Electron Paramagnetic Resonance (EPR) Spectroscopy

(a.k.a. ESR, EMR)

Lecture I. Basic principles of EPR spectroscopy

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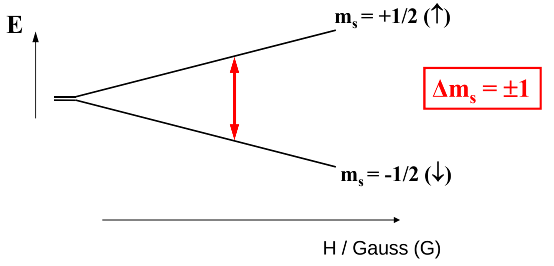
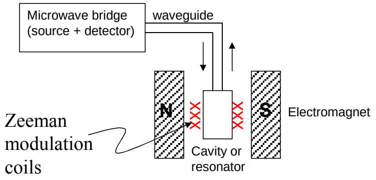
EPR Spectroscopy

- The electron spin equivalent of NMR
- Requires **unpaired electrons** ($S \geq ½$)
- information on the **environment of the unpaired electron** → electronic structure, geometric structure, physical properties, reactivity, dynamics, etc.
- EPR transition = **flipping the electron spin**. E.g. for $S = ½$…

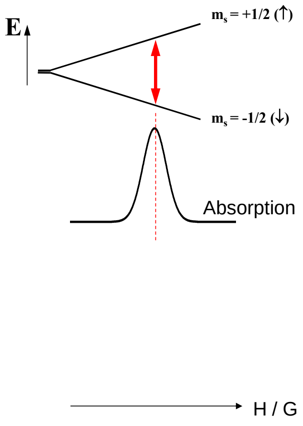


$\boxed{\Delta m_s = \pm 1}$

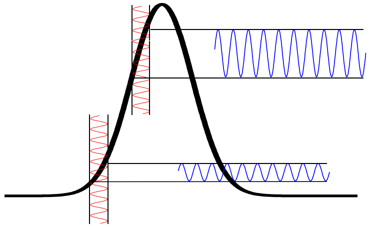
Basics of the experiment



- **Fixed frequency, magnetic field swept**
  –back-to-front! Disadvantage.

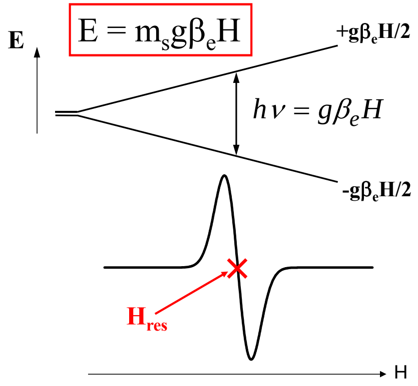


- Detected as **1st derivative** of absorption signal
  -Zeeman modulation



The resonance condition

$$\boxed{E = m_s g \beta_e H}$$



$$h\nu = g\beta_e H$$

$$\boxed{g = \frac{h\nu}{\beta_e H_{res}} = 714.5\frac{\nu\,(\text{GHz})}{H_{res}\,(\text{G})}}$$

h = Planck’s constant
= 6.6261×10^{-34} J s
β_e = Bohr magneton
= 9.2740×10^{-24} J T^{-1}
= 4.6686×10^{-5} $cm^{-1}G^{-1}$

Frequency vs. Field

- Microwaves appropriate for convenient lab magnets
- Can use different fixed frequencies.
- Advantages to both up- and down-frequency/field

Frequency band	υ / GHz	H_{res} / G for g_e
S	**4.0**	**~1400**
X (most common)	**9.0**	**~3200**
Q	**34**	**~12000**
W	**94**	**~33000**

S, X, Q: Electromagnets

W: ← Supercon magnet

↑ Microwave frequencies

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Lecture II. Isotropic (fluid solution) spectra

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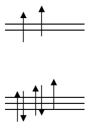
The g-value

•Free electron: g_e = 2.002319… a fundamental constant, related to the magnetic moment of the electron due to its **spin** (ang. mom.). [Nb: gyromagnetic ratio $\gamma_e = g_e\beta_e/\hbar$; magn. mom., $\mu_e = -g_e\beta_e\sqrt{S(S+1)}$

- In real materials, **measured $g \neq g_e$**.

$\boxed{g \propto 1/H_{res} \Rightarrow \textbf{higher g at lower field.}}$

- …because of **orbital angular momentum** contribution to the magnetic moment.
- Can be:

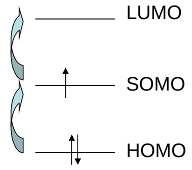


(i) Ground state (T or E terms) → large orbital moment; need to treat spin-orbit split states. Complicated, and won't consider further here.

e.g. O_h Co^{2+}; ^4T

The g-shift

(ii) Mixing with **excited states** via **spin-orbit coupling (SOC)** → small orbital moment ∝ **1/ΔE**.
g ~ g_e for orbital singlets (A or B terms).
Normal range 3 > g > 1.



$$\boxed{g = g_e - \frac{a^2 n\lambda}{\Delta E}}$$

Often discussed as the *g-shift*:

$$\Delta g = g - g_e$$

λ = SOC constant - larger for heavier elements.
a^2 (≤ 1) = covalency parameter
n = quantum mechanical coefficient

Trends in g-shift

$$\boxed{g = g_e - \frac{a^2 n \lambda}{\Delta E}}$$

Consequently:
(i) Organic free-radicals: usually large ΔE (colourless), small λ.
hydrocarbon radicals → $g \approx 2.002\text{-}2.003$
N/O-based radicals $g \approx 2.003\text{-}2.006$
S-based radicals $g \approx 2.007\text{-}2.010$

