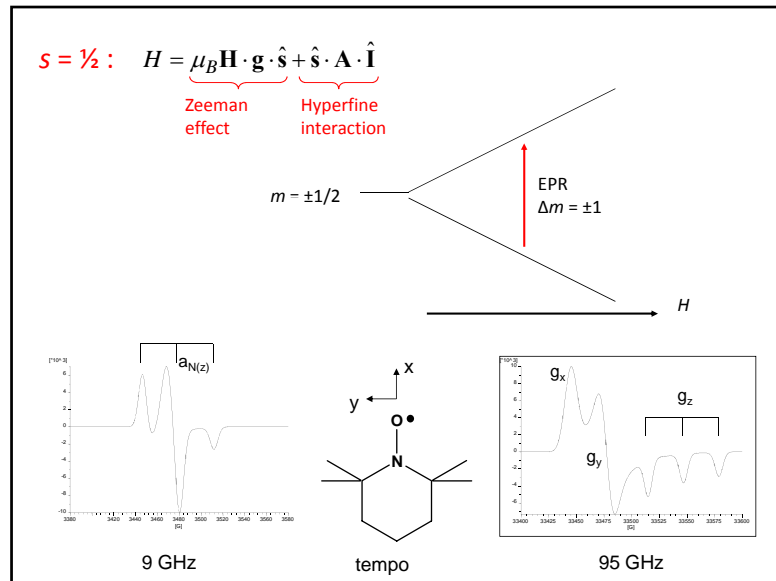


Electron Paramagnetic Resonance (EPR) Spectroscopy

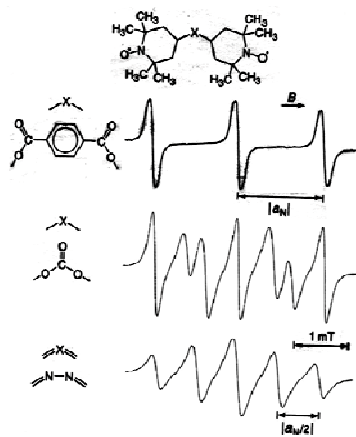
(a.k.a. ESR, EMR)

Lecture VI. More than one unpaired electron, $S > \frac{1}{2}$ (1)

Eric McInnes & David Collison, EPSRC UK National EPR Facility & Service
Photon Science Institute, The University of Manchester
eric.mcinnnes@manchester.ac.uk david.collison@manchester.ac.uk



Interaction between two unpaired electrons $s = \frac{1}{2}$ → total spin states S (= 0 and 1)



- States are separated in energy by the isotropic exchange parameter, J
- When J is very small, comparable to the hyperfine interaction, A : referred to as *bi-radicals*
- Form of fluid spectra depends on magnitude of J versus A

More than one unpaired electron in degenerate orbitals

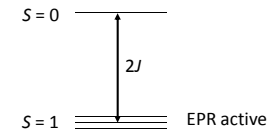
- Electron 1: $s_1 = 1/2$ Electron 2: $s_2 = 1/2$



- Define a total spin S with possible values $s_1 + s_2$ and $s_1 - s_2$

- Hund's rule: ground state has maximum S

- $S = 1$ and 0 : a spin triplet and spin singlet.

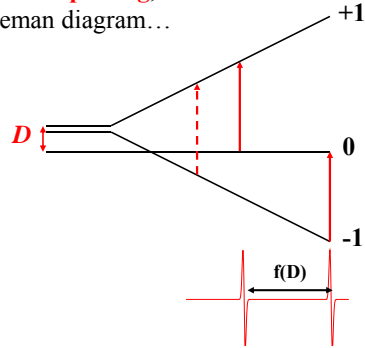


- Differ in energy because of differing electron-electron repulsions.
- Repulsion less in triplet \Rightarrow Hund's rule
- Quantified by the exchange constant (or integral), J
- Very large ($> 10^3 \text{ cm}^{-1}$) for electrons on same paramagnetic centre.

- For EPR can consider as isolated $s = 1$

More than one unpaired electron: $S = 1$

- Now have to consider e-e interactions (usually $\gg e-n$).
- \rightarrow **zero-field splitting, D**
- New Zeeman diagram...



- In general, $2S$ allowed transitions per orientation: **fine structure**.
- Spectra spread over much larger field ranges

Zero-Field Splitting

- Two mechanisms:
 - (i) Dipolar e-e interaction ($\propto 3\cos^2\theta - 1$). Dominant for organics
 - (ii) Spin-orbit coupling. Dominant for transition ions

- Anisotropic: have D_x , D_y and D_z parameters
- If purely dipolar then: $D_x + D_y + D_z = 0$
- (hence no fine structure in fluid solution)

• ... then only two independent parameters and can define...

