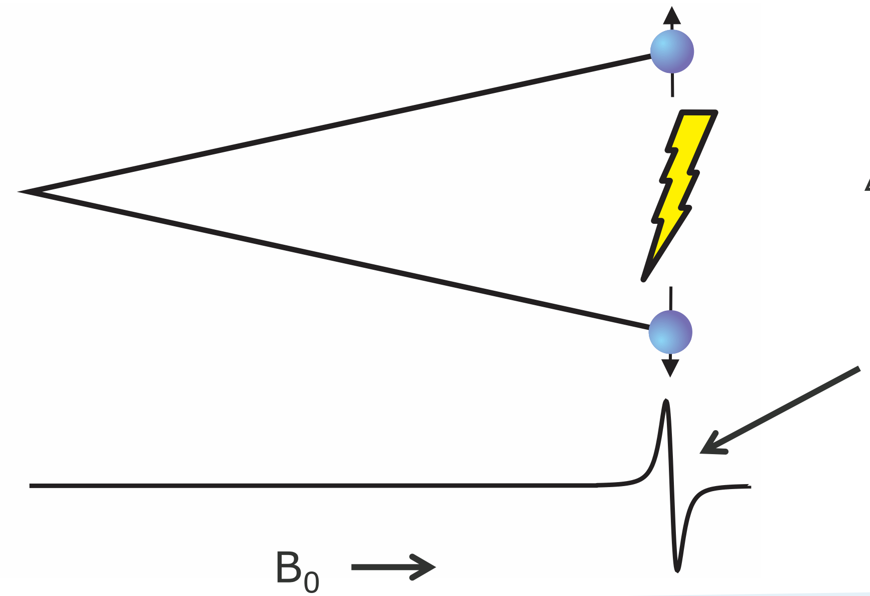
Placing the spins into a magnetic field will lead to alignment of the spins.

An electron spin will assume one of two spins states, aligned either with or against the magnetic field. We call these up and down spin states.



The Zeeman Interaction





$$\Delta E = h\nu = g\mu_B B_0 S$$

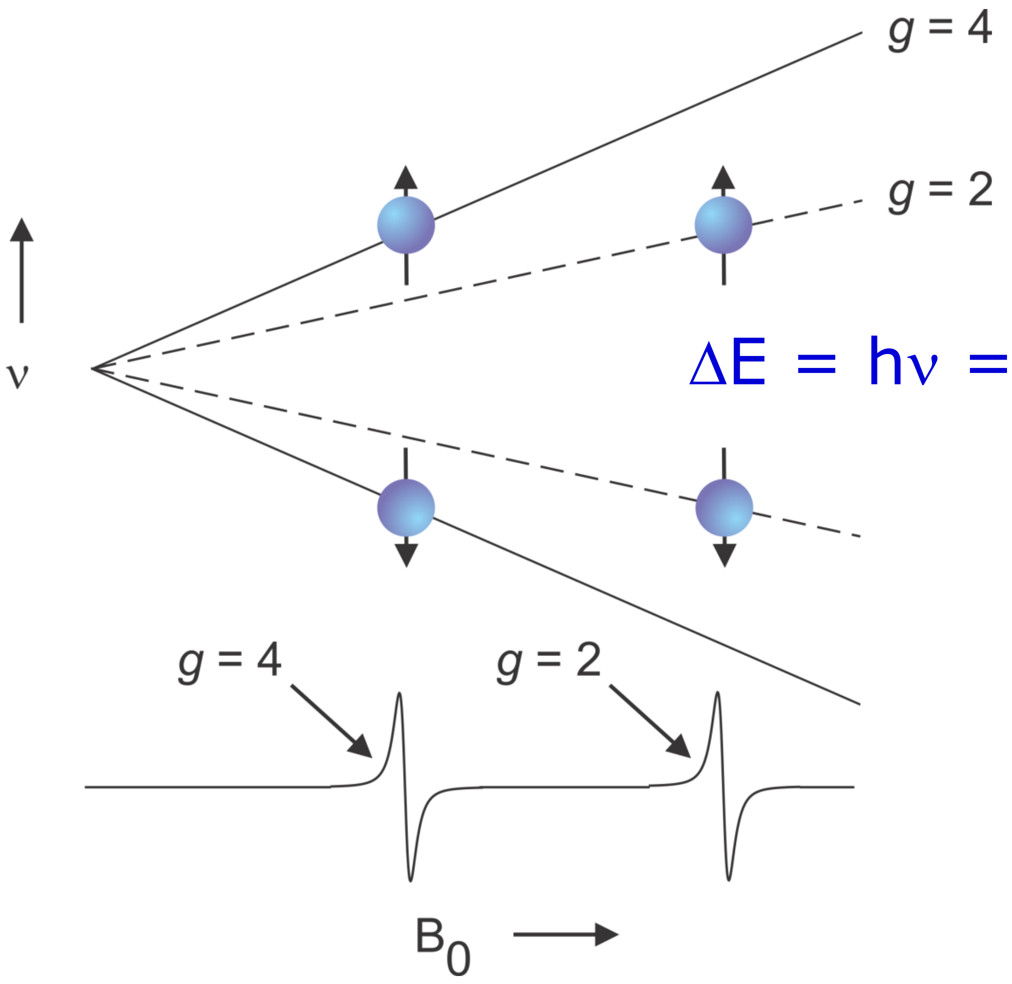
EPR Signal

The Zeeman Interaction

- $B_{EPR} = \frac{h\nu}{g\beta_e} = 714.4775\frac{\nu}{g}$
- ν is the microwave frequency in GHz and the magnetic field, B_{EPR} is in G
- $g = 2.00232$ for a free electron

Microwave Band	Frequency (GHz)	B_{EPR} (G)
L	1.1	390
S	4.0	1430
X	9.8	3480
Q	34.0	12100
W	94.0	33500

The g-Factor



$$\Delta E = h\nu = g\mu_B B_0 S$$

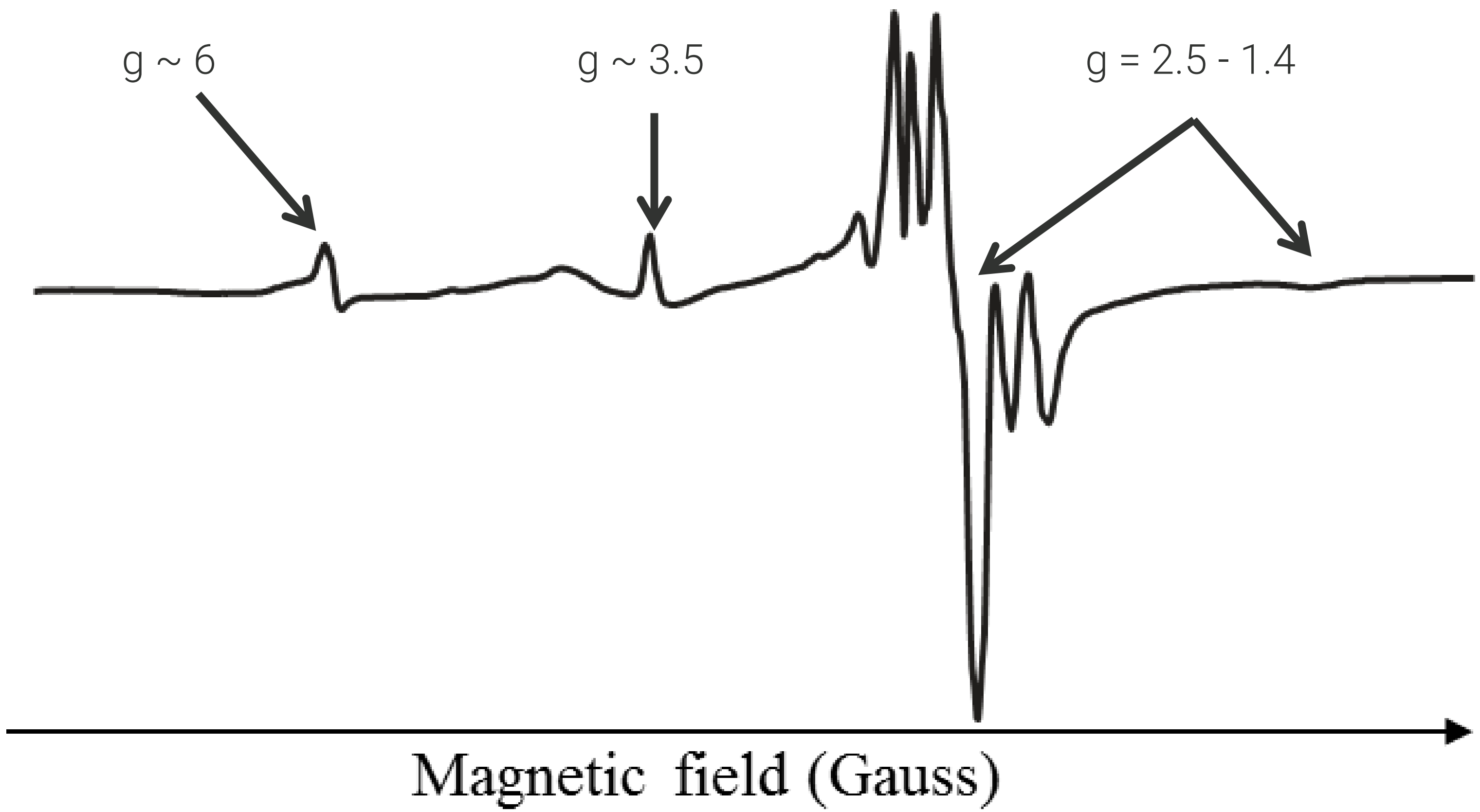
The g-Factor

- The deviation of the g-value from the free electron g-value (2.0023) is akin the ***chemical shift in NMR***
- If chemical shift is usually due to chemical screening and measured in Parts per million (ppm), the g-factors often vary by Parts per part and this variation is mainly due to spin-orbital coupling.
- The spin-orbit coupling mixes *J*, *L* and *S* and shifts ***g***, the shift can yield ***g***<2 or ***g***>2.
- *Landé splitting factor for a metal atom with quantum numbers J, S and L*

$$g = 1 + \frac{J(J+1)+S(S+1)-L(L+1)}{2J(J+1)}$$

- Light atoms, *i.e.* 'organic' radicals and first row transition metals with a single unpaired electron usually have *g* close to 2.0
- Heavier atoms, and molecules or atoms with more than one unpaired electron can have g-values very different from 2

Identifying the species
EPR Fingerprints: the g-value



Identifying the species
EPR Fingerprints: the g-value

	g-value
Flavin semiquinone, ubiquinone, ascorbate, etc	2.0030 - 2.0050
Nitroxide spin labels and traps	2.0020 - 2.0090
sulphur radicals : S-S, S-H	2.02 - 2.06
Mo^V (in aldehyde oxidase)	1.94
Cu^{2+}	2.0 - 2.4
Fe^{3+} (low spin)	1.4 - 3.1
Fe^{3+} (high spin)	2.0 - 10

The Hyperfine Interaction

Nuclei often have a nuclear spin, I

They have spin states, m_I

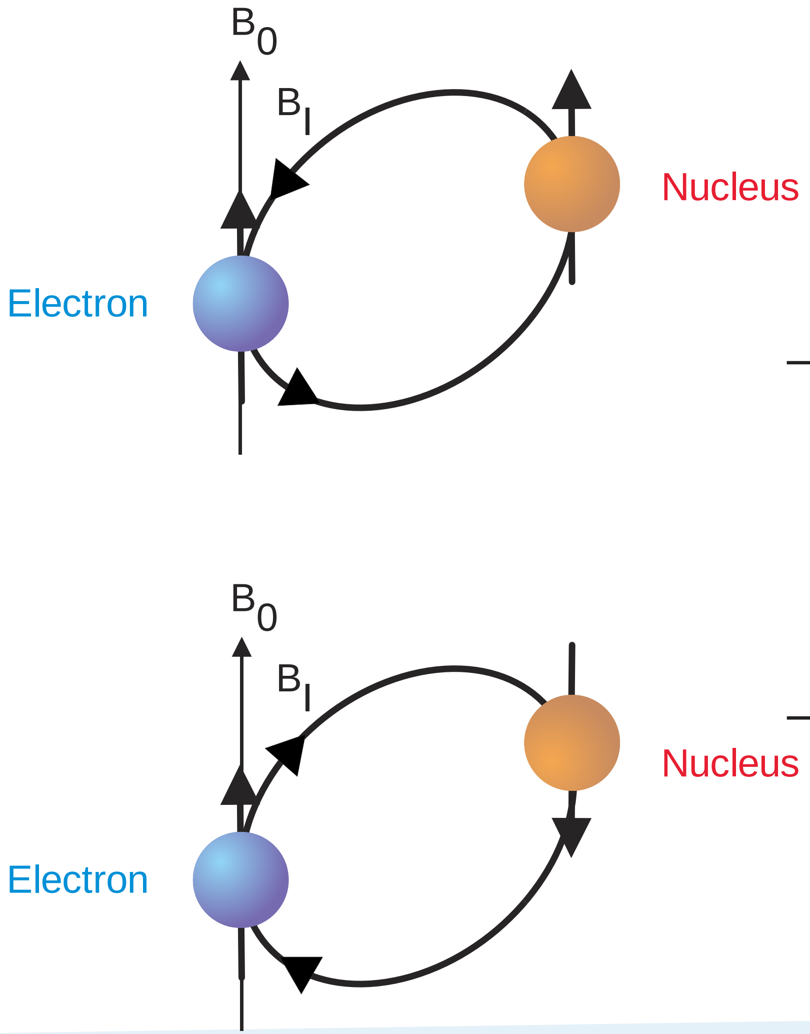
They can create a local magnetic field at the electron, B_I

It either adds to or subtracts from our applied magnetic field, B_0

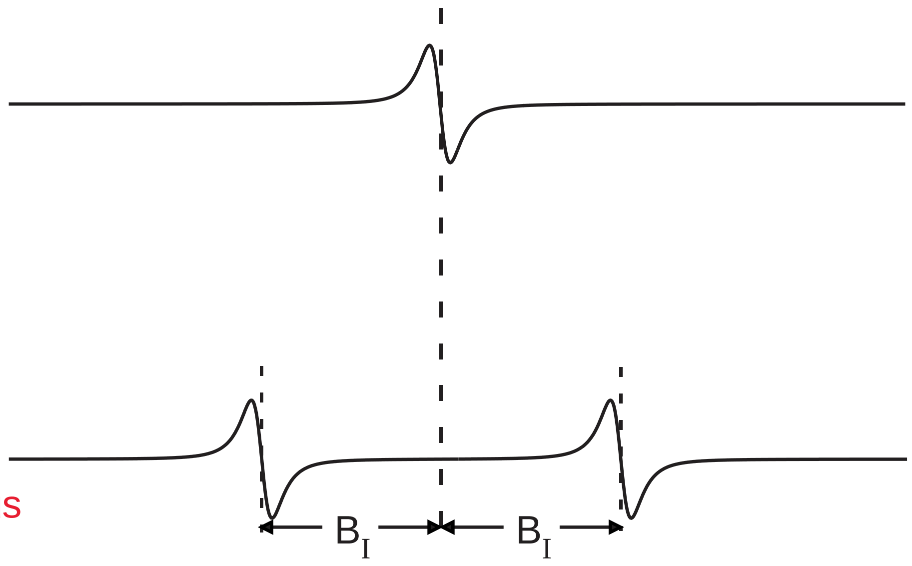
The field splits the EPR signal into two signals (for I=1/2) separated by $2B_I$

This is called the nuclear hyperfine interaction, a

The Hyperfine Interaction

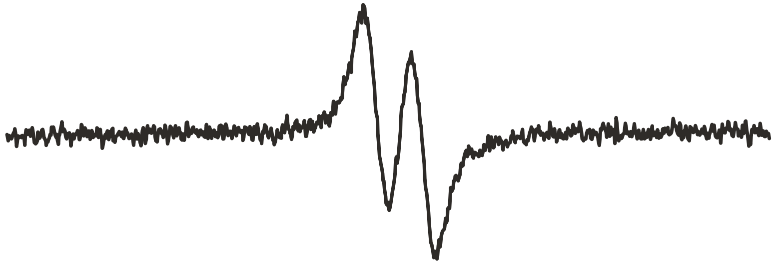


Akin j-j coupling in NMR



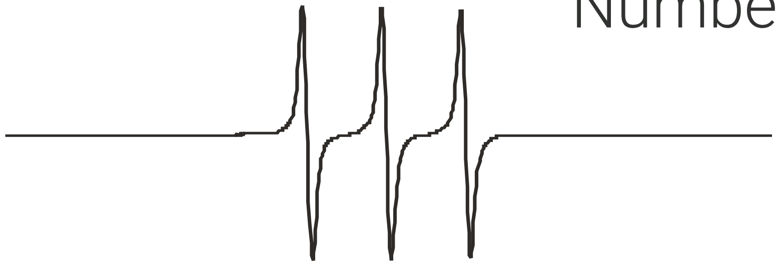
The Hyperfine Interaction

Hydrogen
$I = 1/2$

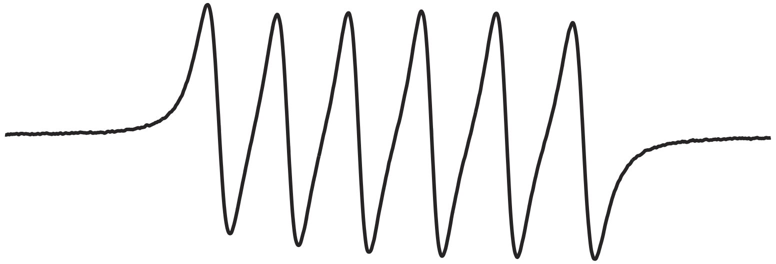


Number of Lines = $2I + 1$

Nitrogen
$I = 1$

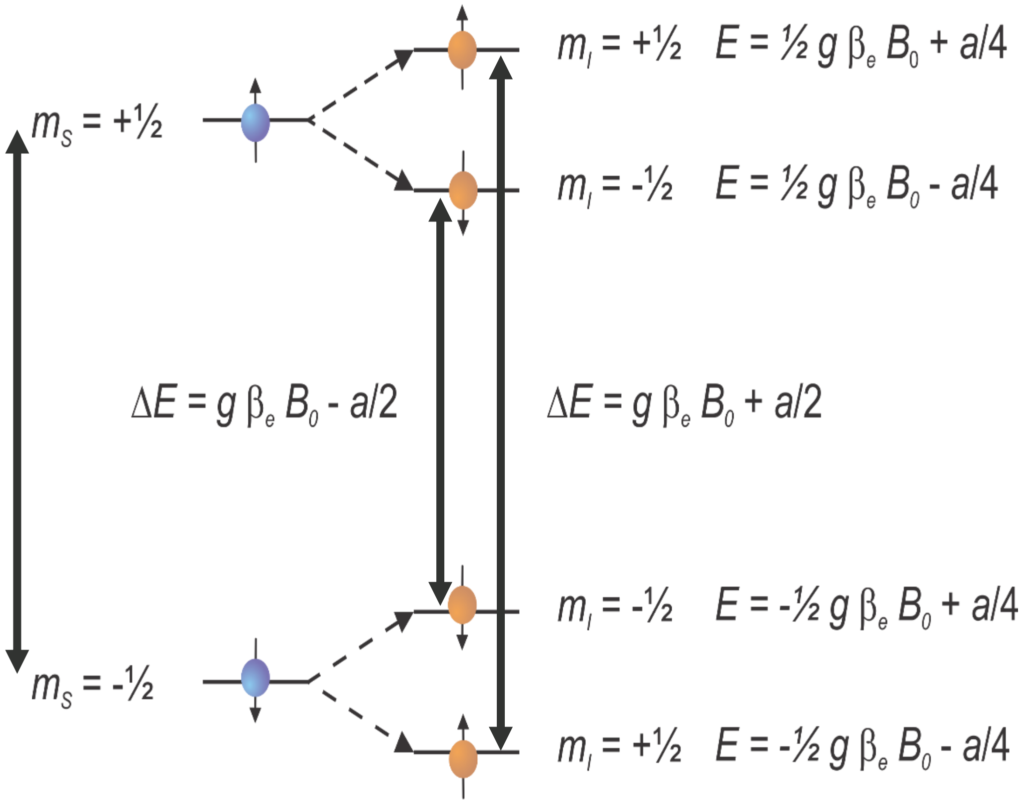


Manganese
$I = 5/2$



The Hyperfine Interaction

- $E \ = g\beta_e B_0 \, m_S + a m_S m_I$
- m_I is the nuclear spin state
- a is the (HFS) HyperFine Splitting
- The allowed EPR transitions occur between states in which there is no change in m_I