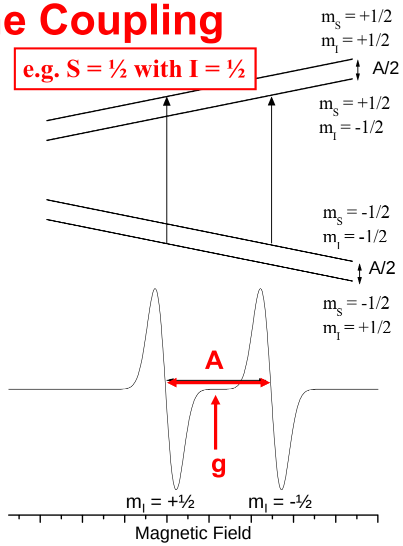
(ii) transition metal ions: small ΔE (coloured; crystal field splittings), big λ → g significantly different from g_e.

(iii) g can be < or > g_e.
Coupling with filled orbital → +ve contribution to Δg.
Coupling with empty orbital → -ve contribution to Δg.

e.g. $\{V^{IV}O\}^{2+}$, d^1 typical $g \approx 1.9$
e.g. Cu^{2+}, d^9 typical $g \approx 2.1$

Hyperfine Coupling

- If electron spin interacts with **nuclear spin (I)** → **hyperfine structure**, with coupling constant A (or a).
- Analogous to nuclear spin-nuclear spin (J) coupling in NMR.
- **2nd selection rule: $\Delta m_I = 0$**
- Each transition corresponds to a given value of m_I →2I+1 transitions.



e.g. S = ½ with I = ½

Coupling Patterns

- Coupling to **n equivalent spin I nuclei** → 2nI+1 multiplet.
- Relative intensities from **triangles** or **stick spectra** (as for NMR).

- E.g. for coupling to n equivalent I = ½ nuclei…Pascal's triangle

"add up 2*I* + 1 numbers to obtain the next row"

n							0		1		0							#	Σ
1						0		1		1		0						2	2
2					0		1		2		1		0					3	4
3						1		3		3		1						4	8
4					1		4		6		4		1					5	16
5				1		5		10		10		5		1				6	32
6			1		6		15		20		15		6		1			7	64
7		1		7		21		35		35		21		7		1		8	128
8	1		8		28		56		70		56		28		8		1	9	256

Triangles for I > 1/2 nuclei

n × (*I* = 1); add up 2*I* + 1 = 3 numbers

n					0	0	1	0	0					#	Σ
1				0	0	1	1	1	0	0				3	3
2			0	0	1	2	3	2	1	0	0			5	9
3				1	3	6	7	6	3	1				7	27
4			1	4	10	16	19	16	10	4	1			9	81
5		1	5	15	30	45	51	45	30	15	5	1		11	243
6	1	6	21	50	90	126	141	126	90	50	21	6	1	13	729

n × (*I* = $^3/_2$); add up 2*I* + 1 = 4 numbers

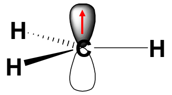
n							0		0		0		1		0		0		0							#	Σ
1				0		0		0		1		1		1		1		0		0		0				4	4
2							1		2		3		4		3		2		1							7	16
3				1		3		6		10		12		12		10		6		3		1				10	64
4	1		4		10		20		31		40		44		40		31		20		10		4		1	13	256

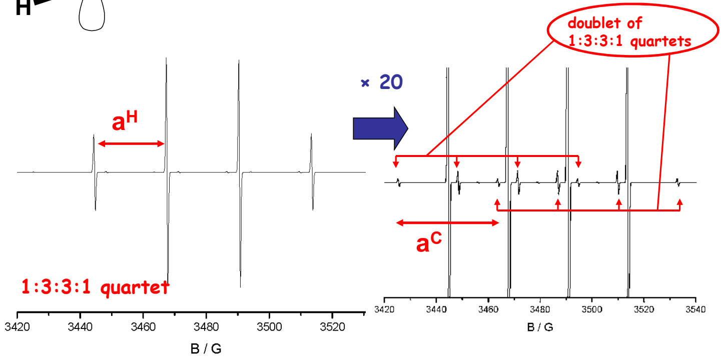
n × (*I* = $^5/_2$); add up 2*I* + 1 = 6 numbers

n						0		0		0		0		0		1		0		0		0		0		0						#	Σ
1											1		1		1		1		1		1											6	6
2						1		2		3		4		5		6		5		4		3		2		1						11	36
3	1		3		6		10		15		21		25		27		27		25		21		15		10		6		3		1	16	216

Can observe coupling to quadrupolar nuclei, even if in low symmetry

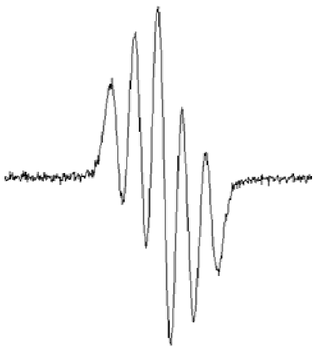
Methyl radical

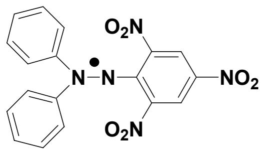




^{13}C, 1.1% nat. ab., $I = ½$

2,2-diphenyl-1-picrylhydrazyl (dpph)