ZFS parameters, D and E :

$$D = D_z - (D_x + D_y)/2$$

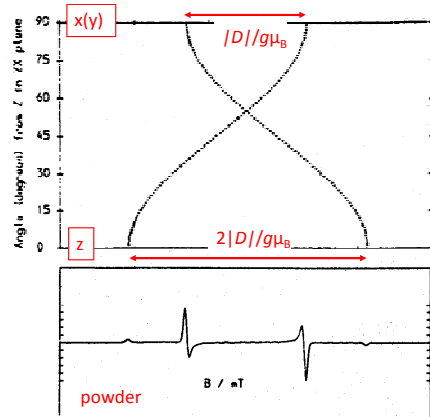
Axial term

$$E = (D_x - D_y)/2$$

Rhombic term

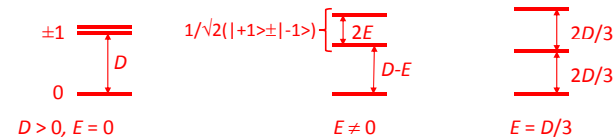
- Symmetry: isotropic ($D = E = 0$), axial ($D \neq 0, E = 0$), rhombic ($E \neq 0$).

$s = 1$, axial symmetry, road map and powder spectrum:



In general for $s > 1/2$, cannot derive analytical expression for resonance fields at arbitrary orientation. Need to diagonalise matrix at each θ, ϕ .

$s = 1$ in zero field.



- E mixes states differing by $\Delta M_s = \pm 2$, and breaks degeneracy

- Can define "rhombicity", $\lambda = |E/D|$
- $\lambda = 0$ (axial) to $1/3$ (rhombic limit)
- $\lambda > 1/3 \Rightarrow$ redefinition of axes

$s = 1$, effect of $E \neq 0$

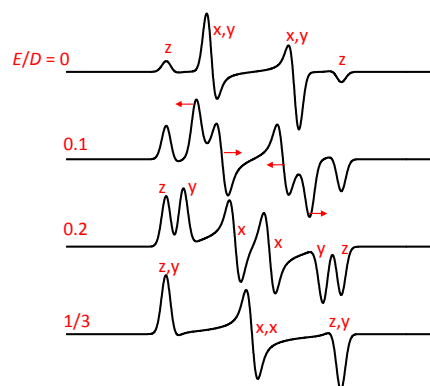
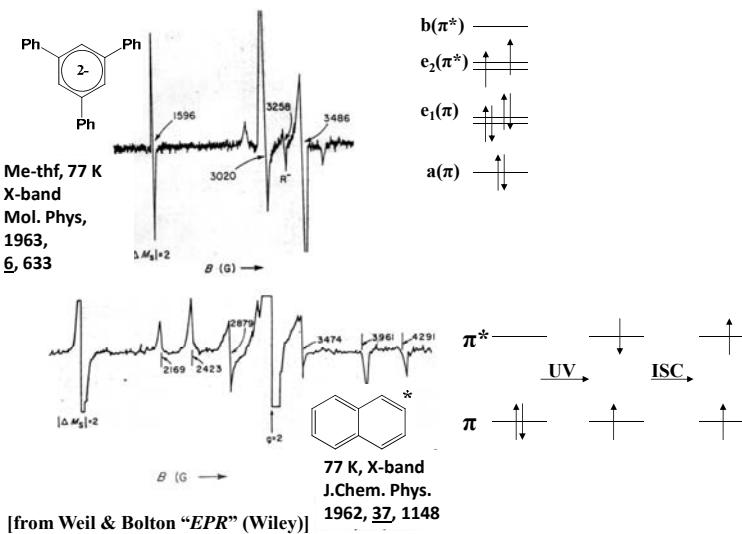
$$D = D_{zz} - (D_{xx} + D_{yy})/2$$

$$E = (D_{xx} - D_{yy})/2$$

Special cases:

$$E = 0 \Rightarrow D_{xx} = D_{yy} \neq D_{zz}$$

$$E/D = 1/3 \Rightarrow D_{yy} = -D_{zz}, D_{xx} = 0$$

 $0 \leq |E/D| \leq 1/3$ by convention
 **$s = 1$, some examples: ground state and excited state triplets****ZFS for some organic spin triplets**