$m_S = +½$

$m_S = -½$

$m_I = +½ \quad E = ½\, g\, \beta_e\, B_0 + a/4$

$m_I = -½ \quad E = ½\, g\, \beta_e\, B_0 - a/4$

$m_I = -½ \quad E = -½\, g\, \beta_e\, B_0 + a/4$

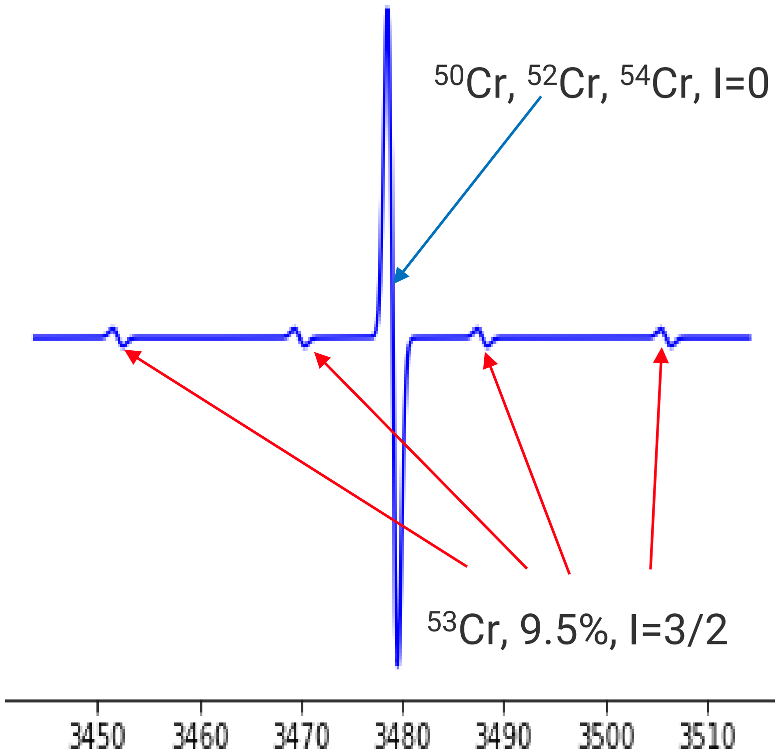
$m_I = +½ \quad E = -½\, g\, \beta_e\, B_0 - a/4$

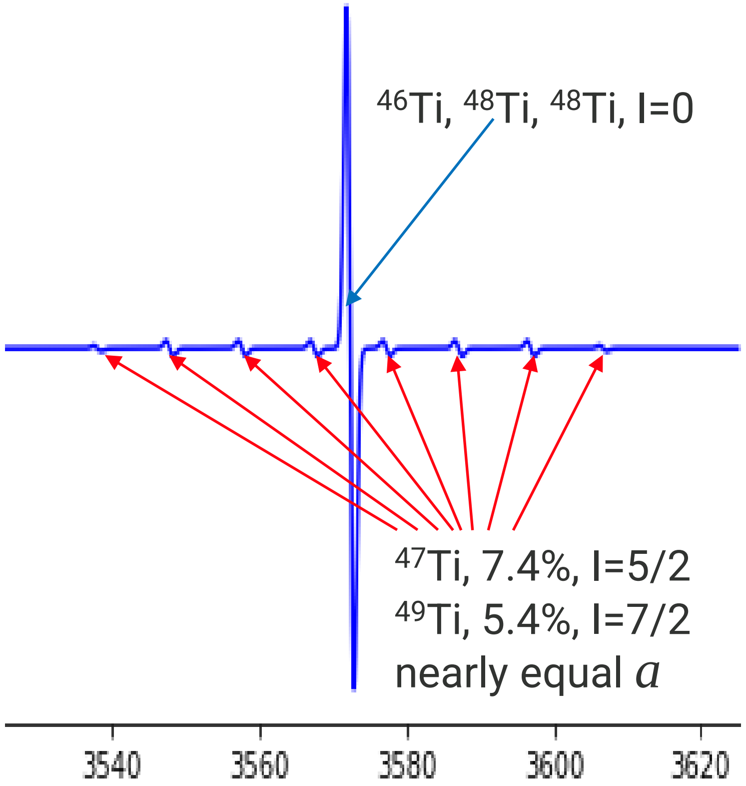
$\Delta E = g\, \beta_e\, B_0 - a/2$

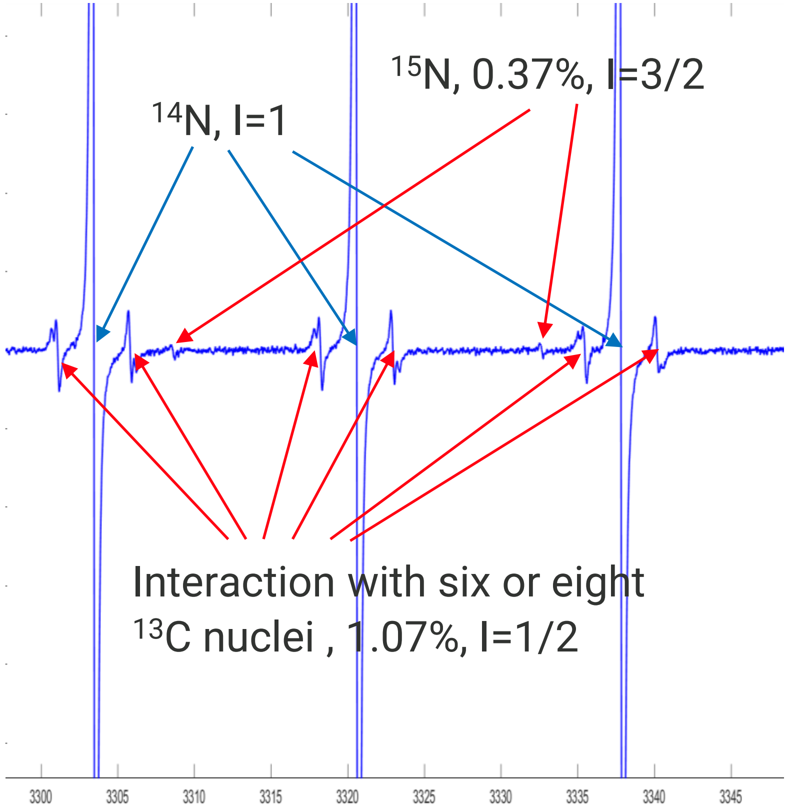
$\Delta E = g\, \beta_e\, B_0 + a/2$

The hyperfine interaction: Satellite lines

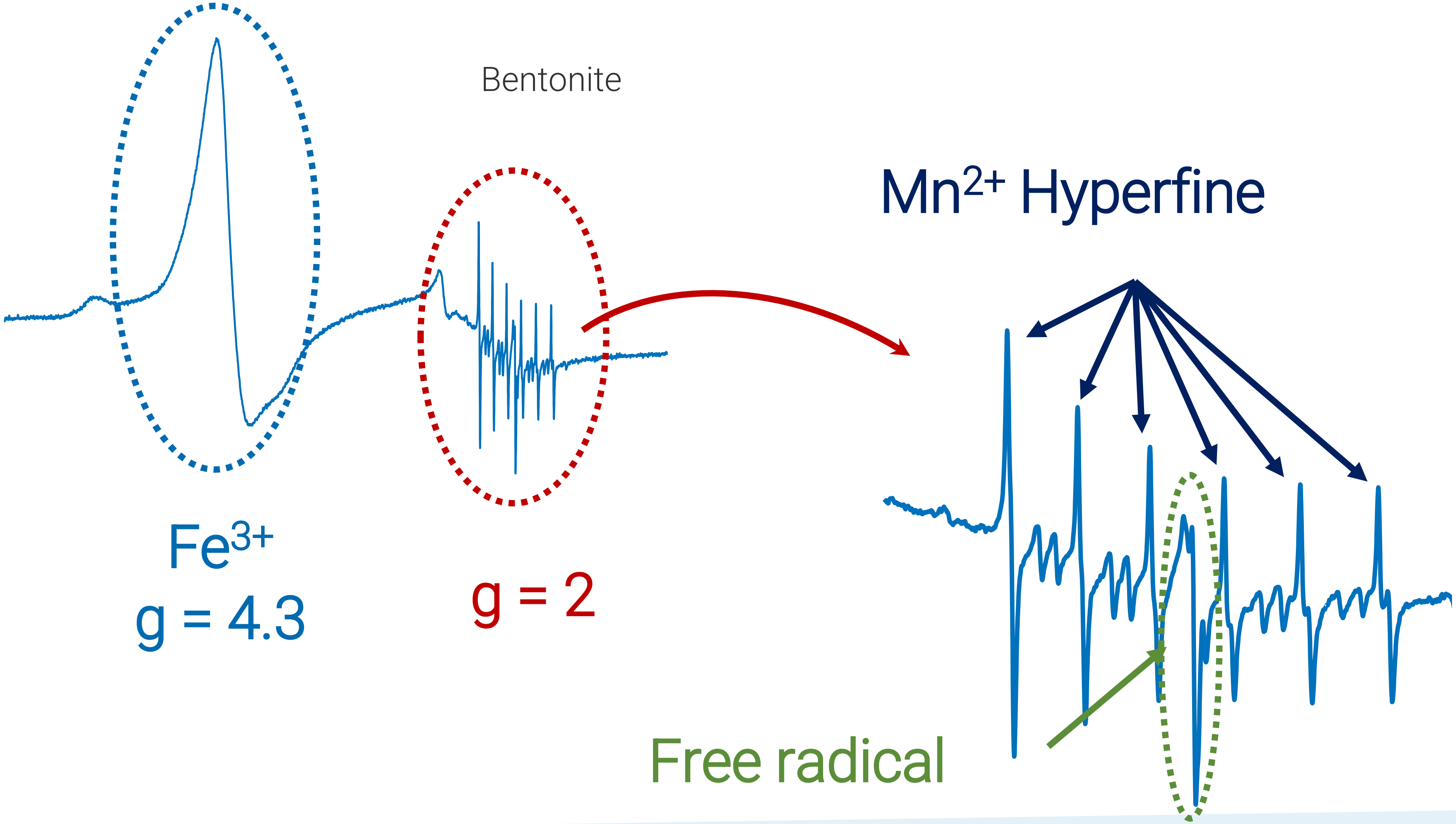
Different isotopes can have different nuclear spin and different hyperfine patterns:







Identifying species via their EPR fingerprints



Bentonite

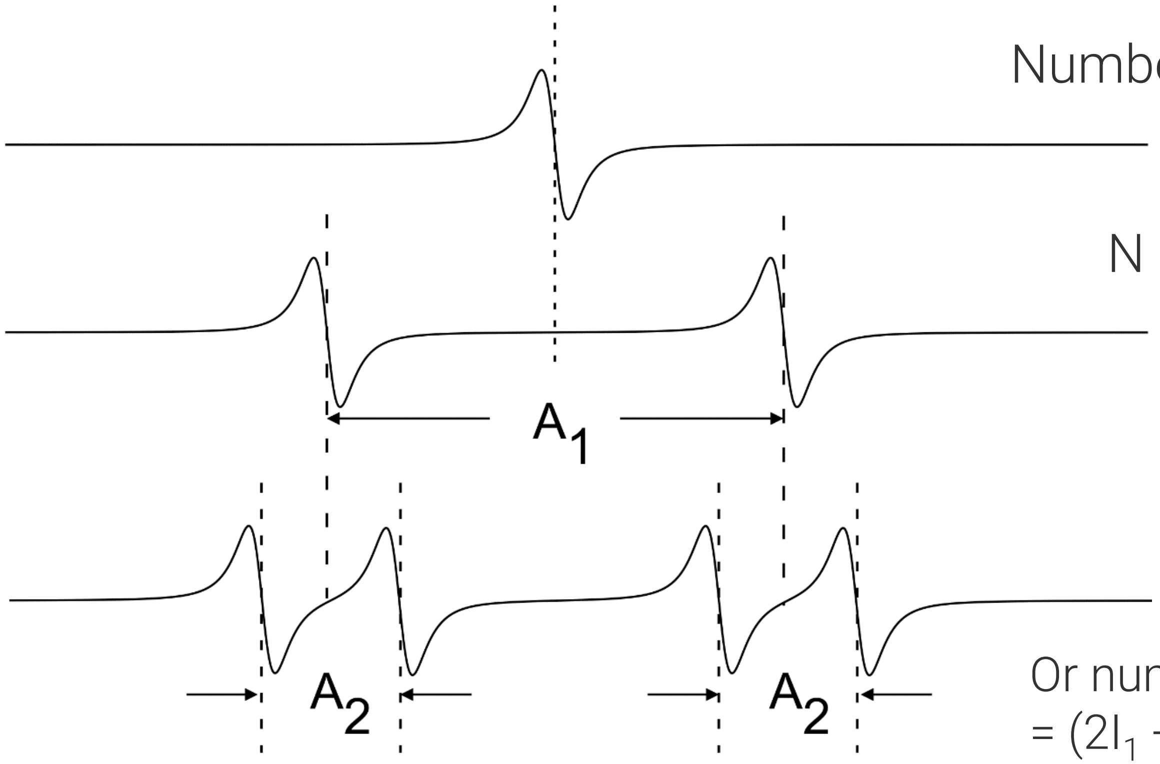
Fe^{3+}
g = 4.3

g = 2

Mn^{2+} Hyperfine

Free radical

Hyperfine interactions, non-equivalent nuclei

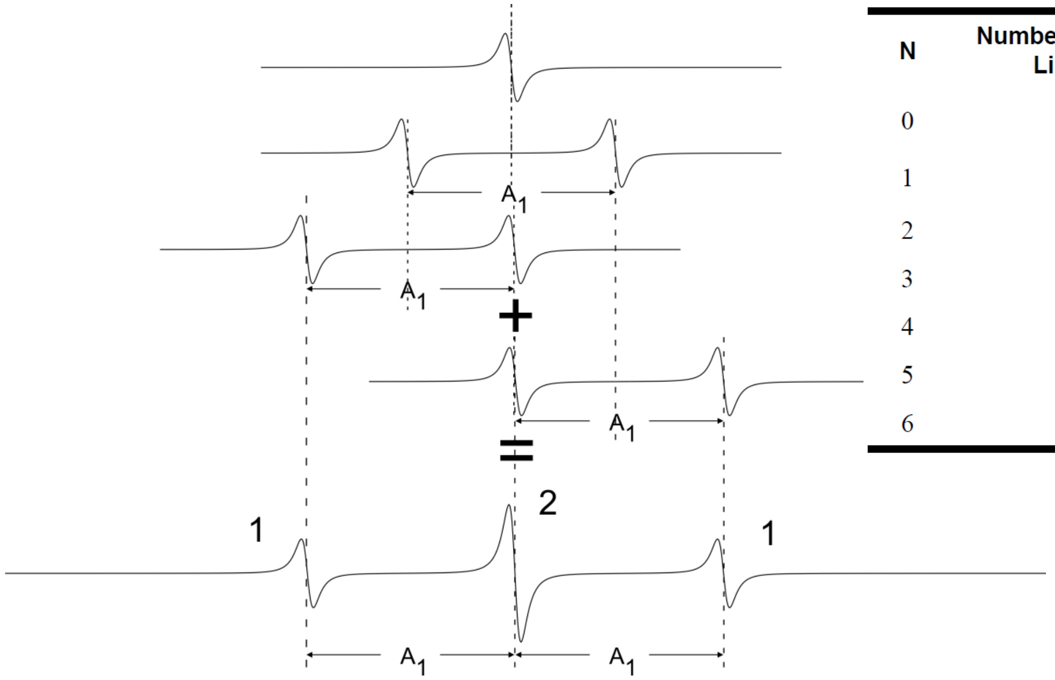


Number of Lines = $(2I + 1)^N$

N = Number of nuclei

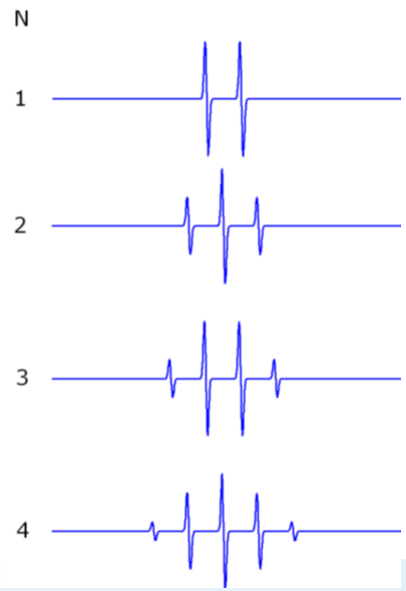
Or number of Lines
= $(2I_1 + 1)$x $(2I_2 + 1)$ for two nuclei with
different nuclear spin numbers