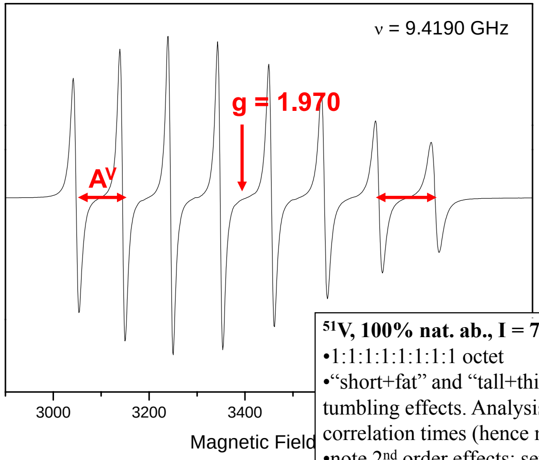


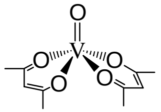
- ^{14}N, 100% nat. ab., I = 1
- Two very similar couplings
- **1:2:3:2:1 pentet**

g = 2.00354

Used as a standard for g-value calibration

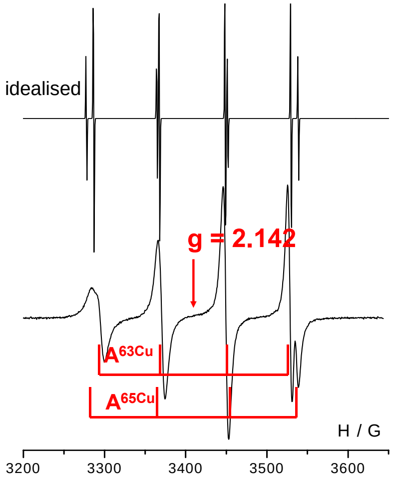
[VO(acac)$_2$]: V^{IV}, d^1

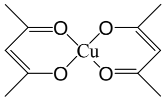




^{51}V, 100% nat. ab., I = 7/2.
- 1:1:1:1:1:1:1:1 octet
- "short+fat" and "tall+thin" lines due to tumbling effects. Analysis → rotational correlation times (hence mobility etc)
- note 2nd order effects: separations not even; g offset from centre.

[Cu(acac)$_2$]: Cu^{II}, d^9



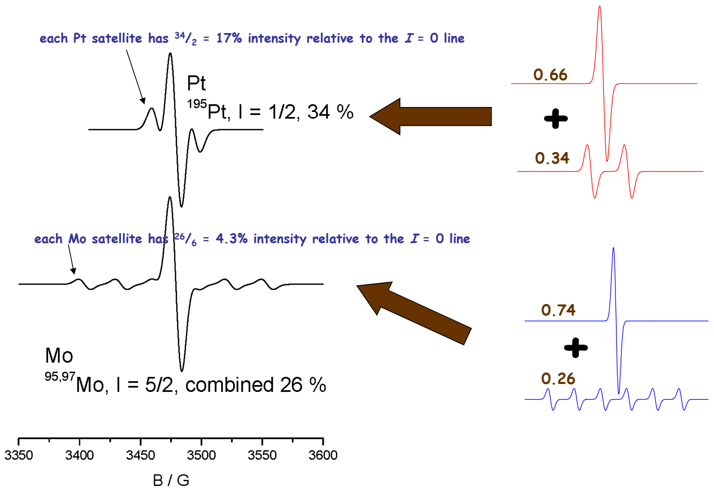


^{63}Cu 69% nat. ab.
^{65}Cu 31 % nat. ab.
Both I = 3/2

- **Same g, different A**
- A(^{63}Cu)/A(^{65}Cu) = ratio of nuclear magnetic moments ($g_n\beta_nI$) hence **nuclear g_n-values**…

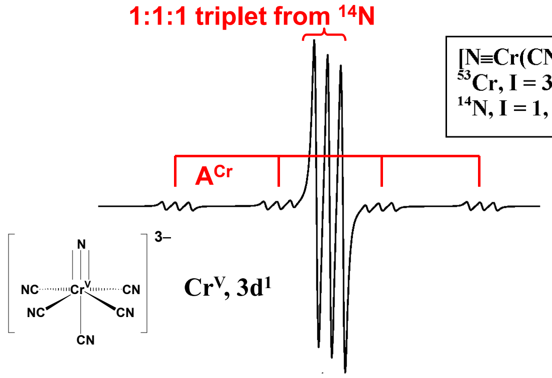
= 1.484/1.588 = 0.935

Other poly-isotopic examples


each Pt satellite has $^{34}/_{2}$ = 17% intensity relative to the I = 0 line

each Mo satellite has $^{26}/_{6}$ = 4.3% intensity relative to the I = 0 line

"Superhyperfine" = ligand hyperfine



$[N{\equiv}Cr(CN)_5]^{3-}$
^{53}Cr, I = 3/2, 10%
^{14}N, I = 1, 100%

- Unpaired electron must be partly delocalized out to ^{14}N nucleus.
- Superhyperfine coupling is direct evidence for **covalency** in coordination compounds.