Hyperfine interactions, equivalent nuclei: Pascal's Triangle



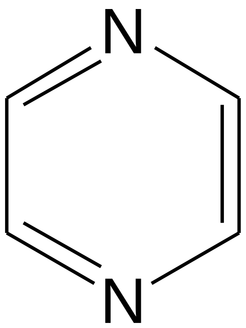
N	Number of EPR Lines	Relative Intensities
0	1	1
1	2	1 1
2	3	1 2 1
3	4	1 3 3 1
4	5	1 4 6 4 1
5	6	1 5 10 10 5 1
6	7	1 6 15 20 15 6 1

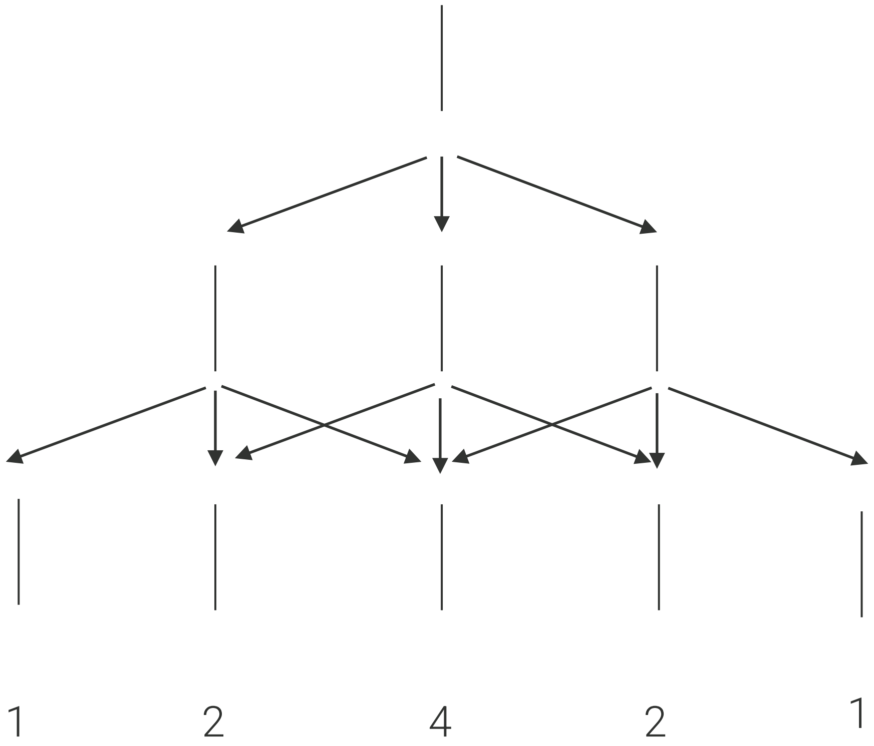
Number of Lines = 2N+ 1



General case: Number of Lines = $\prod_i (2N_i I_i + 1)$ where *i* is the number of groups of non-equivalent nuclei with a spin I_i, and *N* is a number of equivalent nuclei in each group.

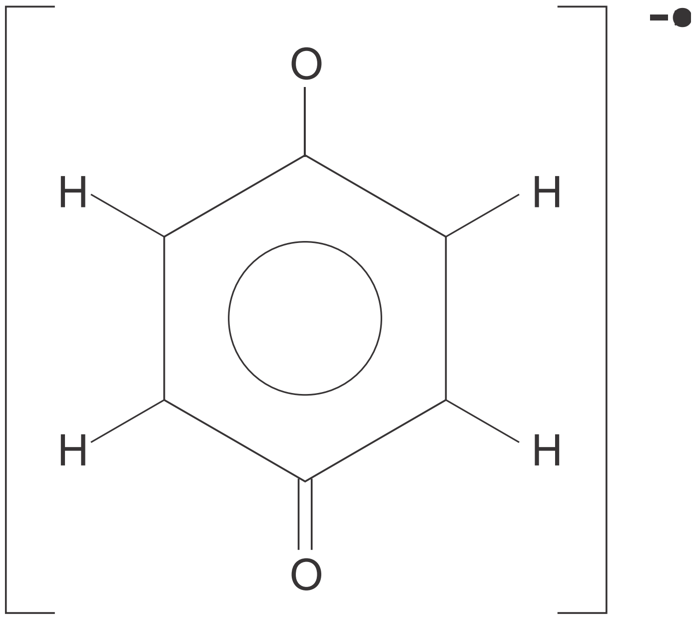
Hyperfine interactions, equivalent nuclei



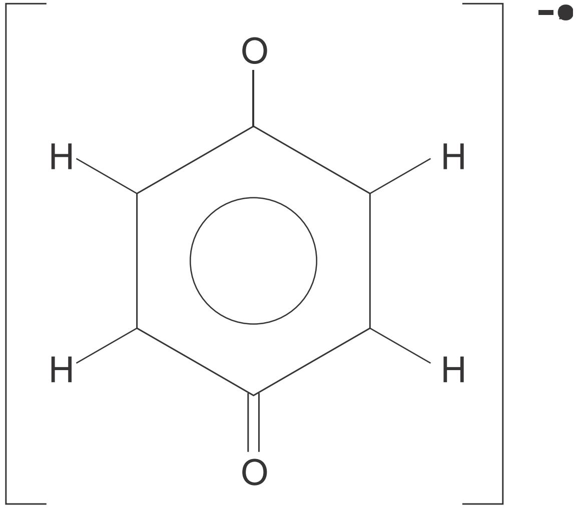


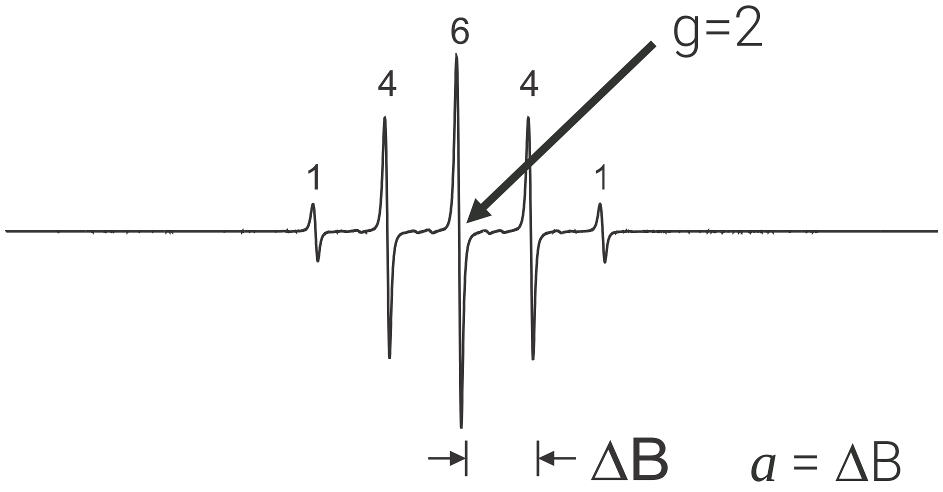
Hyperfine interactions: Semiquinone Radicals

- ^{12}C: $I = 0$
- ^{16}O: $I = 0$
- ^{1}H: $I = \frac{1}{2}$
- Four protons



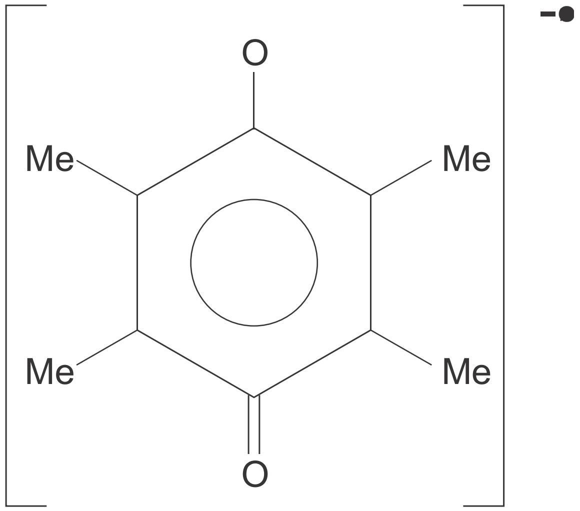
Hyperfine interactions: Semiquinone Radicals

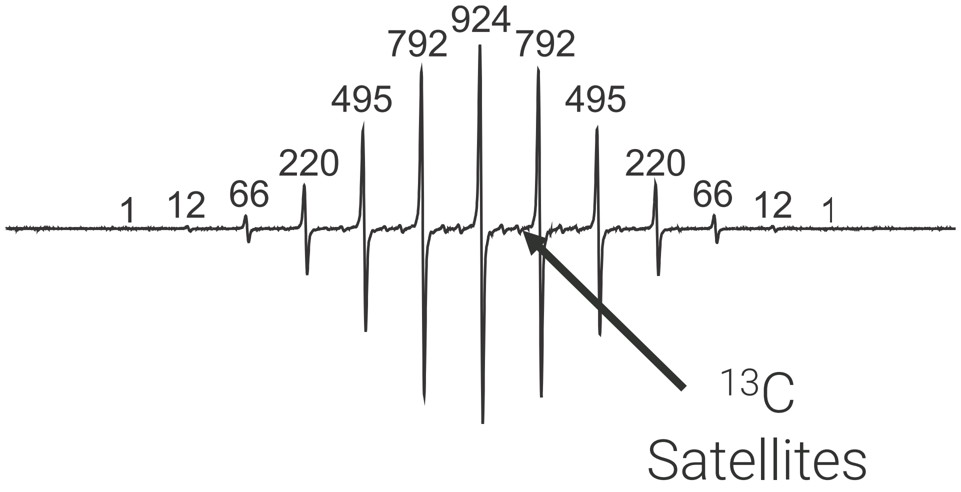




$$\text{Number of Lines} = \prod (2 \cdot N \cdot I + 1)_n = \left(2 \cdot 4 \cdot \frac{1}{2} + 1\right) = 5$$

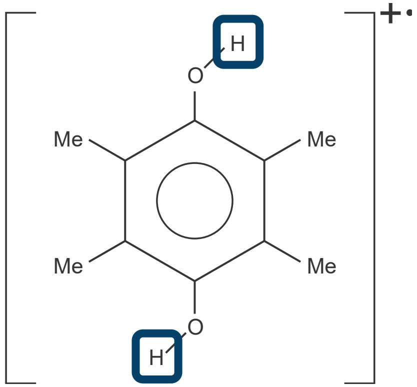
Hyperfine interactions: Semiquinone Radicals

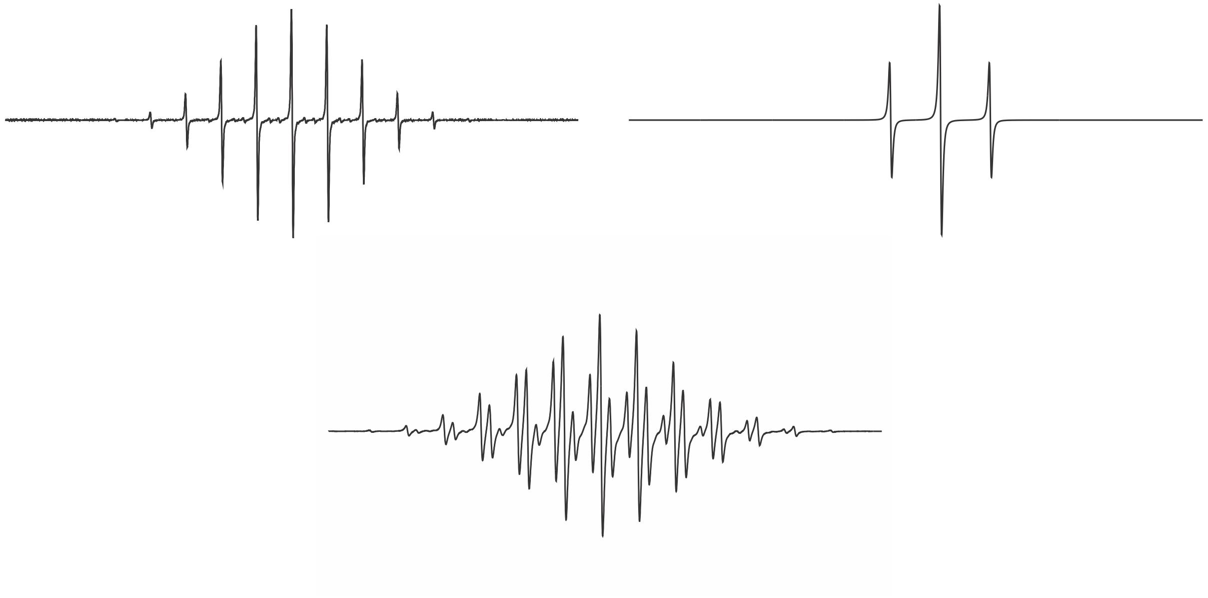




$$\text{Number of Lines} = \prod (2 \cdot N \cdot I + 1)_n = \left(2 \cdot 12 \cdot \frac{1}{2} + 1\right) = 13$$

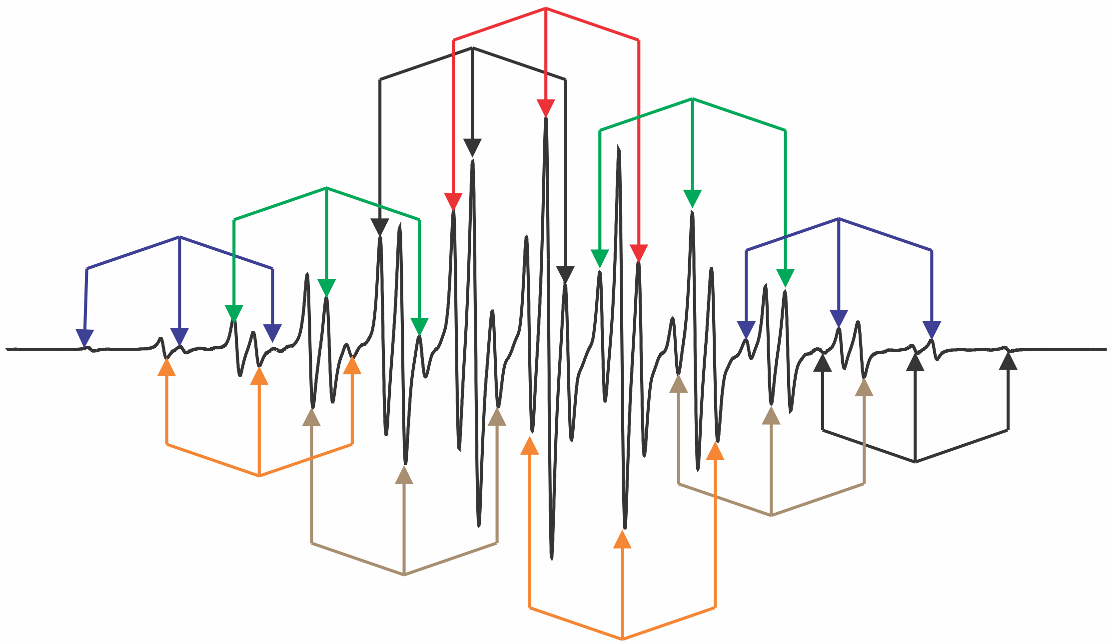
Hyperfine interactions: Semiquinone Radicals





$$\text{Number of Lines} = \prod (2 \cdot N \cdot I + 1)_n = \left(2 \cdot 12 \cdot \frac{1}{2} + 1\right) \cdot \left(2 \cdot 2 \cdot \frac{1}{2} + 1\right) = 39$$

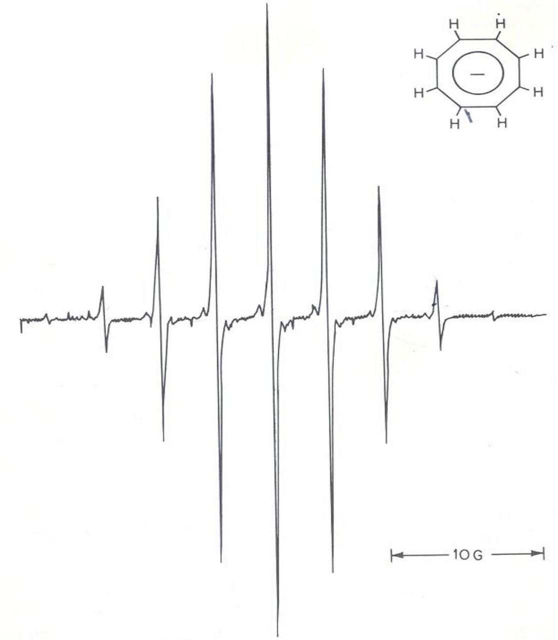
Hyperfine interactions: Semiquinone Radicals



$$\text{Number of Lines} = \prod(2 \cdot N \cdot I + 1)_n = \left(2 \cdot 12 \cdot \frac{1}{2} + 1\right) \cdot \left(2 \cdot 2 \cdot \frac{1}{2} + 1\right) = 39$$

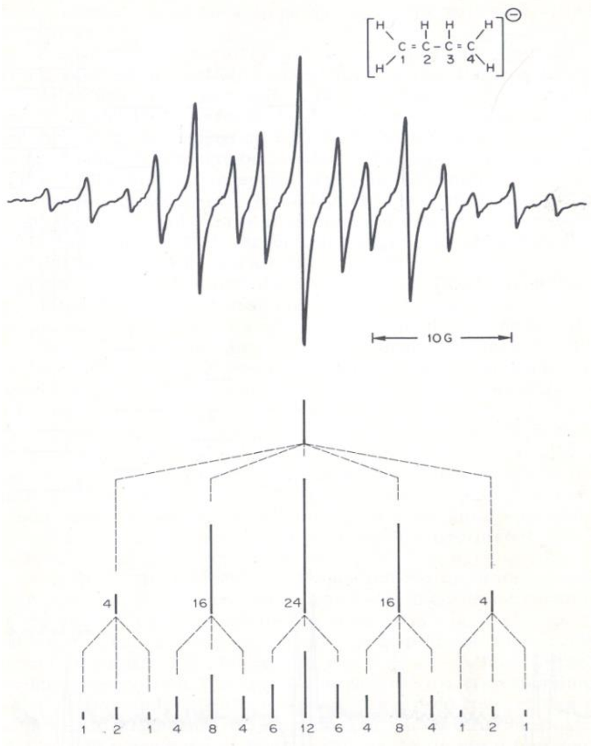
Hyperfine interactions: organic radicals in liquids

Cyclooctatetraen anion



Observation of the 1:8:28:56:70:56:28:8:1 spectrum shows that eight protons are equivalent

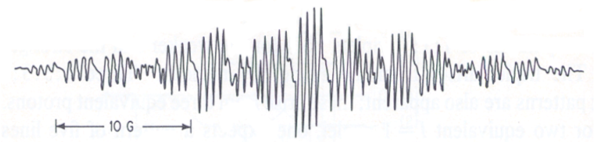
Butadien ion in liquid NH_3



Two sets of equivalent protons: 2 and 4

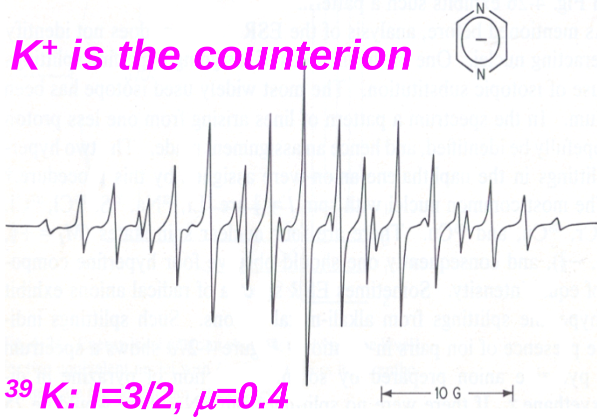
Pyrazine anion

Na^+ is the counterion



^{23}Na: I=3/2, μ=2.22

K^+ is the counterion



^{39}K: I=3/2, μ=0.4

(14641) by (12421) pattern

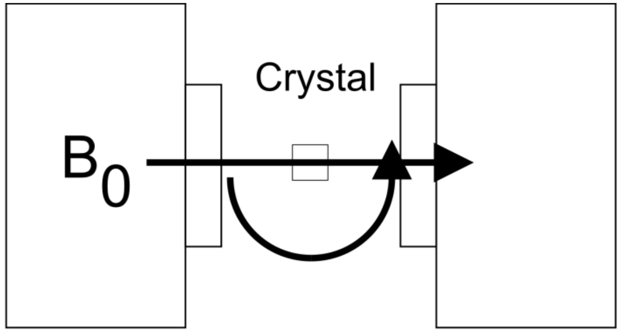
The figures are taken from the textbook by Wertz&Bolton

g-factor vs hyperfine splitting: important difference

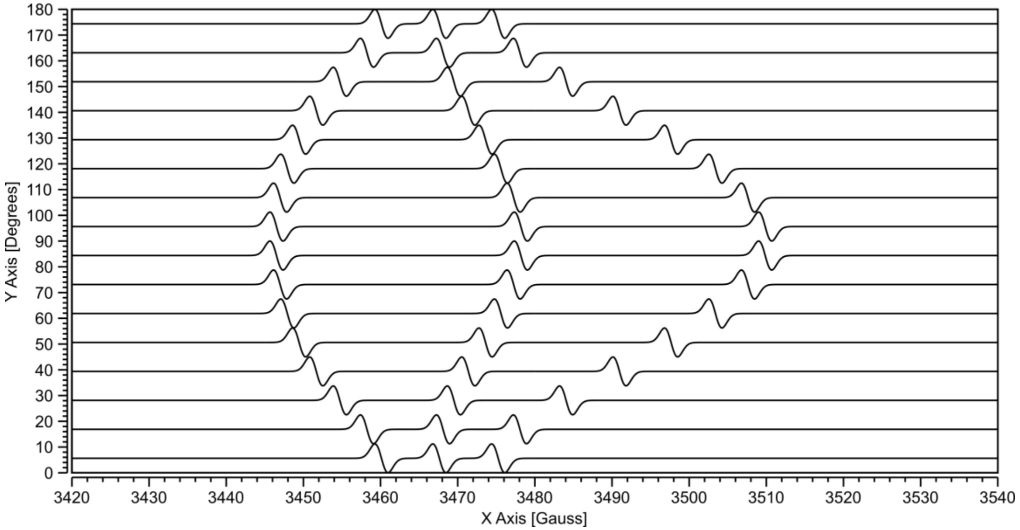
- Spectral splitting between features with different g-factor value increase with increasing EPR frequency
- Spectral splitting due to hyperfine interactions do not depend on the EPR frequency

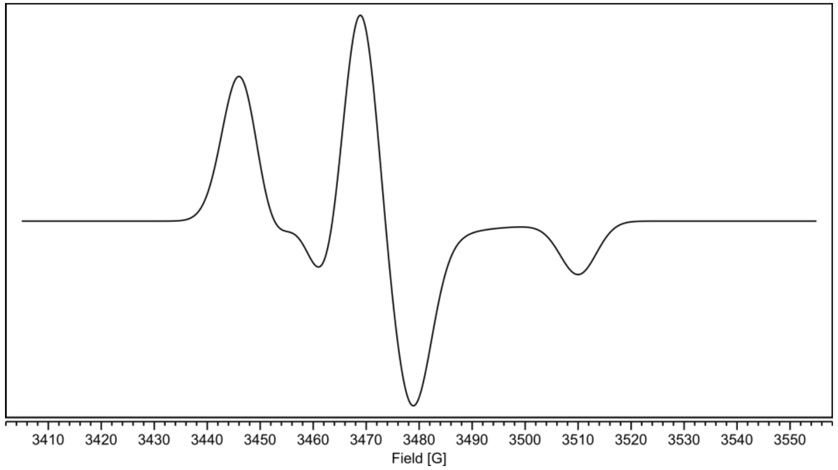
- It is one of the reasons to do EPR at multiple frequencies (Multi Frequency EPR) – and there are more!

Anisotropy of the g-factor and hyperfine interactions



A single crystal





Powder Pattern

Anisotropy of the g-factor and hyperfine interactions

$$\boldsymbol{g} = \begin{bmatrix} g_x & 0 & 0 \\ 0 & g_y & 0 \\ 0 & 0 & g_z \end{bmatrix} \qquad \boldsymbol{A} = \begin{bmatrix} A_x & 0 & 0 \\ 0 & A_y & 0 \\ 0 & 0 & A_z \end{bmatrix}$$

$$g_{eff}^2(\theta, \varphi) = g_x^2\, cos^2\theta cos^2\varphi + \ g_y^2 sin^2\theta cos^2\varphi + g_z^2 sin^2\varphi$$

$$A_{eff}^2(\theta, \varphi) = A_x^2\, cos^2\theta cos^2\varphi + \ A_y^2 sin^2\theta cos^2\varphi + A_z^2 sin^2\varphi$$

Axially symmetric g- and A- matrices: $g_\perp = g_x = g_y \neq g_\parallel = g_z$, $A_\perp = A_x = A_y \neq A_\parallel = A_z$

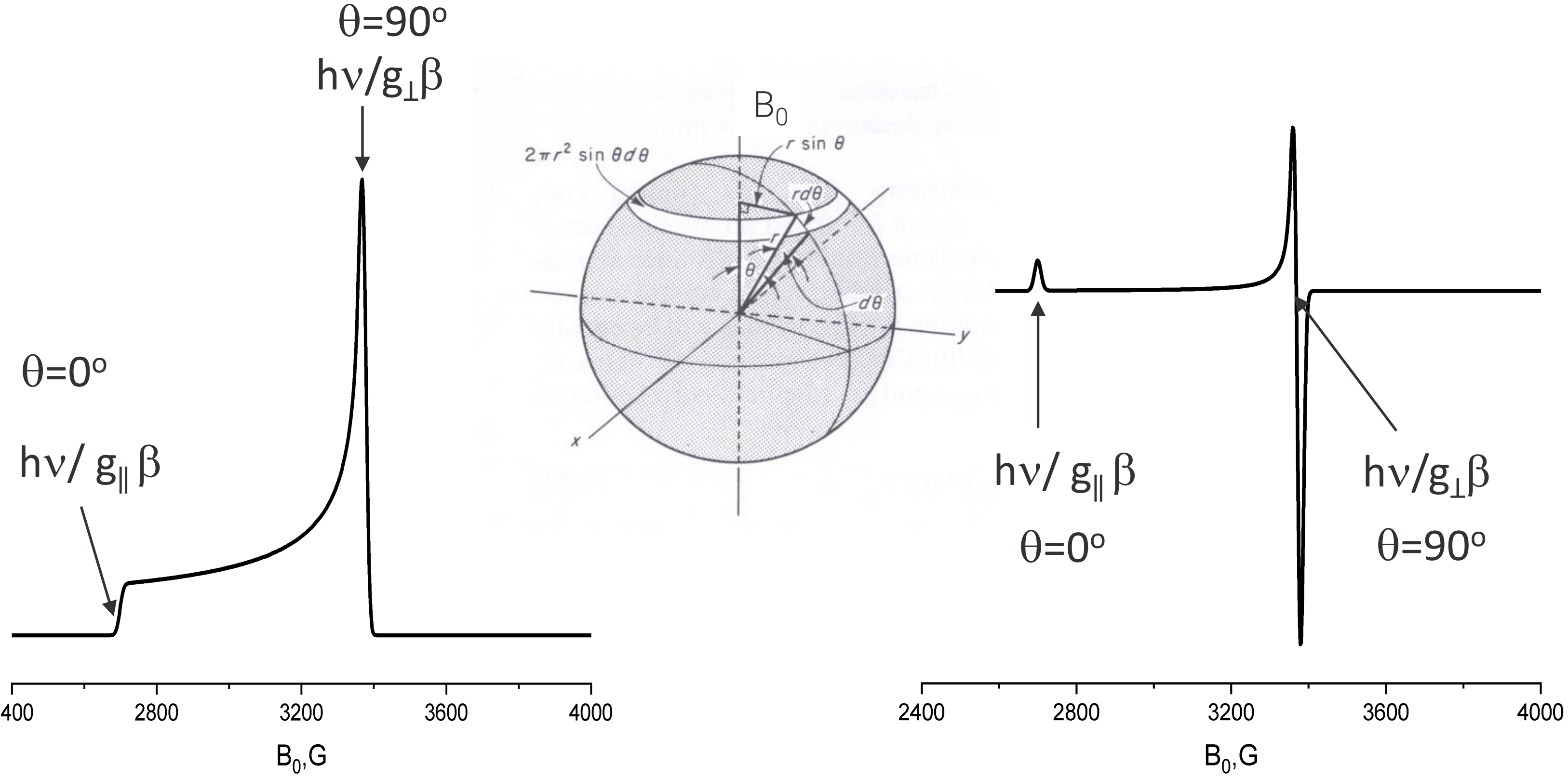
$$g_{eff}^2(\theta) = g_\parallel^2\, cos^2\theta + \ g_\perp^2\, sin^2\theta$$

$$A_{eff}^2(\theta) = A_\parallel^2\, cos^2\theta + \ A_\perp^2\, sin^2\theta$$

Powder spectrum of a radical with an axially symmetric g-factor

$$B_\theta^{res} = \frac{h\nu}{g_{eff}\beta} = \frac{h\nu}{\beta}[g_{II}^2\cos^2\theta + g_\perp^2\sin^2\theta]^{-1/2}$$

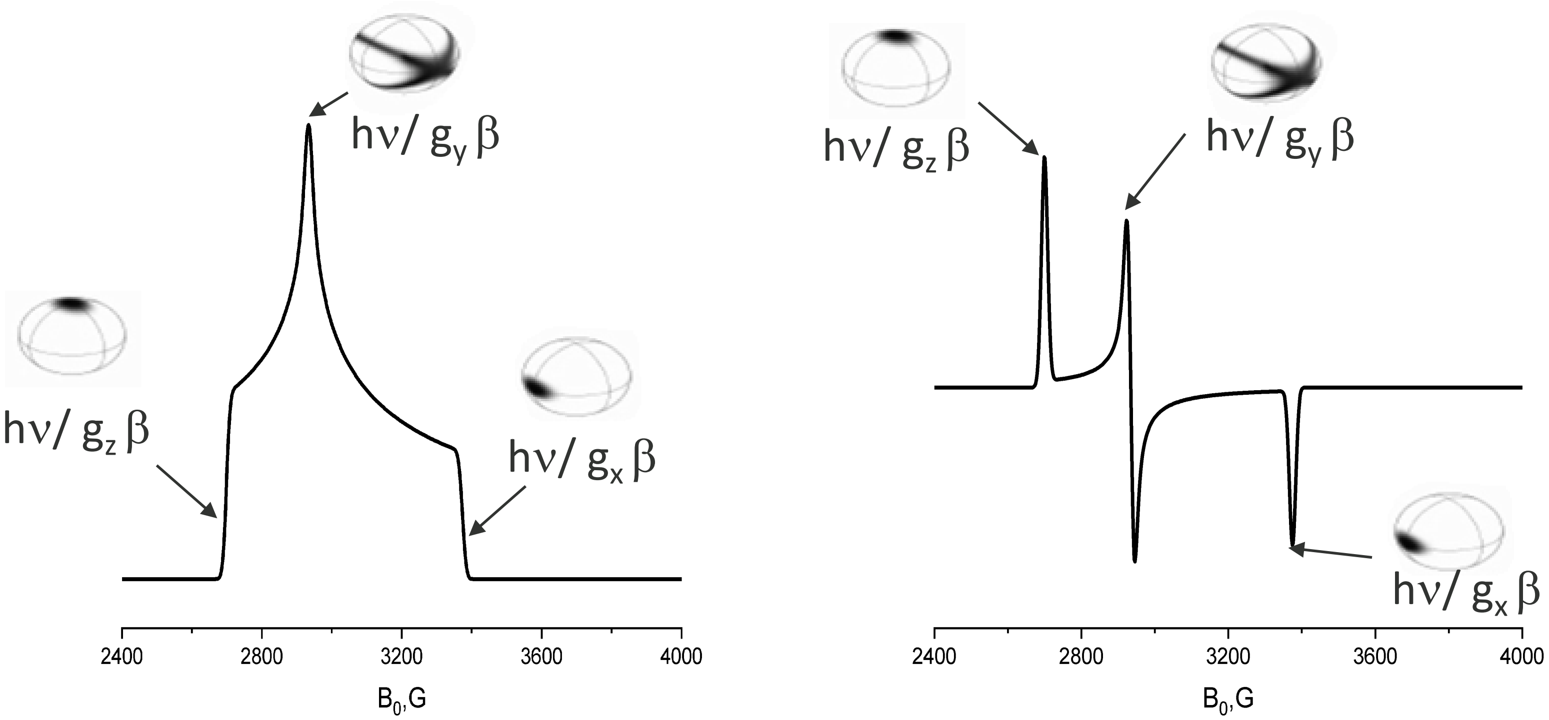
$g_x = g_y = g_\perp < g_z = g_\parallel$



Powder spectrum of a radical with a rhombic g-factor

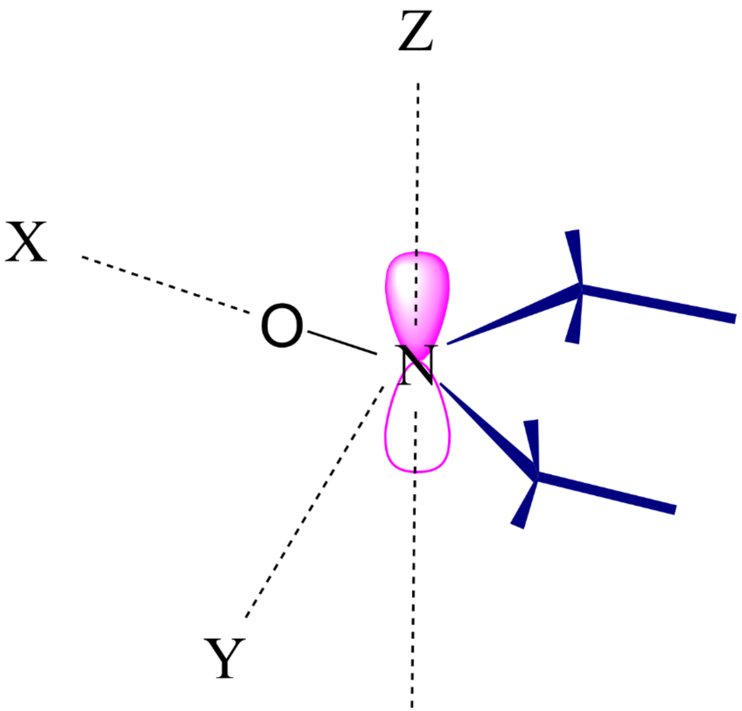
$$B_\theta^{res} = \frac{h\nu}{g_{eff}\beta} = \frac{h\nu}{\beta}\left[g_x^2 cos^2\theta cos^2\varphi + \ g_y^2 sin^2\theta cos^2\varphi + g_z^2 sin^2\varphi\right]^{-1/2}$$