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Lecture III. Meaning of hyperfine interaction

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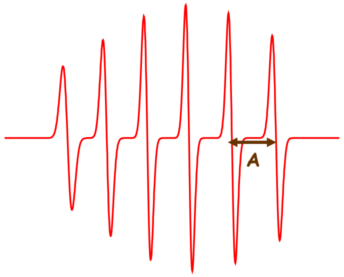
Units for hyperfine coupling

- Measured in field units, but coupling constant is an interaction energy
- Need to convert to energy (or equivalent) units…



g_{iso} = 2.00

A_{iso} = 100 Gauss

From: $\Delta E = h\nu = g\beta_e H_{res}$

β_e in cm^{-1} G^{-1}

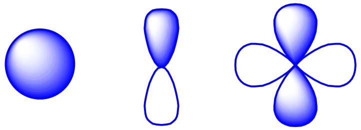
$$A(\text{cm}^{-1}) = g \times \beta_e \times A(G)$$
$$= 2.00 \times \underbrace{4.66858 \times 10^{-5}}_{} \times 100$$
$$= 93.4 \times 10^{-4}\ \text{cm}^{-1}$$

$$A(\text{MHz}) = g \times A(G) / 0.7145$$
$$= 2.00 \times 100 / 0.7145$$
$$= 279.9\ \text{MHz}$$

Conversion from field to energy units depends on the *g*-value

Hyperfine (e-n) Mechanisms

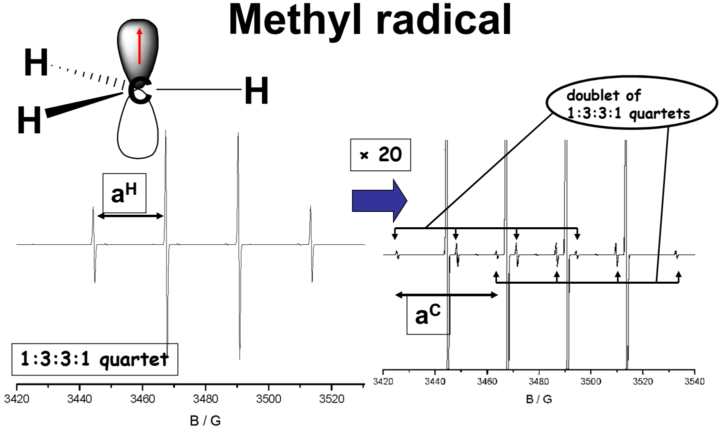
- **Dipolar** (through space): Depends on e-n distance and orientation w.r.t. applied field.
$A_{dip} \propto 3\cos^2\theta - 1$ - **Averages to zero in fluid solution.**



- Spin density **at the nucleus** (**Fermi contact**): Direct contribution only possible if upe is (at least partly) in an **s-orbital** (p,d,f orbitals have **nodes** at the nucleus).
- **Spin-orbit coupling** [$\propto \Delta g$]: important for d-block

⇒Should **only see s-electron density in solution**, but…

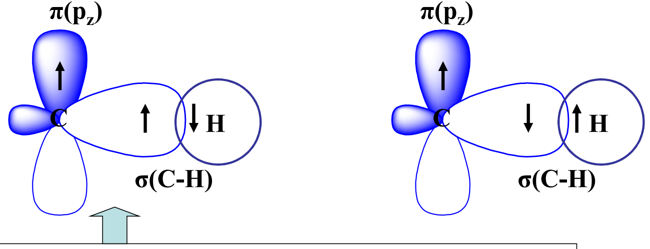
Methyl radical



Often see solution hyperfine where symmetry should preclude it!

Spin Polarisation

- Unpaired electron interacts differently with the ↑ and ↓ electrons in a filled orbital
- →the paired electrons have slightly different spatial distributions.



- Slightly favoured by spin correlation (cf. Hund's rule)
- "excess" spin up at C; spin down at H – including nucleus.

- Or, configuration interaction between $p_z^1\sigma^2$ with excited states
- Similar arguments for observation of ^{13}C splitting or, e.g., metal hyperfine in d-block complexes

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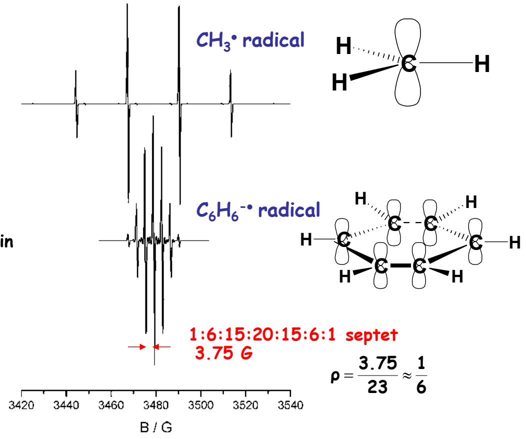
McConnell analysis

Calculation of spin population of $2p_z$ orbital in π-radical from hyperfine coupling to bound H

$$\boxed{a_{iso}^H = \rho Q}$$

Spin density in C $2p_z$ orbital

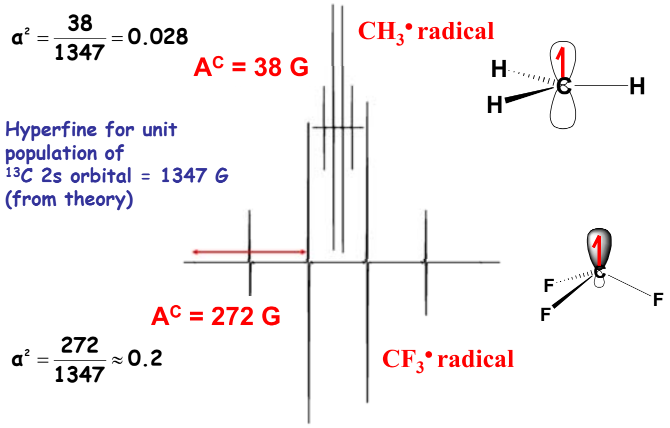
$\rho = 1$, $Q = 23$ G



$\rho = \frac{3.75}{23} \approx \frac{1}{6}$

Structural information from hyperfine

- Radical identification
- Geometric structure can be inferred, e.g…



$$a^2 = \frac{38}{1347} = 0.028$$

$$a^2 = \frac{272}{1347} \approx 0.2$$

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Lecture IV. What happens when we immobilise the sample?