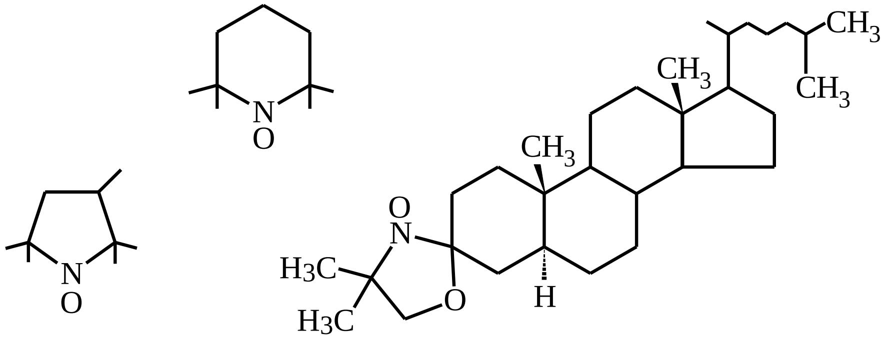
$g_x<g_y<g_z$



Two angles for summation: θ and φ

Anisotropy: Nitroxide Radicals



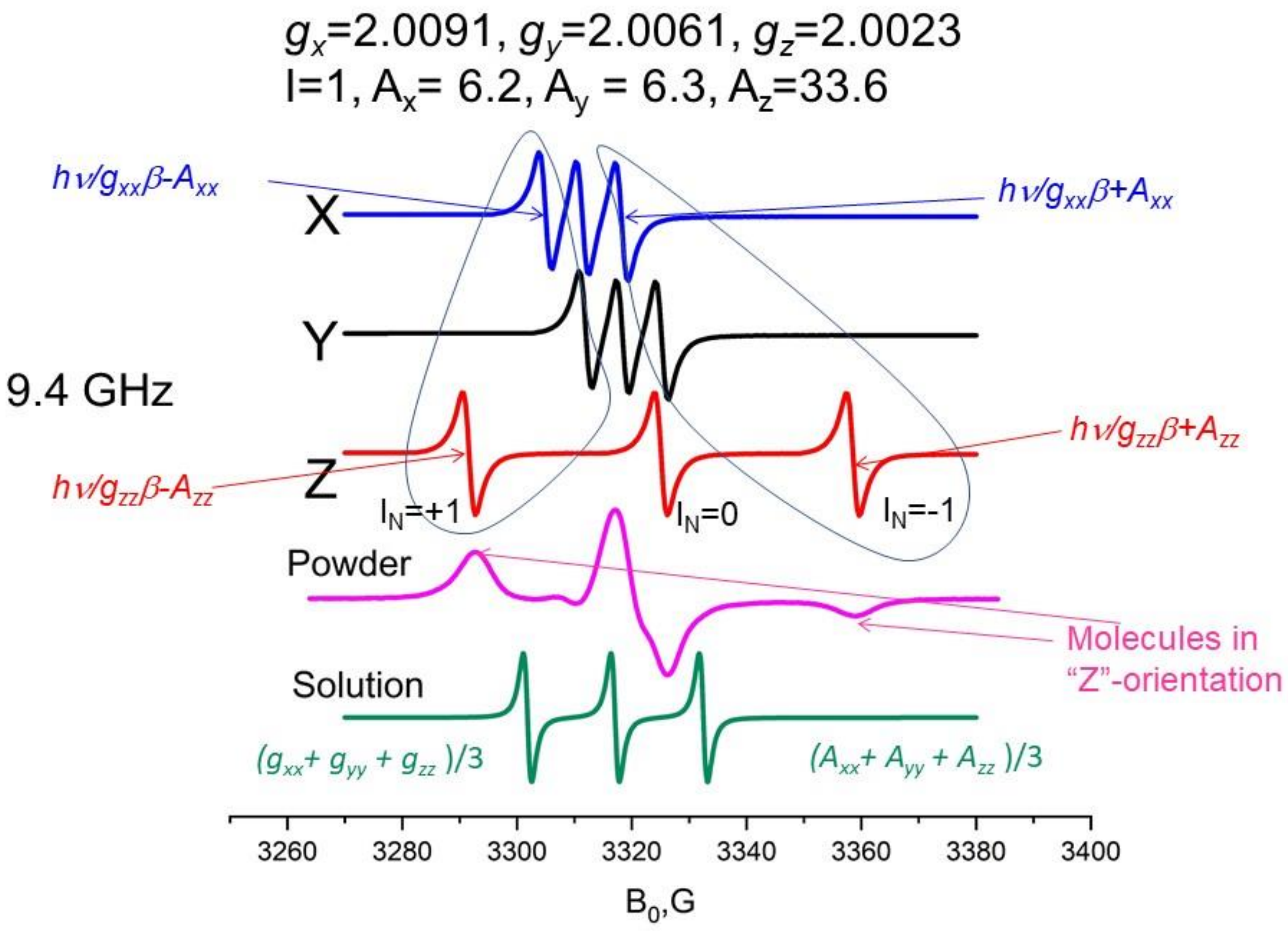


The most used molecules in EPR

The g- and A-tensor frame for a nitroxide radical

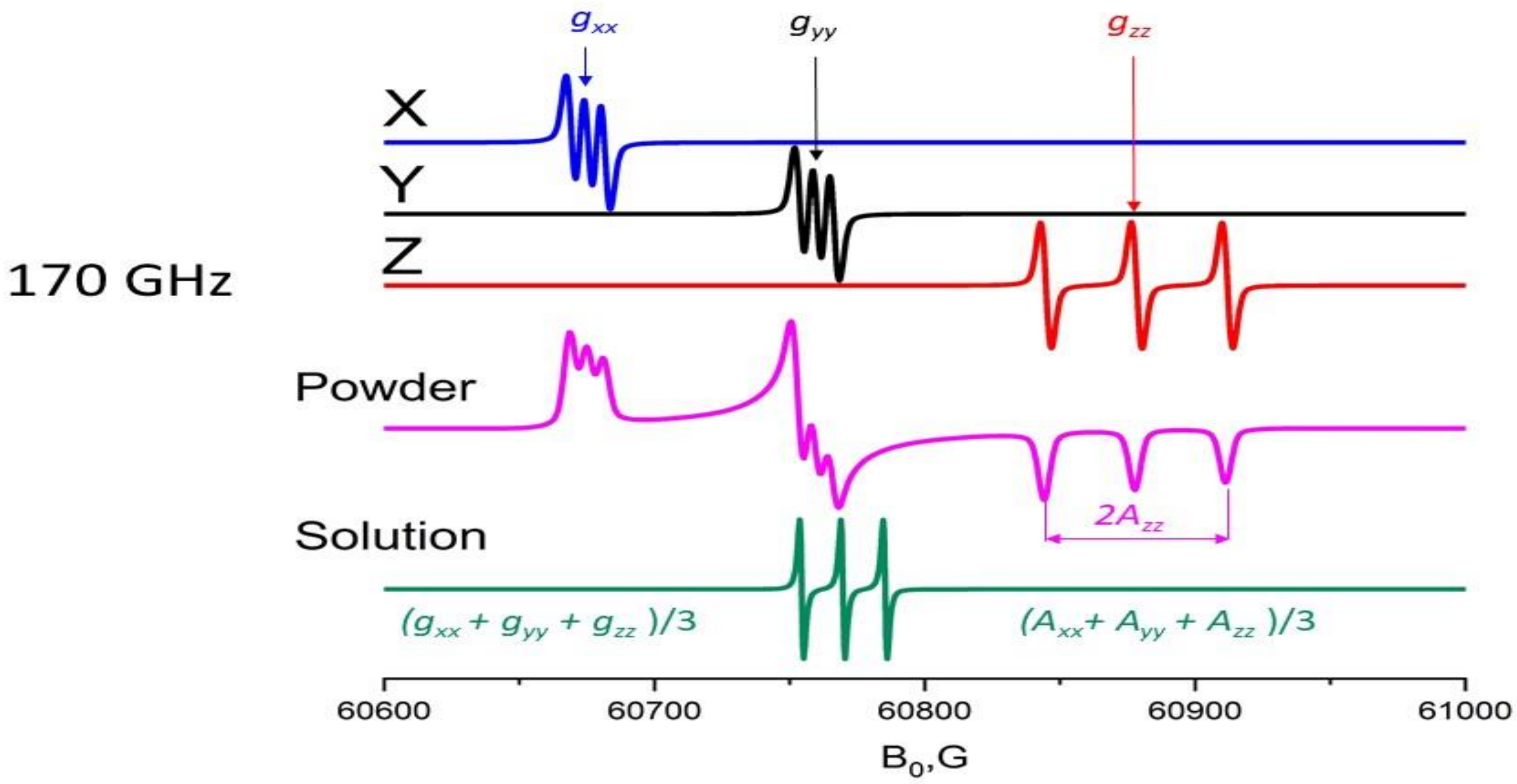
g_x=2.0091, g_y=2.0061, g_z=2.0023
I=1, A_x= 6.2, A_y = 6.3, A_z=33.6

Anisotropy: Nitroxide Radicals



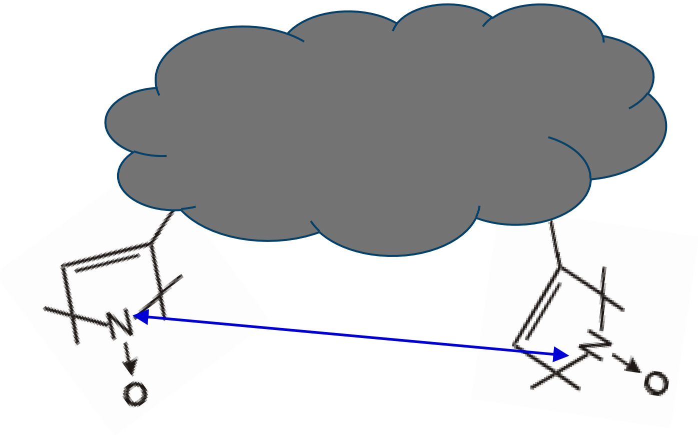
Anisotropy: Nitroxide Radicals. What we see with High Field EPR?

The regions corresponding different orientations of the magnetic axis relative to the external magnetic field do not overlap in the high field EPR spectrum

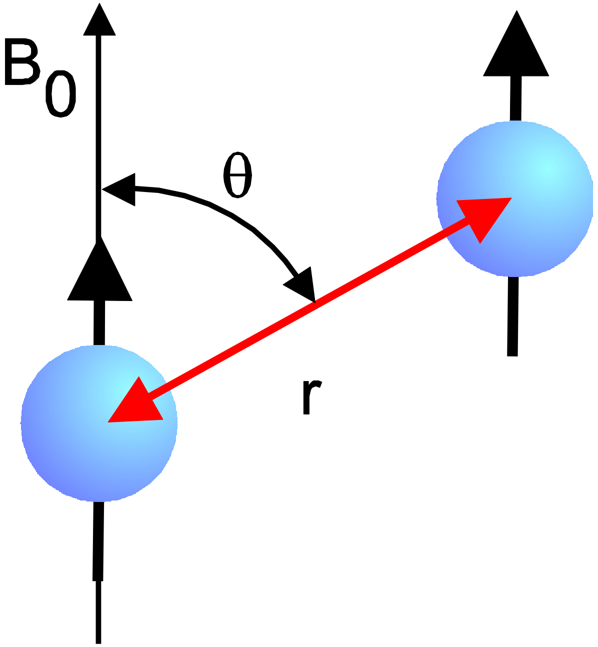


Molecules with S>1/2. Electron-Electron Dipolar Interaction

- Electron-electron dipolar interaction.



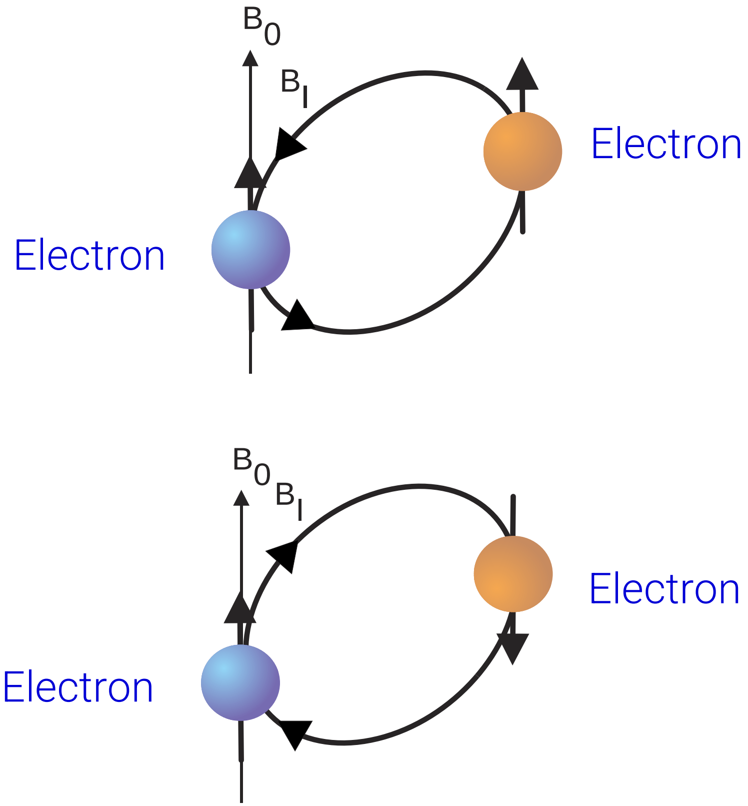
Example: two nitroxide spin labels on the same molecule



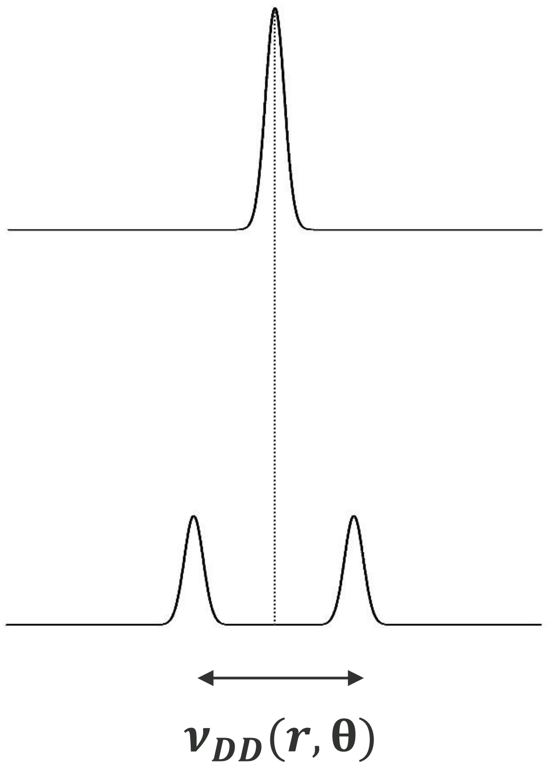
$$\nu_{DD}(r,\theta) = \frac{1}{r^3} g_e^2 \mu_B^2 (3\cos^2\theta - 1)$$

Axially symmetric

Dipolar Splitting for a Single Orientation

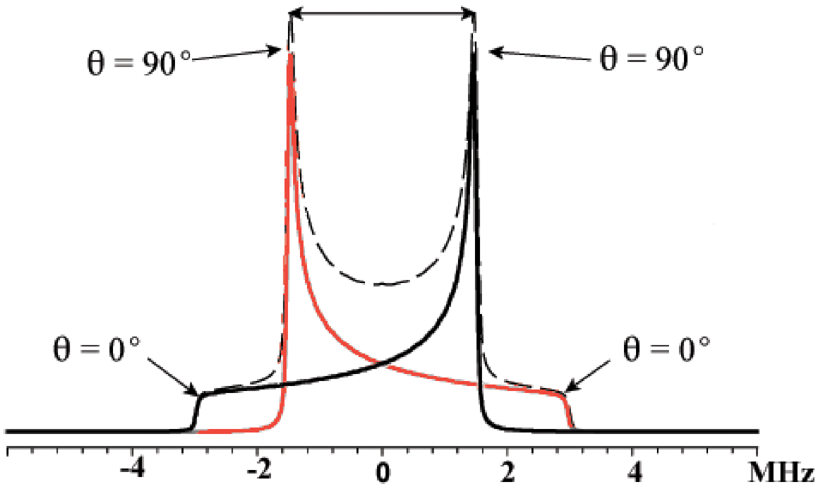


Dipolar Splitting



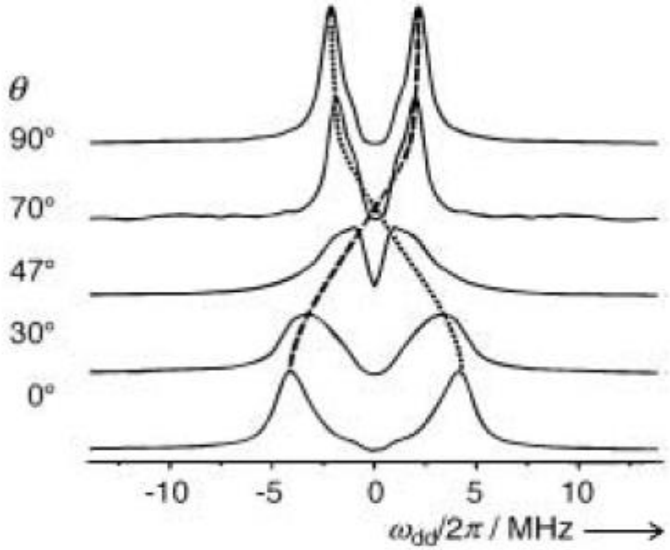
Pake Pattern – a Superposition of all Orientations