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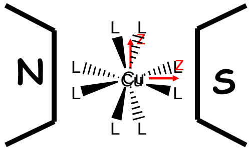
Sample phase and orientation

- in **fluid solution** molecules tumbling rapidly (mostly) on timescale of experiment.
- Magnetic field “sees” **average orientation** of the molecule.
→ “isotropic” spectrum.

- …but molecules are not, in general, isotropic. They look different from different orientations.
- As with ALL spectroscopies, spectrum depends on the orientation of the molecule (e.g. polarisation of optical transitions). EPR easy to measure on powders, single crystals, frozen solutions etc.



- e.g. sq. planar Cu^{II} (D_{4h})
- g and A will depend on orientation of molecule (can define by C_4) w.r.t. H.

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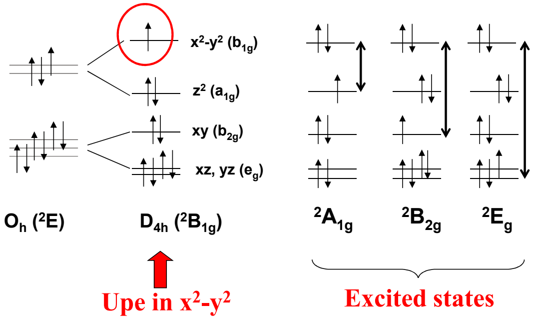
g anisotropy

- Remember $g \neq g_e$ due to excited state orb. ang. mom. via SOC.
- **Different excited states** contribute to magnetic moment (hence g) in different orientations. Easiest to see by example.

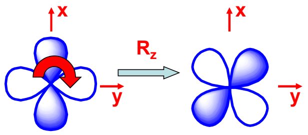
- **Consider a square planar Cu(II) complex, D_{4h} symmetry.**



Hand-wavey approach

- Non-zero orbital ang. mom. if orbitals can be transformed by rotation about an axis. E.g…

(i) x^2-y^2 transforms to xy via R_z



- ∴contribution to magn. moment along z from xy excited state
- and contribution to **g measured with H parallel to z** - "g_z"

$$g_z = g_e - \frac{a^2 n\lambda}{E_{x^2-y^2} - E_{xy}}$$

…or from group theory

D_{4h}	E	$2C_4$ (z)	C_2	$2C'_2$	$2C''_2$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$		
A_{1g}	+1	+1	+1	+1	+1	+1	+1	+1	+1	+1	-	x^2+y^2, z^2
A_{2g}	+1	+1	+1	-1	-1	+1	+1	+1	-1	-1	R_z	-
B_{1g}	+1	-1	+1	+1	-1	+1	-1	+1	+1	-1	-	x^2-y^2
B_{2g}	+1	-1	+1	-1	+1	+1	-1	+1	-1	+1	-	xy
E_g	+2	0	-2	0	0	+2	0	-2	0	0	(R_x, R_y)	(xz, yz)
A_{1u}	+1	+1	+1	+1	+1	-1	-1	-1	-1	-1	-	-
A_{2u}	+1	+1	+1	-1	-1	-1	-1	-1	+1	+1	z	-
B_{1u}	+1	-1	+1	+1	-1	-1	+1	-1	-1	+1	-	-
B_{2u}	+1	-1	+1	-1	+1	-1	+1	-1	+1	-1	-	-
E_u	+2	0	-2	0	0	-2	0	+2	0	0	(x, y)	-

- Orb. ang. mom. along z, x or y axes has rotational vector symmetry rep., R_i (think about "orbiting about that axis").
- Multiply **symmetry rep. of ground state** by $\mathbf{R_i}$.

B_{1g} (x^2-y^2) . A_{2g} (R_z) = B_{2g}

∴ SOC along z mixes B_{1g} ground state with B_{2g} excited state (xy)

…or from group theory

D_{4h}	E	$2C_4$ (z)	C_2	$2C'_2$	$2C''_2$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$		
A_{1g}	+1	+1	+1	+1	+1	+1	+1	+1	+1	+1	-	x^2+y^2, z^2
A_{2g}	+1	+1	+1	-1	-1	+1	+1	+1	-1	-1	R_z	-
B_{1g}	+1	-1	+1	+1	-1	+1	-1	+1	+1	-1	-	x^2-y^2
B_{2g}	+1	-1	+1	-1	+1	+1	-1	+1	-1	+1	-	xy
E_g	+2	0	-2	0	0	+2	0	-2	0	0	(R_x, R_y)	(xz, yz)
A_{1u}	+1	+1	+1	+1	+1	-1	-1	-1	-1	-1	-	-
A_{2u}	+1	+1	+1	-1	-1	-1	-1	-1	+1	+1	z	-
B_{1u}	+1	-1	+1	+1	-1	-1	+1	-1	-1	+1	-	-
B_{2u}	+1	-1	+1	-1	+1	-1	+1	-1	+1	-1	-	-
E_u	+2	0	-2	0	0	-2	0	+2	0	0	(x, y)	-

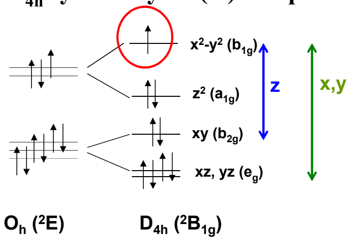
- SOC along x(y)…

B_{1g} (x^2-y^2) . E_g ($R_{x,y}$) = E_g

∴ SOC along x(y) mixes B_{1g} ground state with E_g (xz,yz)

Result…

- **D_{4h} symmetry Cu(II) complex.**



$$g_z = g_e - \frac{a^2 n\lambda}{E_{x^2-y^2} - E_{xy}}$$

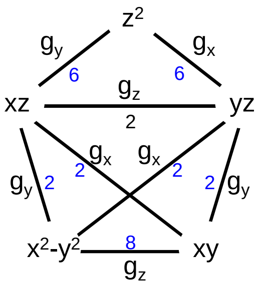
$$g_x = g_y = g_e - \frac{a^2 n\lambda}{E_{x^2-y^2} - E_{xz,yz}}$$

- g-values are anisotropic
- Can predict that $\mathbf{g_z > g_x = g_y}$ ($> \mathbf{g_e}$)
- *Exercise*: z^2 ground state for d^9 (e.g. Jahn-Teller compressed Cu^{II}).
- Should find $\mathbf{g_x = g_y > g_z}$ ($= \mathbf{g_e}$)

Pattern of g-values tells you about the orbital in which the unpaired electron is located.

The magic pentagon

- Contributions to g-values summarised in…



$$g = g_e - \frac{a^2 n\lambda}{\Delta E}$$

- Start at a vertex for a given ground state
- Links give contributions to g_i-values
- Coefficients n also given

How does this affect spectra?

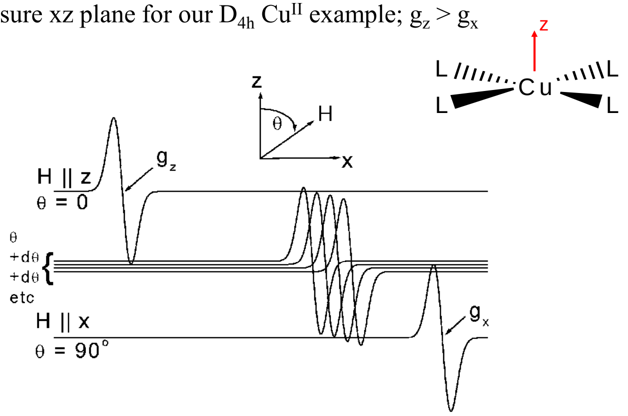
- **Fluid solution**: field "sees" **AVERAGE** orientation

- Measure **average g-value**, labelled $\mathbf{g_{iso}}$

$$\boxed{g_{iso} = \frac{g_x + g_y + g_z}{3}}$$

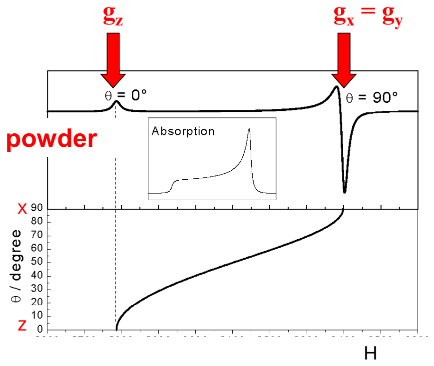
Single orientation spectra (e.g. single crystal)

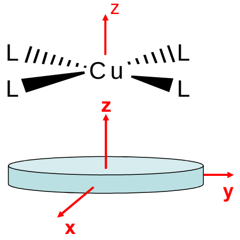
- Each spectrum looks "isotropic"
- e.g. measure xz plane for our D_{4h} Cu^{II} example; $g_z > g_x$



- **If we sum these, the "in-between" orientations cancel out**

Powder spectra and "road maps"

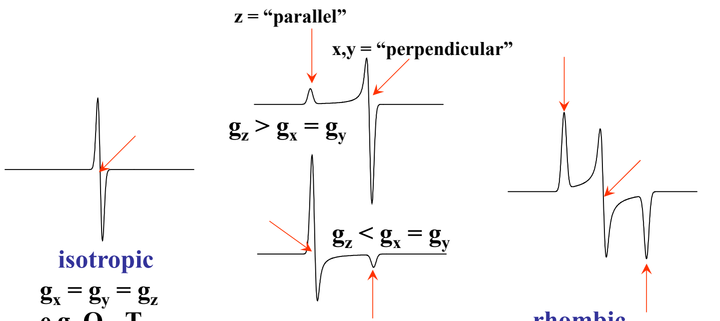




- Molecule has axial (disc-like) symmetry (D_{4h})
- Unique z
- Whole plane of xy

- **Powder spectrum is the SUM over ALL orientations**
- Features observed at turning points in road map
- Different shapes and intensities due to summation

Powder spectra and symmetry



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

Arrows denote positions used to measure *g*-values

Electron Paramagnetic Resonance (EPR) Spectroscopy

(a.k.a. ESR, EMR)

Lecture V. Information about electronic structure

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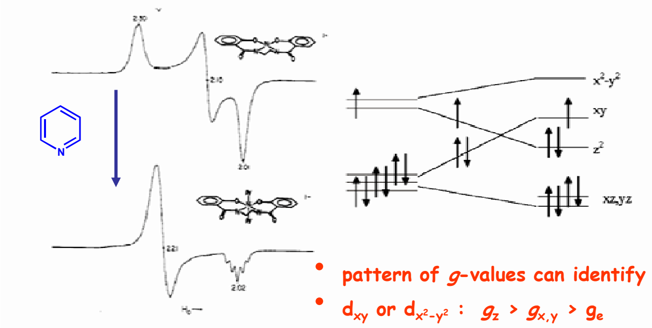
Information from g-values