$\nu_{DD}(r, \pi/2)$



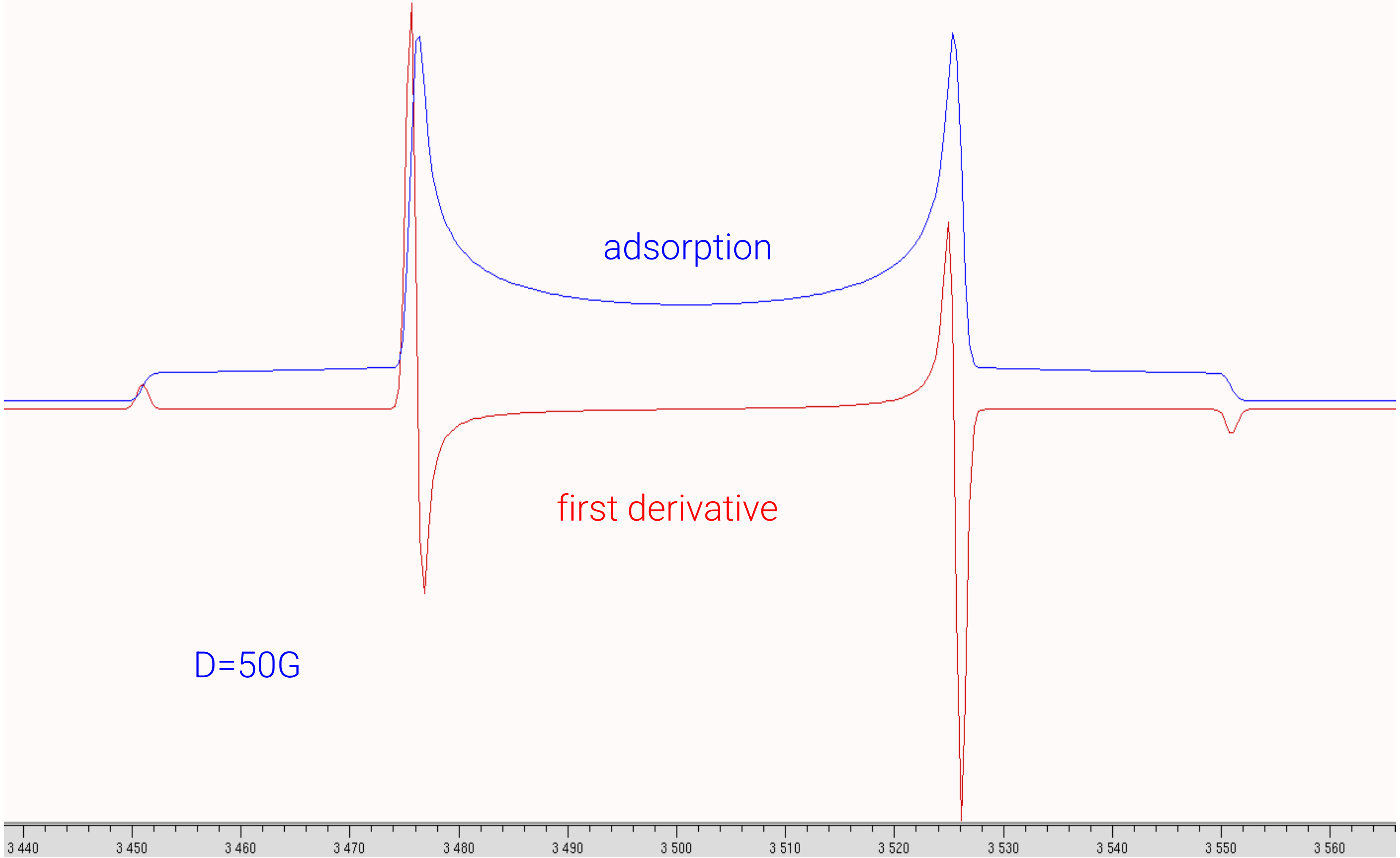
$$\nu_{DD}(r, \theta) = \frac{1}{r^3} g_e^2 \mu_B^2 (3\cos^2\theta - 1)$$

A rigid biradical in the Merck nematic liquid crystal phase



G. Jeschke. Distance Measurements in The Nanometer Range by Pulse EPR. CHEMPHYSCHEM 3, 927-932 (2002)

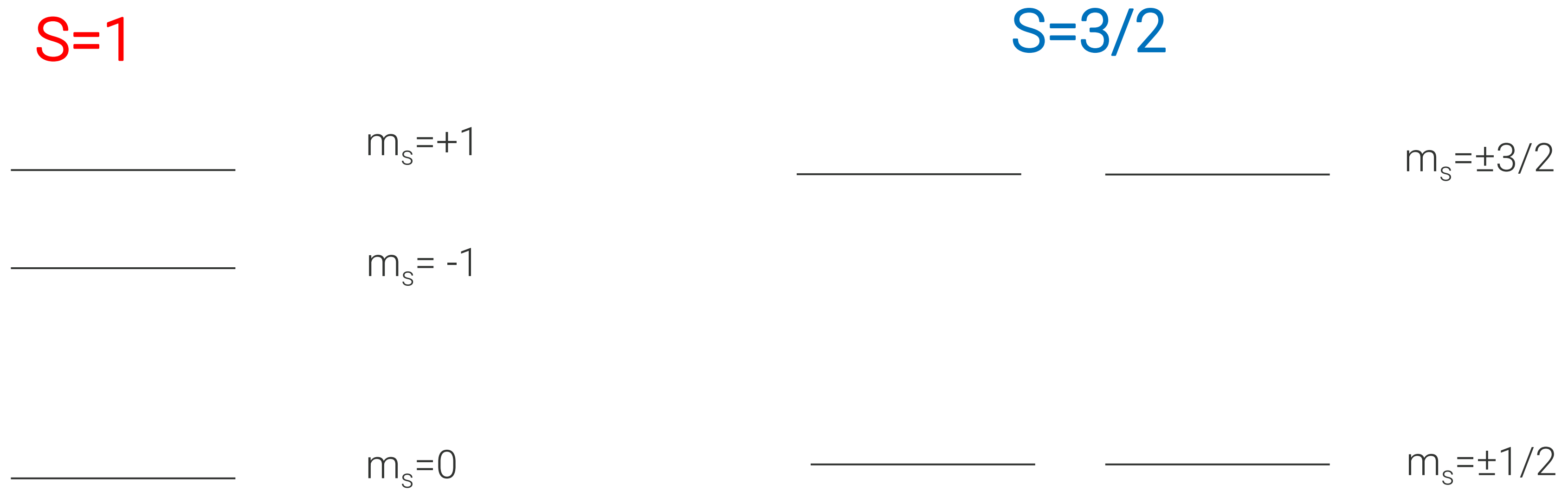
Pake Doublet



Zero-field splitting

A paramagnetic atom having multiple electrons:

- spin-spin and spin-orbit coupling are both involved in the splitting of spin states
- for example, for S=1 we have a singlet and triplet states



S=1

m_s=+1

m_s= -1

m_s=0

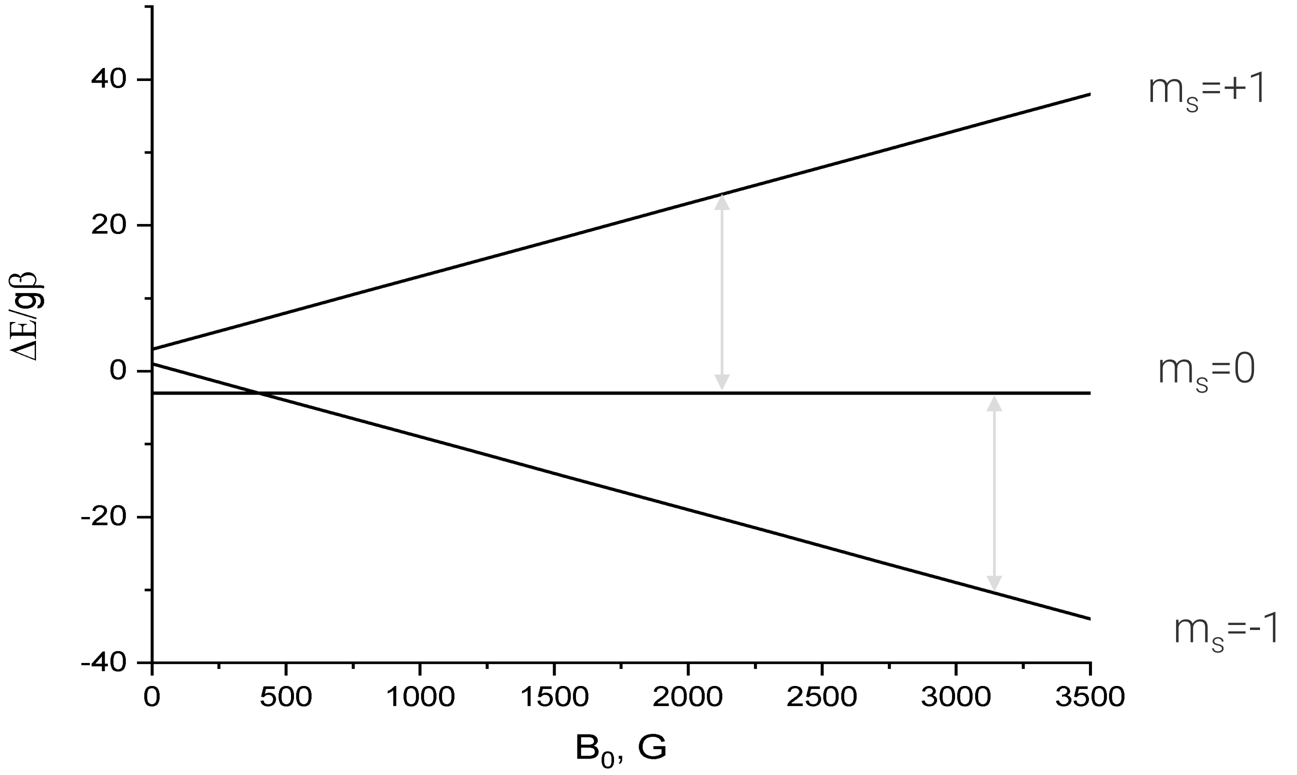
S=3/2

m_s=±3/2

m_s=±1/2

Zero-field splitting

Two EPR transition because of ZFS



Zero-field splitting

$$\hat{H}_{ZFS} = \mathbf{S{\cdot}D{\cdot}S}$$

$$[S_x \quad S_y \quad S_z] \times \begin{bmatrix} D_{xx} & 0 & 0 \\ 0 & D_{yy} & 0 \\ 0 & 0 & D_{zz} \end{bmatrix} \times \begin{bmatrix} S_x \\ S_z \\ S_z \end{bmatrix}$$

$$\hat{H}_{ZFS} = D_{XX}\,\hat{S}_X{}^2 + D_{YY}\,\hat{S}_Y{}^2 + D_{ZZ}\,\hat{S}_Z{}^2$$

Traceless matrix

$$D_{XX} + D_{YY} + D_{ZZ} = 0$$

$$\hat{S}^2|\psi\rangle = S(S+1)\,|\psi\rangle$$

$$D = \begin{bmatrix} -\frac{1}{3}D + E & 0 & 0 \\ 0 & -\frac{1}{3}D - E & 0 \\ 0 & 0 & \frac{2}{3}D \end{bmatrix}$$

D and E are directly measurable parameters

$$\hat{H}_{ZFS} = D\,[\hat{S}_Z{}^2 - S(S+1)/3] + E\,(\hat{S}_X{}^2 - \hat{S}_Y{}^2)$$

Zero-field splitting. Rhombicity

E/D ratio called *rhombicity* of the zero-field splitting:

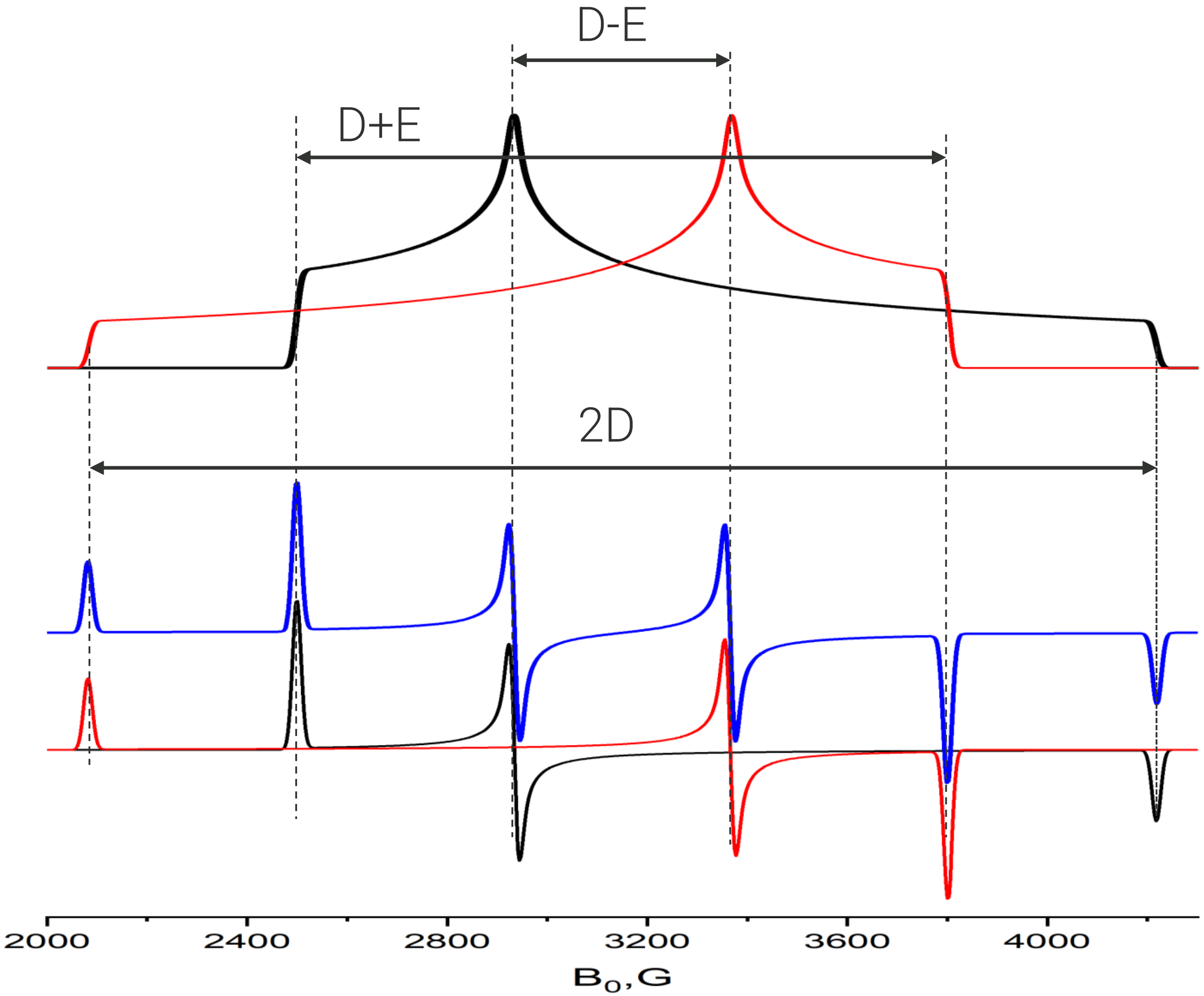
$0 \geq$ *rhombicity* $\geq 1/3$

$D=0$, $E=0$ for an isotropic system

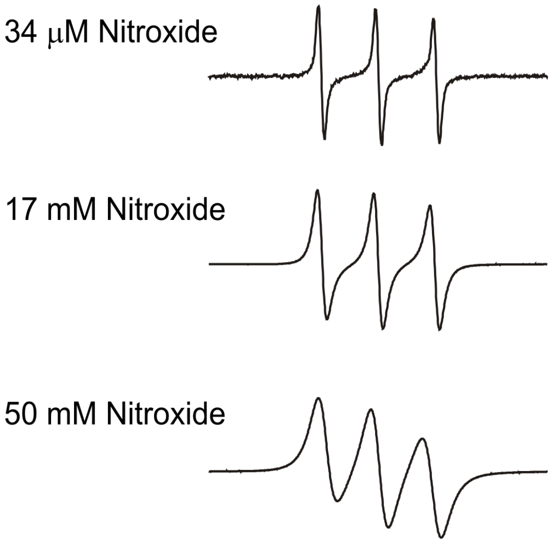
$D \neq 0$, $E=0$ for an axial system

$D \neq 0$, $E \neq 0$ for a rhombic system

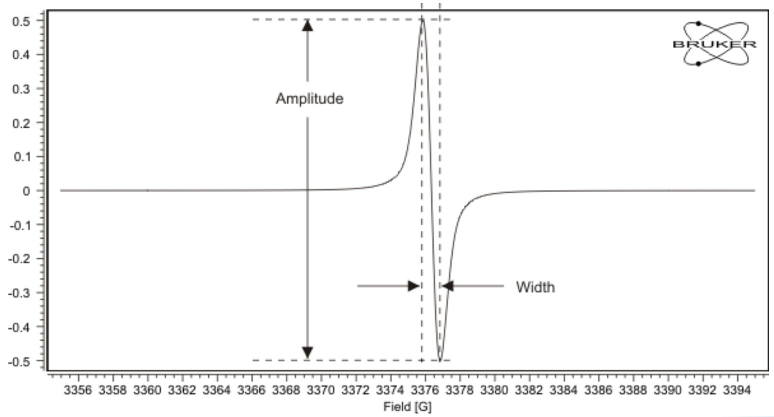
Zero-field splitting

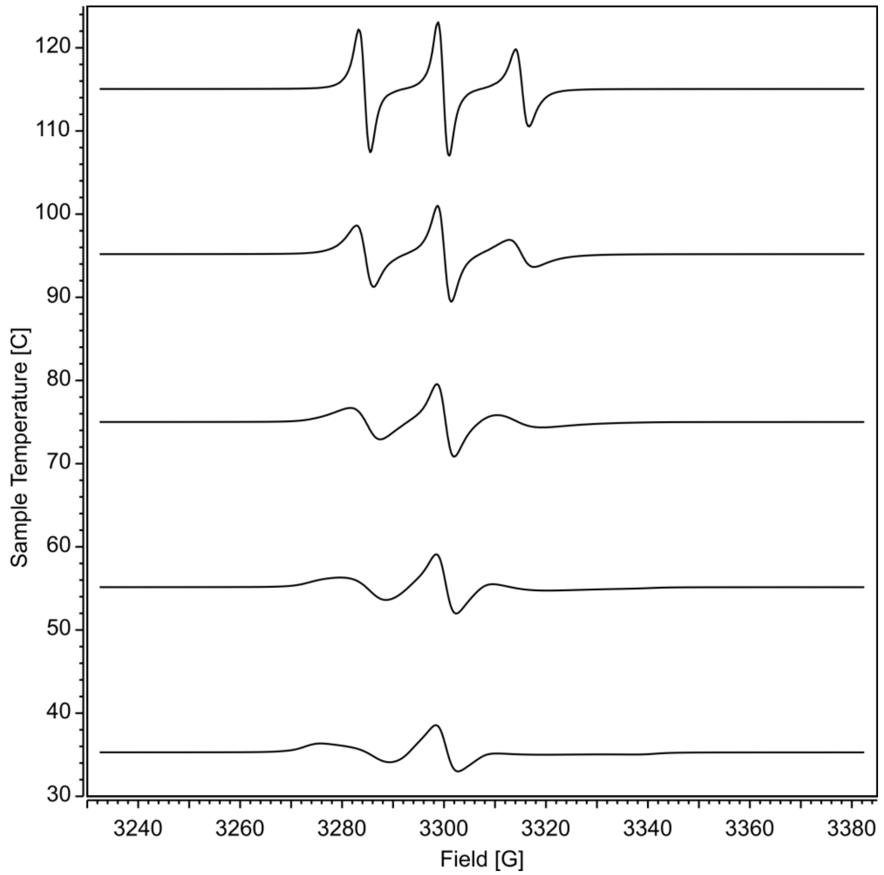


Lineshape and Linewidth



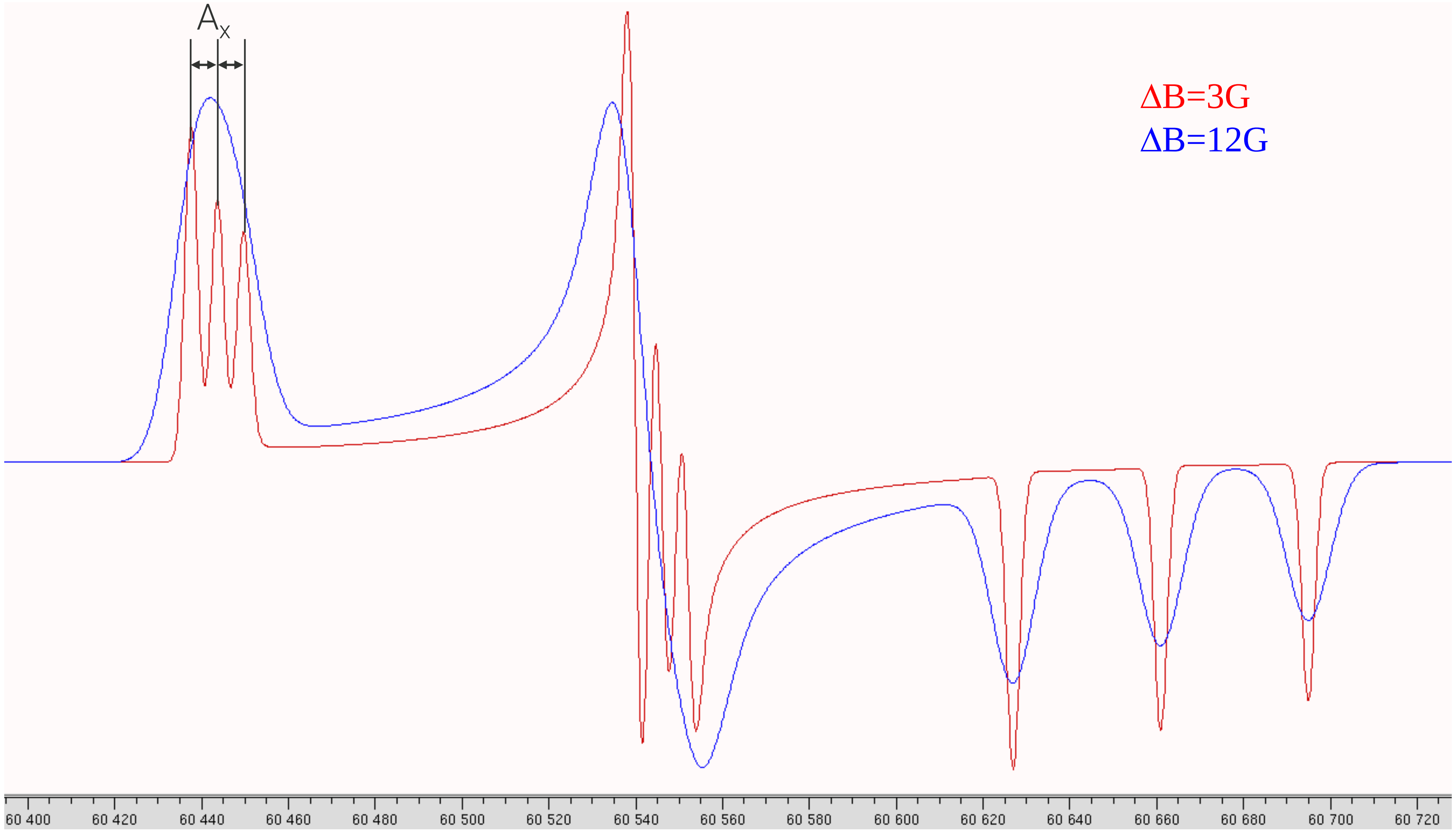
Concentration effect





Motional dynamics effect

Intrinsic Linewidth



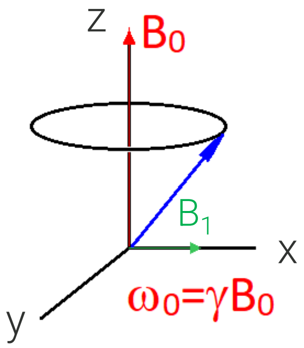
Relaxation processes

Relaxation is described by the Bloch equations

$$\frac{dM_{x'}}{dt} = (\omega_0 - \omega)M_{y'} - \frac{M_{x'}}{T_2}$$

$$\frac{dM_{y'}}{dt} = -(\omega_0 - \omega)M_{x'} - \frac{M_{y'}}{T_2}$$

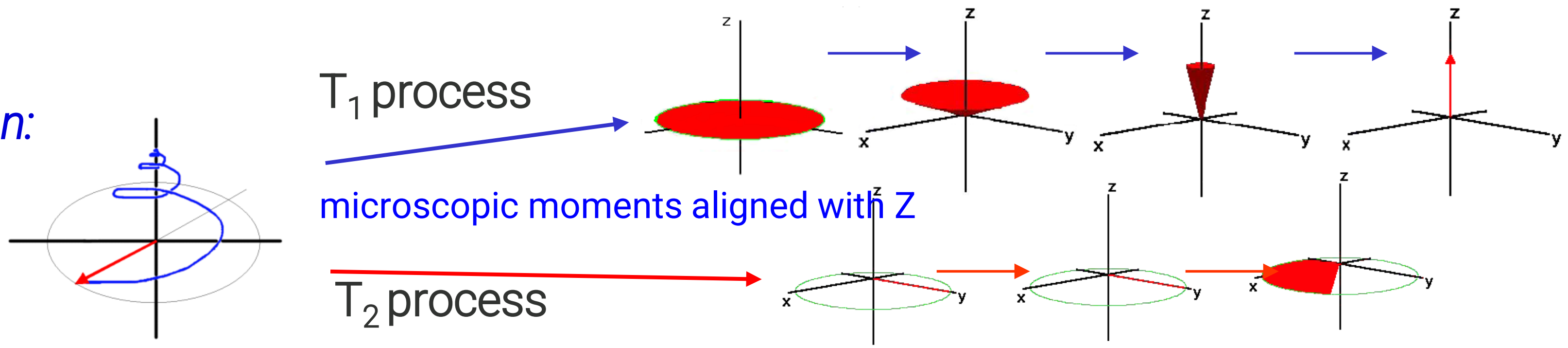
$$\frac{dM_z}{dt} = -\frac{(M_z - M_{z_0})}{T_1}$$



$M_{x'}, M_{y'}, M_z$ – magnetization components in the *rotating frame*

$\omega_0=\gamma_e B_0$ – the *Larmor Frequency*

Relaxation:



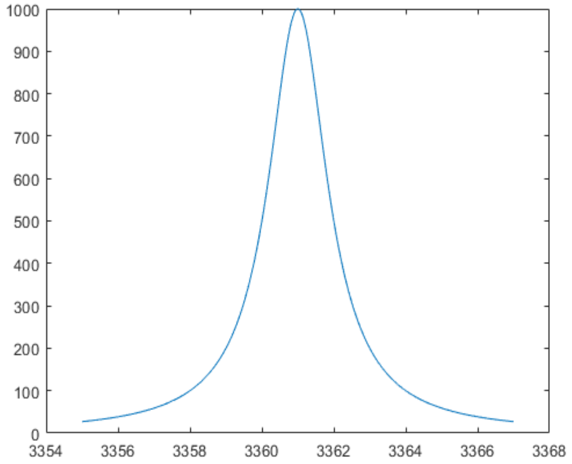
T_1 process

microscopic moments aligned with Z

T_2 process

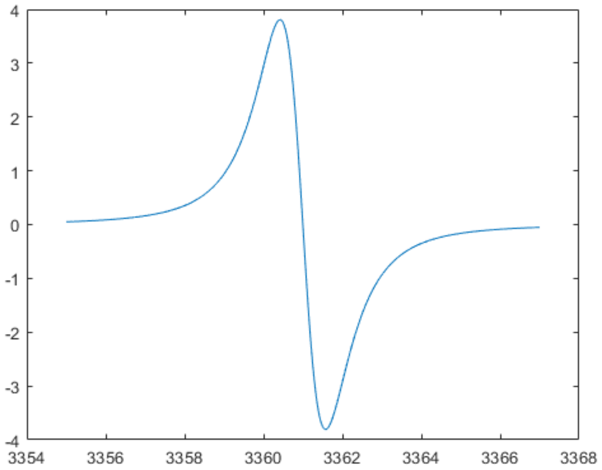
The microscopic moments are still precessing, but the coherence is lost and their vector sum is collinear with Z

EPR Line Shapes. Lorentzian Line: homogeneous broadening



$$F(H) = \frac{\gamma T_2}{\pi} \frac{1}{1 + \gamma^2 T_2^2 (B - B_0)^2}$$

Ex: for T_2=1ns, Linewidth~115G



$$\frac{1}{T_2'} = \gamma_e \Delta B$$

$$\gamma_e = 1.76 \bullet 10^7 \, rad/(s \cdot G)$$

ΔB: *half width at half height*

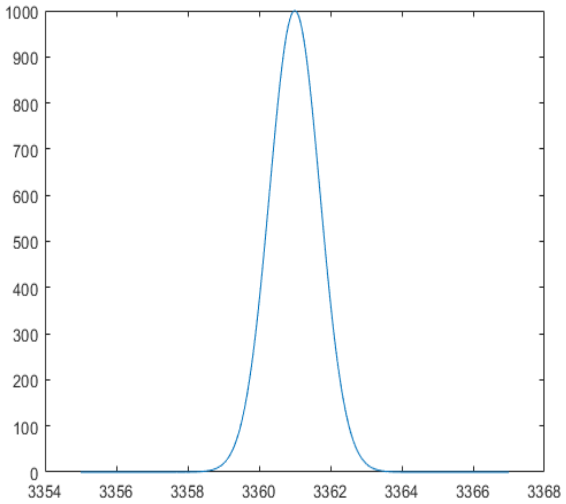
Lorentzian Line Shape is related to the ***Lifetime Broadening***:

ΔWΔt≥h/2π *Heisenberg uncertainty principle for energy and time*

Small value of *Δt* value will lead to a large *ΔW* and hence to a smearing of the energy levels and broadening of EPR lines.

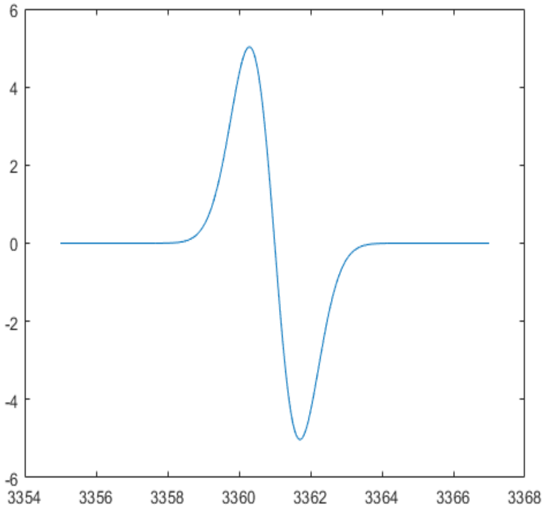
EPR Line Shapes. Gaussian Line

Due to inhomogeneous broadening: non-uniform magnetic field on the sample, unresolved hyperfine splitting etc.



$$F(H) = Amp \times \exp(-\frac{(B-B_0)^2}{(\Delta B)^2} ln2)$$

$$\Delta B \; half \; width \; at \; half \; height$$

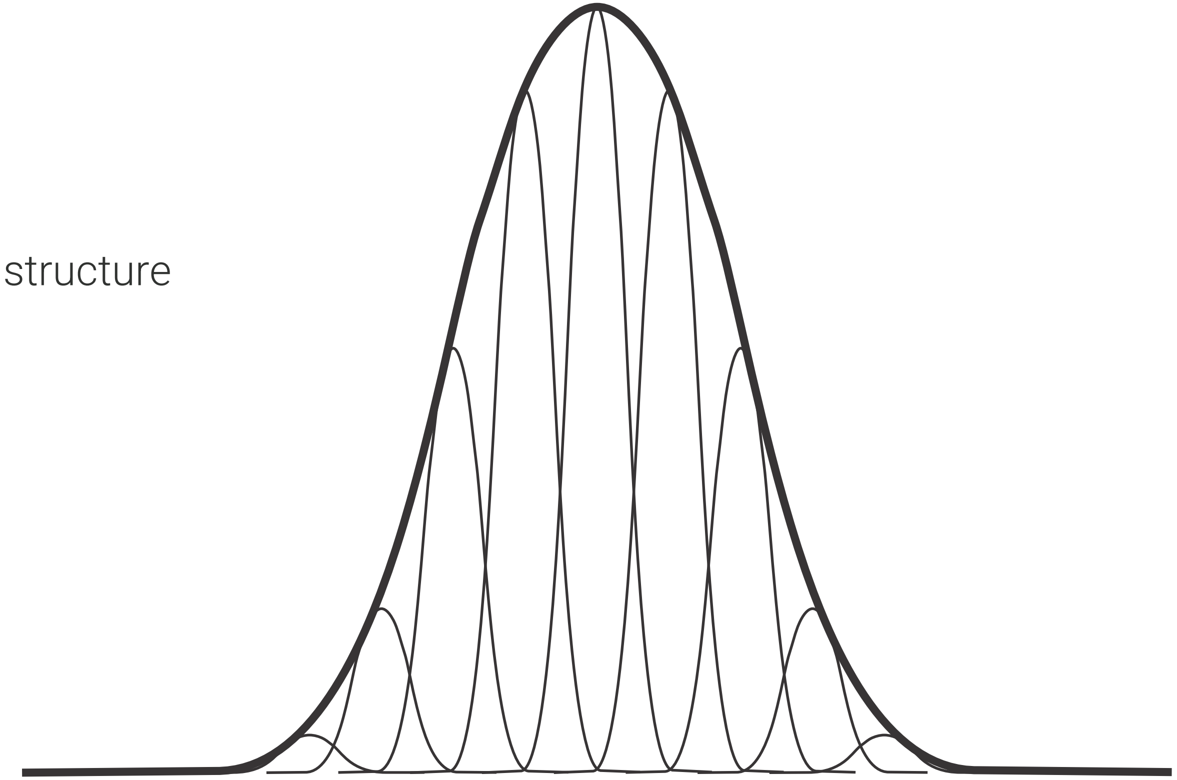


Voigtian line, obtained by convolution of Lorentzian and Gaussian:

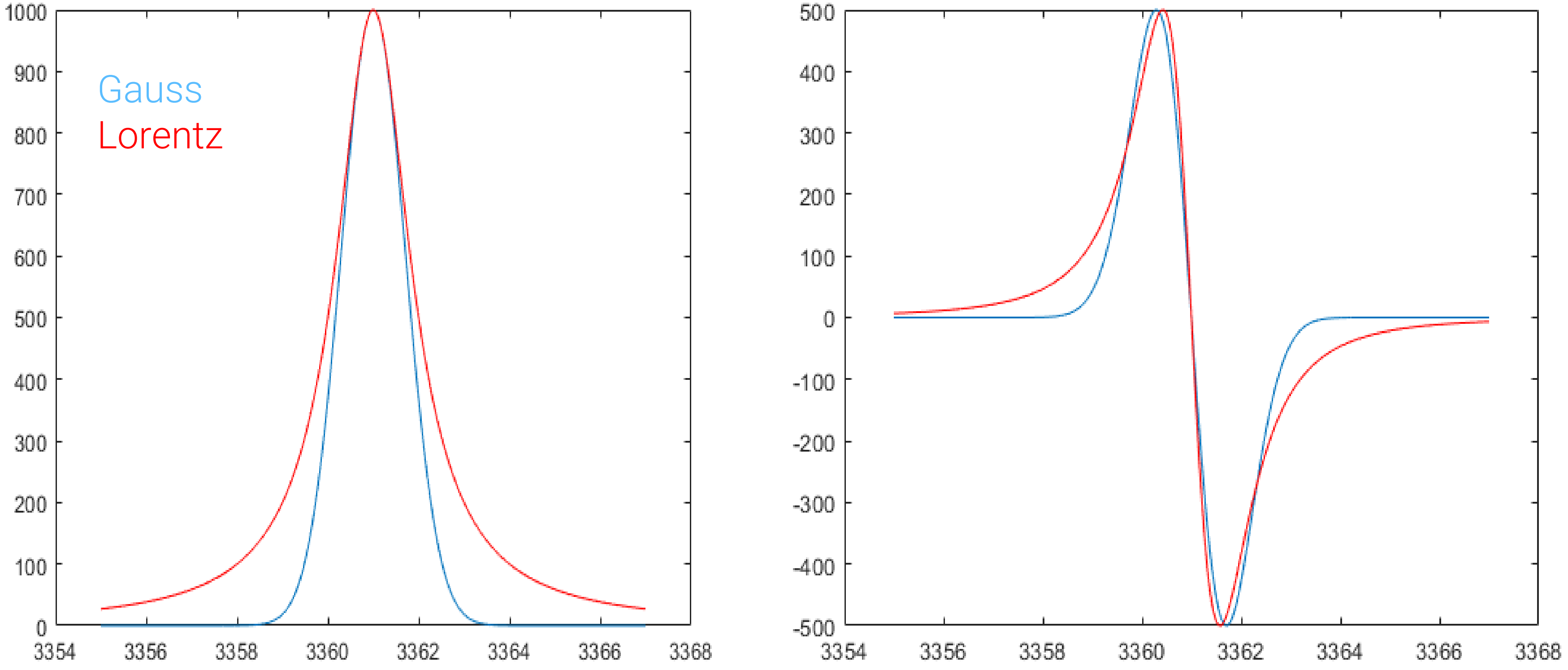
$$F(H) = \int_{-\infty}^{+\infty} G(B_1) \times L(B_1 - B) dB_1$$