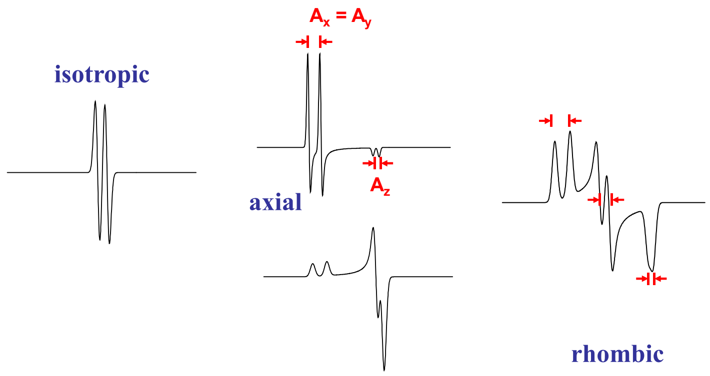
Ni^{3+}, $3d^7$



- pattern of *g*-values can identify *SOMO*
- d_{xy} or $d_{x^2-y^2}$: $g_z > g_{x,y} > g_e$
- d_{z^2} : $g_{x,y} > g_z = g_e$

Krüger and Holm, *Inorg. Chem.*, 1987, 26, 3645.

Powder spectra with hyperfine: I = 1/2



isotropic

$A_x = A_y$

A_z

axial

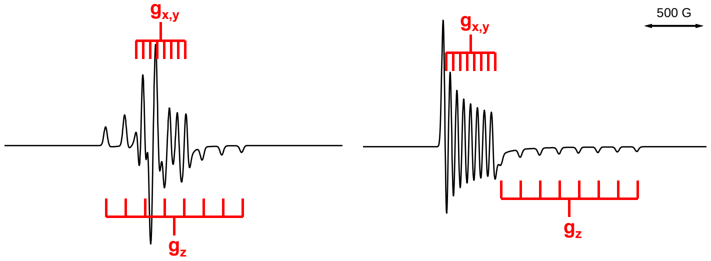
rhombic

•Each g-feature is split by hyperfine.

•**Hyperfine coupling is also anisotropic, determined by symmetry**.

Powder spectra: A *vs.* g-anisotropy

- If A > separation between g in field units, then “parallel” and “perp” regions will overlap. Very common.
- E.g. typical $\{VO\}^{2+}$: $g_z = 1.93$, $g_{x,y} = 1.98$, $A_z = 170$ G, $A_{x,y} = 60$ G



9.4 GHz

$H_0(g_{x,y})-H_0(g_z) = 88$ G

94 GHz

$H_0(g_{x,y})-H_0(g_z) = 880$ G

More on hyperfine

- **Fluid solution**: field “sees” **AVERAGE** orientation
- Measure **average A-value**, labelled $\mathbf{A_{iso}}$

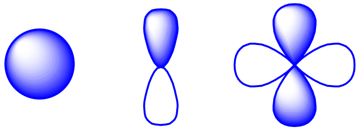
$$\boxed{A_{iso} = \frac{A_x + A_y + A_z}{3}}$$

In energy (cm^{-1}) or frequency units (MHz) – **NOT** field units.

- A_{iso}, A_x, A_y and A_z can be either sign. No **direct** information in spectrum, BUT…
- Can get **relative signs** from averaging to A_{iso}.

- Can also use A_{iso} to determine unresolved anisotropic component.

Hyperfine Anisotropy



Remember:

- Spin density **at nucleus**: A_s
- SOC [= $P\Delta g_{iso}$]

$\Big\}$ $\mathbf{A_{iso}}$

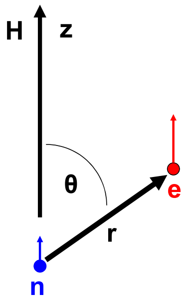
- **Dipolar**, $\mathbf{A_{dip}}$: Depends on e-n distance and orientation w.r.t. applied field.

In solid state, observe SUM of the isotropic and dipolar part.

$$\mathbf{A = A_{iso} + A_{dip}}$$

Dipolar part of hyperfine

$$A_{dip} \propto \mu_{ez}\mu_{nz}\frac{\left(3\cos^2\theta - 1\right)}{r^3}$$



θ = 0° $3\cos^2\theta = +2$

θ = 90° $3\cos^2\theta = -1$

Any dipolar interaction has form +2a, -a, -a

Electron in a p_z-orbital

Angular factor from form of wavefunction

Hyperfine observed for **unit population of a p-orbital** for that isotope. Calcd from theory.[1]

Exptly observed hyperfines

$$A_z = A_{iso} + \frac{4}{5} a^2 P_p$$

$$A_{x(y)} = A_{iso} - \frac{2}{5} a^2 P_p$$

Covalency, $a^2 \leq 1$.
a = MO coefficient of p_z in SOMO.

$$A_z - A_{x(y)} = \frac{6}{5} a^2 P_p$$

Anisotropic hyperfine → composition of molecular orbitals!

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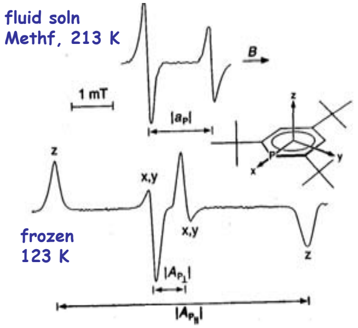
[1] J.R. Morton and K.F. Preston, *J. Mag. Reson*. 1978, **30**, 577; P.H. Rieger, *J. Magn. Reson*. 1997, **124**, 140.