EPR Line Shapes. Gaussian Line

Unresolved hyperfine structure

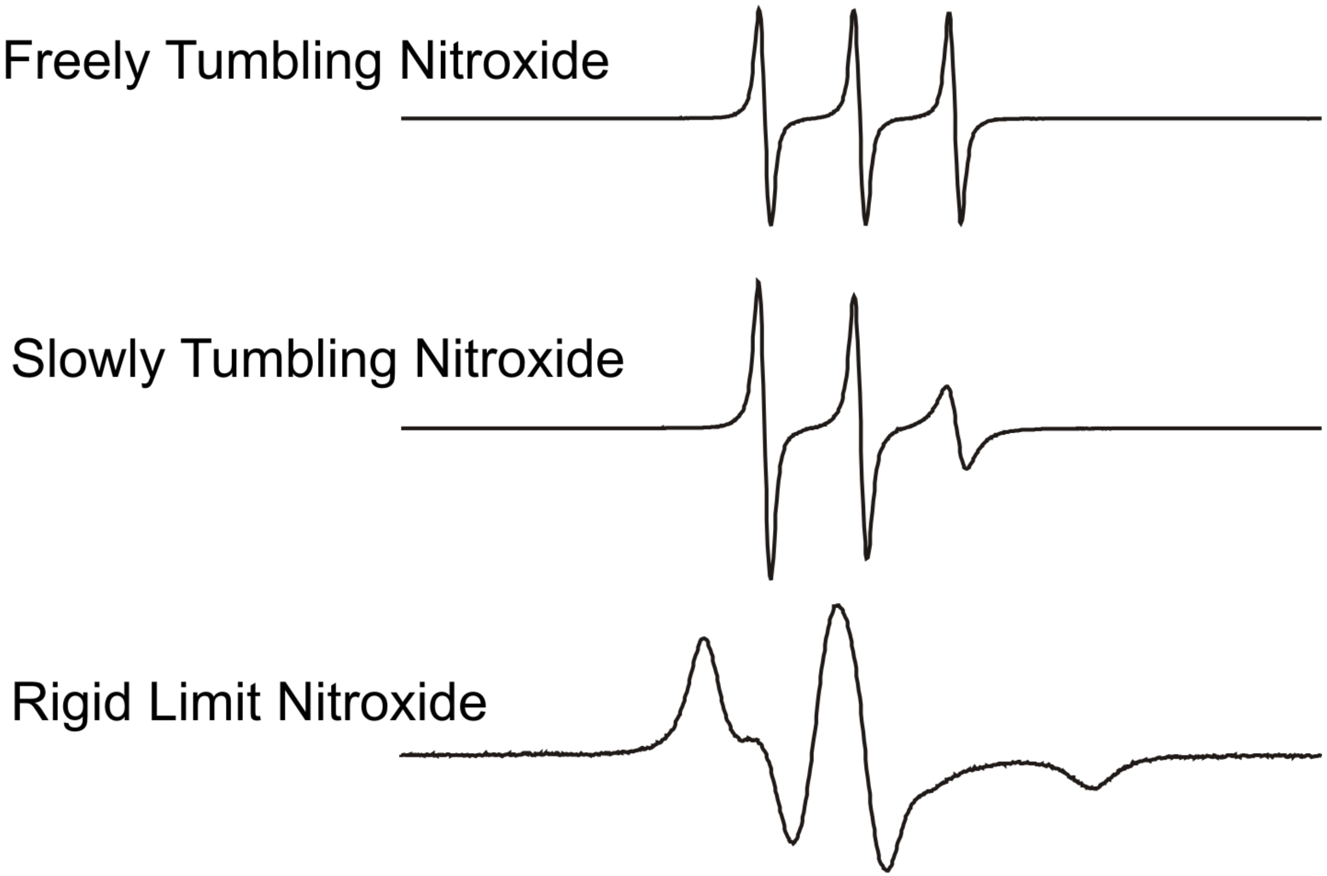


Gauss vs Lorentz

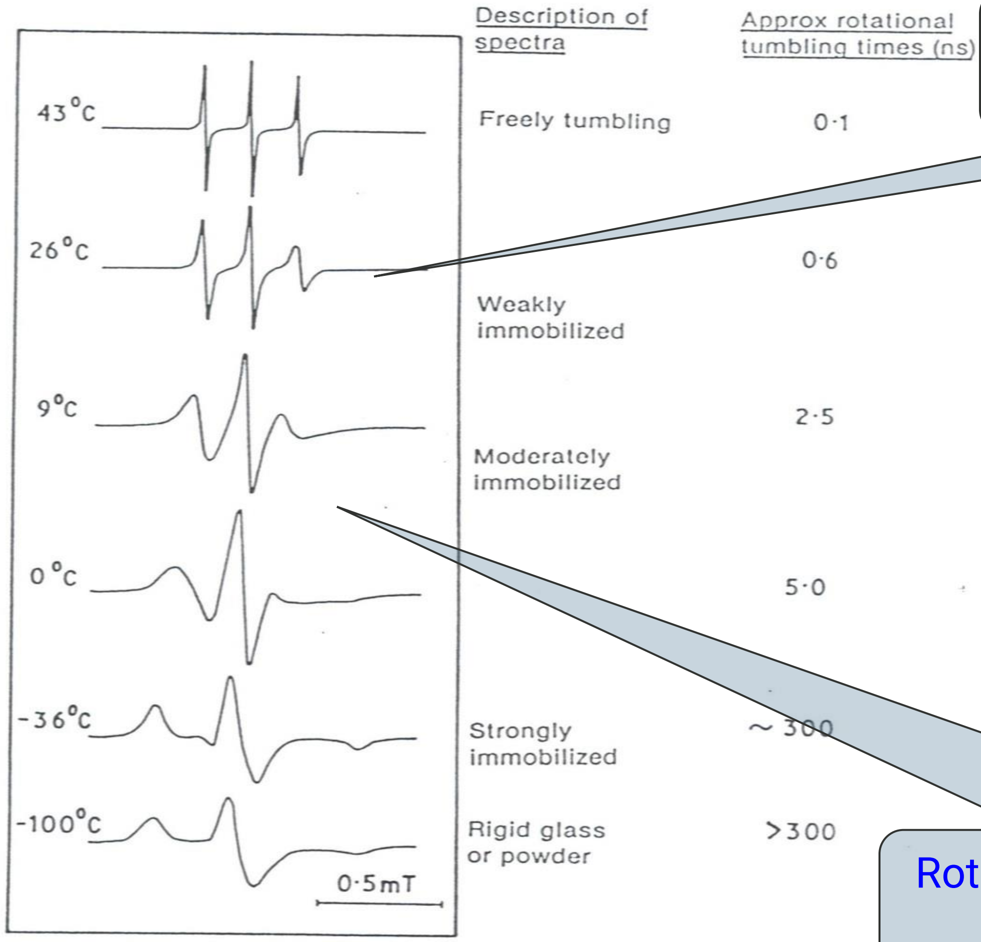


Note a quicker decay of the wings for the Gaussian shape.

Lineshape and Linewidth: Molecular Motion

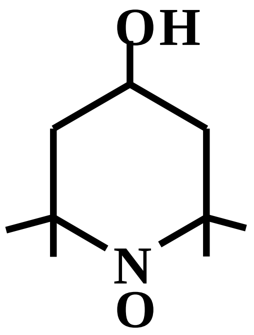


EPR is sensitive to molecular motion – in a very appropriate range for chemistry and biology!



	Description of spectra	Approx rotational tumbling times (ns)
43°C	Freely tumbling	0·1
26°C		0·6
	Weakly immobilized	
9°C		2·5
	Moderately immobilized	
0°C		5·0
-36°C	Strongly immobilized	~ 300
-100°C	Rigid glass or powder	>300

Tempol in water/glycerol at different temperatures

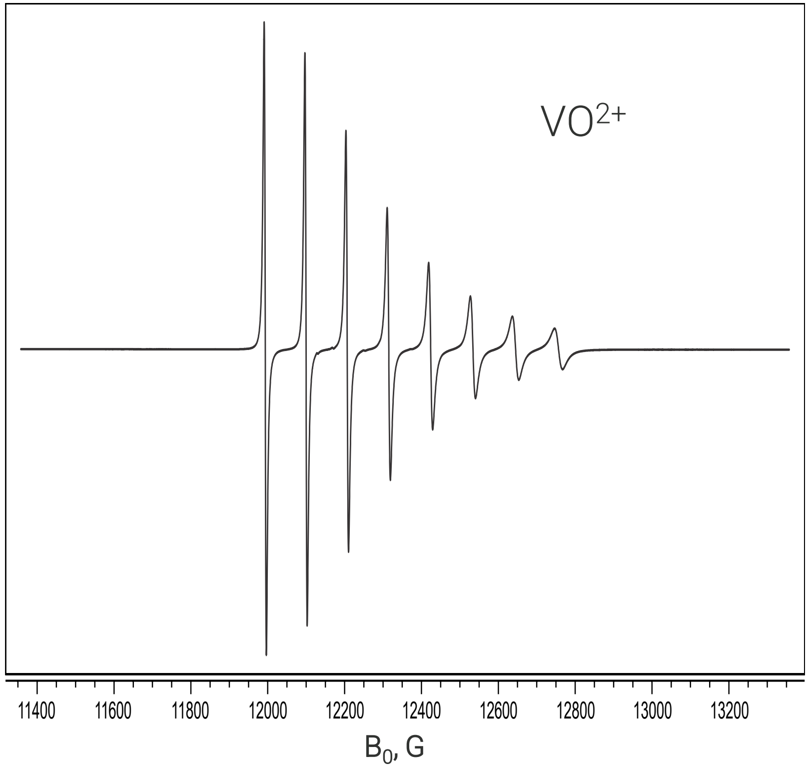


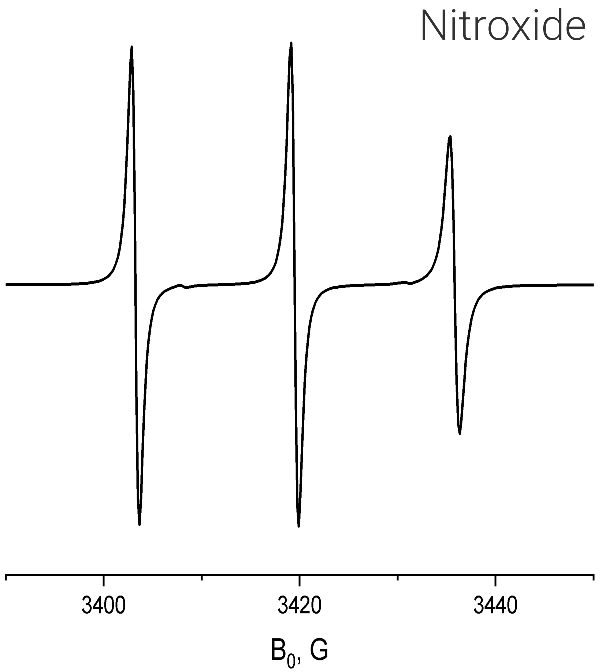
$$\tau = \frac{\eta V}{kT}$$

(Stocks-Einstein)

Rotation correlation times between 10^{-11} and 10^{-6} s are detectable by EPR

Kivelson Theory

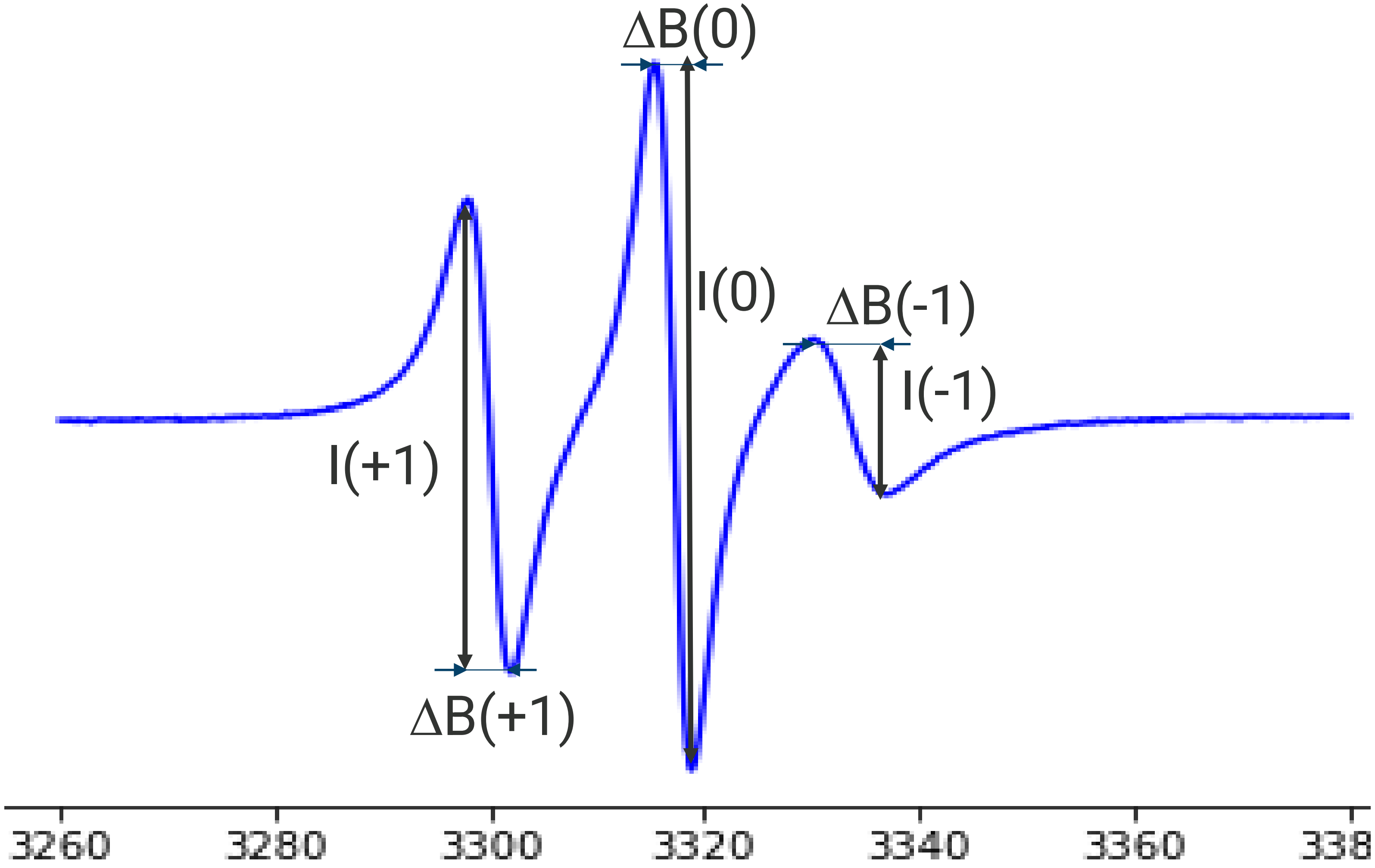




$$\text{Linewidth } = A + Bm_I + Cm_I^2$$

$$\text{Integrated Intesity} \propto = Amplitude \cdot Line\ Width^2$$

Kivelson Theory



Kivelson Theory: nitroxide radicals

Calculation of rotation correlation times for fast isotropic tumbling

The parameters *B* and *C* are related to peak-to-peak amplitudes, $I(m_I)$ by:

$$B = \frac{1}{2}\left[\sqrt{\frac{I(0)}{I(+1)}} - \sqrt{\frac{I(0)}{I(-1)}}\right] \qquad C = \frac{1}{2}\left[\sqrt{\frac{I(0)}{I(+1)}} + \sqrt{\frac{I(0)}{I(-1)}} - 2\right]$$

The high-field line has $m_I = -1$.
Tumbling correlation times are calculated from B and C using

$$\tau = B\left[\left(\frac{2\hbar}{\sqrt{3}g_o\beta}\right)\left(\frac{4B_o}{15}\right)(b\Delta\gamma)\left(\frac{1}{\Delta B_o}\right)\right]^{-1} \quad \text{and} \quad \tau = C\left[\left(\frac{2\hbar}{\sqrt{3}g_o\beta}\right)\left(\frac{b^2}{8}\right)\left(\frac{1}{\Delta B_o}\right)\right]^{-1}$$

Where $g_o = \frac{1}{3}(g_x + g_y + g_z)$ $\quad B_o = \frac{\hbar\omega}{g_o\beta}$ $\quad \Delta\gamma = \frac{\beta(g_z - 0.5(g_x + g_y))}{\hbar}$

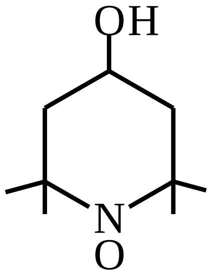
$$b = \frac{2}{3}(A_z - 0.5(A_x + A_y))$$

ΔB_o is the peak-to-peak width of the center line
Hyperfine values (A) are in radians/s
The calculation assumes isotropic tumbling

Kivelson Theory: nitroxide radicals

4-OH-TEMPO (tempol) in 9:1 glycerol:water

$g_x = 2.0094$, $g_y = 2.0059$, $g_z = 2.0023$



$A_x = 2\pi\ 18\mathrm{x}10^6$, $A_y = 2\pi\ 22.5\mathrm{x}10^6$, $A_z = 2\pi\ 103\mathrm{x}10^6$ rad/s

$I(+1) = 13.5$, $I(0) = 16.4$, $I(-1) = 3.4$ (arbitrary units)

$\Delta B_o = 3.52$ G

$\nu = 9.2449\mathrm{x}10^9\ \mathrm{s}^{-1}$

$\beta = 9.274\mathrm{x}10^{-21}$ erg/G

$h = 6.626\mathrm{x}10^{-27}$ erg s

$\tau = 2.1\mathrm{x}10^{-9}$ s from B or $\tau = 2.3\mathrm{x}10^{-9}$ s from C

Determination of microviscosity:

$$\tau = \frac{\eta V}{kT}$$

(Stocks-Einstein)

$$\tau = 6.65 \times 10^{-10} \times \Delta B(+1) \times \left[\sqrt{\frac{I(+1)}{I(-1)}} - 1\right]$$

Simplified formula

Any questions?

Thank you!

BRUKER

Innovation with Integrity