Determining spin density distribution



$A_{iso}(P) = \pm 28$ G → $\pm 26 \times 10^{-4}$ cm^{-1}

$A_z(P) = \pm 118$ G → $\pm 110 \times 10^{-4}$ cm^{-1}
$A_{x,y}(P) = \mp 15$ G → $\mp 14 \times 10^{-4}$ cm^{-1}

- $A_{iso} = (A_x + A_y + A_z)/3 \Rightarrow A_{x,y}$ and A_z must be opposite sign.
- Assume A_z –ve → -ve a^2. Not physically meaningful.
- A_z +ve → $a^2 = 0.45$, i.e. 45% of spin density in P $3p_z$.

$P_p = +306 \times 10^{-4}$ cm^{-1} for ^{31}P (100% nat. ab., $I = ½$)

Electron in a d_{xy/x^2-y^2} orbital

Hyperfine for **unit population of a d-orbital**.

Different angular factor for d-orbitals

SOC (excited state) contribution. Convenient to cast in terms of g-shifts, because these can be measured.

$$A_z = A_{iso} + P_d\left[-\frac{4}{7}a^2 + \frac{2}{3}\Delta g_z - \frac{5}{21}\Delta g_{x,y}\right]$$

$$A_{x,y} = A_{iso} + P_d\left[+\frac{2}{7}a^2 - \frac{1}{3}\Delta g_z + \frac{5}{42}\Delta g_{x,y}\right]$$

Solve for a^2: spin density in d

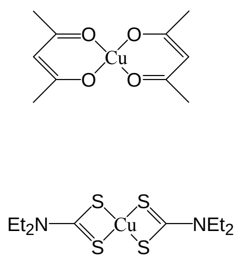
$$\Rightarrow A_z - A_{x,y} = P_d\left[-\frac{6}{7}a^2 + \Delta g_z - \frac{5}{14}\Delta g_{x,y}\right]$$

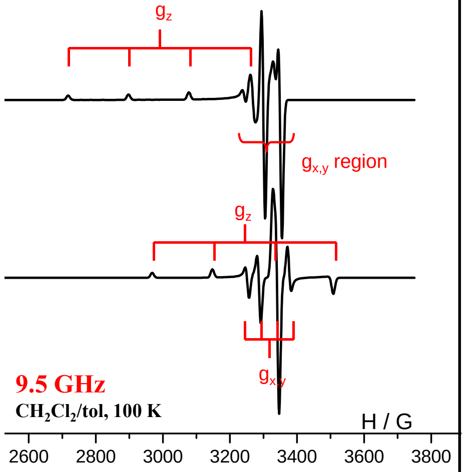
Electron in a d_{z^2} orbital

$$A_z = A_{iso} + P_d\left[+\frac{4}{7}a^2 - \frac{1}{3}\Delta g_z - \frac{17}{21}\Delta g_{x,y}\right]$$

$$A_{x,y} = A_{iso} + P_d\left[-\frac{2}{7}a^2 - \frac{1}{3}\Delta g_z + \frac{17}{42}\Delta g_{x,y}\right]$$

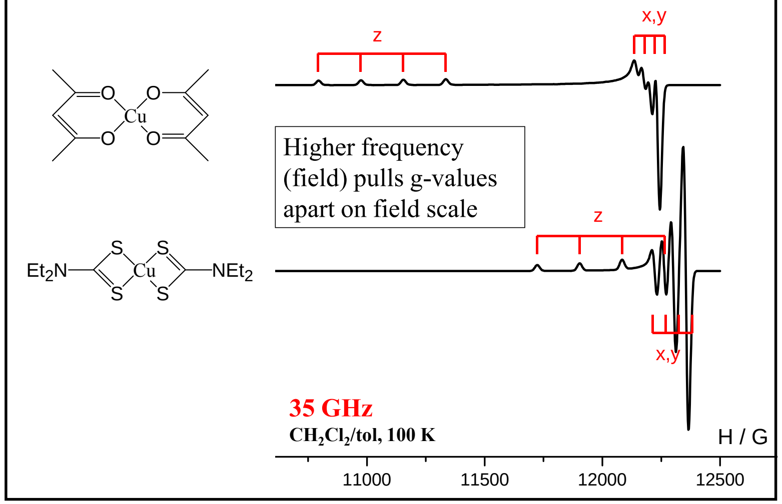
Example: covalency in Cu^{II} complexes





9.5 GHz
CH_2Cl_2/tol, 100 K

Example: covalency in Cu^{II} complexes

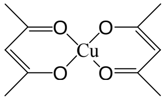


Higher frequency (field) pulls g-values apart on field scale

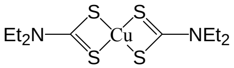
35 GHz

CH_2Cl_2/tol, 100 K

Example: covalency in Cu^{II} complexes



A_{iso} = 76x10^{-4} cm^{-1}
g_z = 2.260, $g_{x,y}$ = 2.050
A_z = 189x10^{-4} cm^{-1}, $A_{x,y}$ = 20x10^{-4} cm^{-1}



A_{iso} = 75x10^{-4} cm^{-1}
g_z = 2.085, $g_{x,y}$ = 2.035
A_z = 175x10^{-4} cm^{-1}, $A_{x,y}$ = 38x10^{-4} cm^{-1}

$$A_z - A_{x,y} = P_d\left[-\frac{6}{7}a^2 + \Delta g_z - \frac{5}{14}\Delta g_{x,y}\right]$$

- A_{iso}, A_z and $A_{x,y}$ all same sign (-ve)
- CFT predicts x^2-y^2 ground state
- → a^2 = 0.77 for O-donor complex
- → a^2 = 0.48 for S-donor complex
- Spin much more delocalised (i.e. greater covalency) for S-donor