	D / cm^{-1}	E / cm^{-1}
	0.157	0.020
	0.100	-0.014
	0.103	-0.016
	0.072	-0.008
	0.068	-0.0314
	0.011	0.001
H ₂ C ^{••}	0.696	0.004
Ph ₂ C ^{••}	0.406	0.019

- Examples are excited state aromatics or ground state carbenes
- D arises from:
 - Dipolar interaction $D \propto r^{-3}$ (dominant in organic radicals) and/or
 - Spin-orbit coupling (dominant in transition metals)

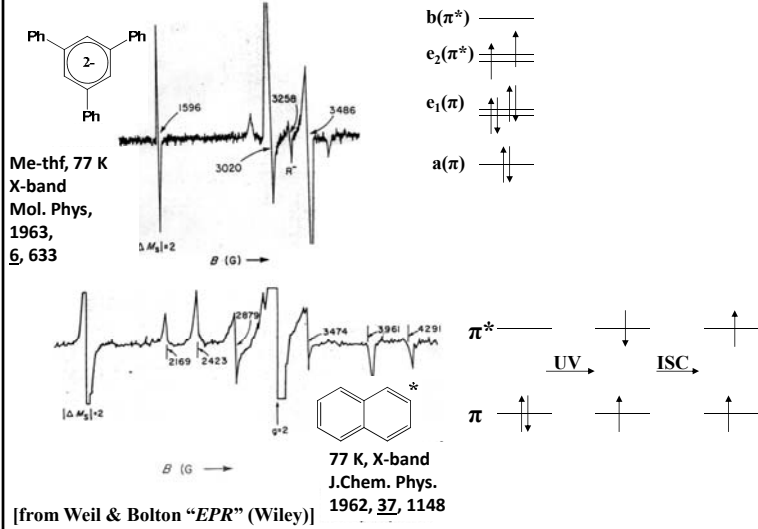
Electron Paramagnetic Resonance (EPR) Spectroscopy

(a.k.a. ESR, EMR)

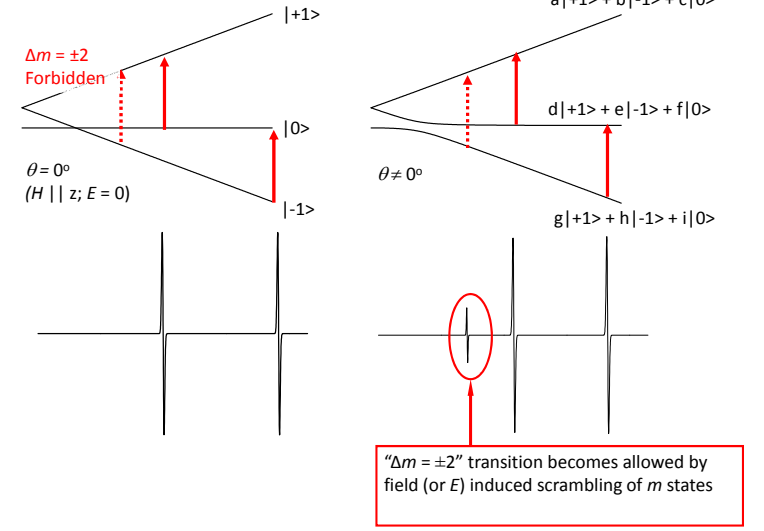
Lecture VII. More than one unpaired electron, $S > 1/2$ (2)

Eric McInnes & David Collison, EPSRC UK National EPR Facility & Service
Photon Science Institute, The University of Manchester
eric.mcinnnes@manchester.ac.uk david.collison@manchester.ac.uk

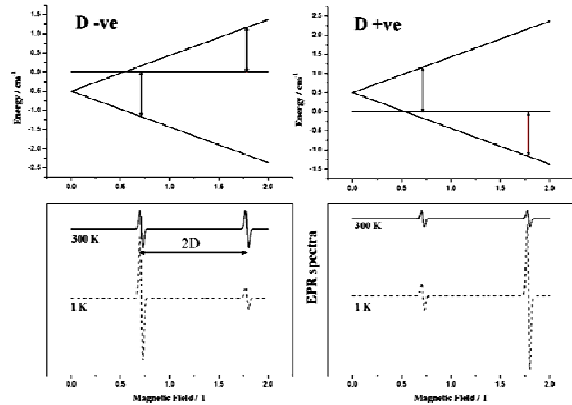
$s = 1$, some examples: ground state and excited state triplets



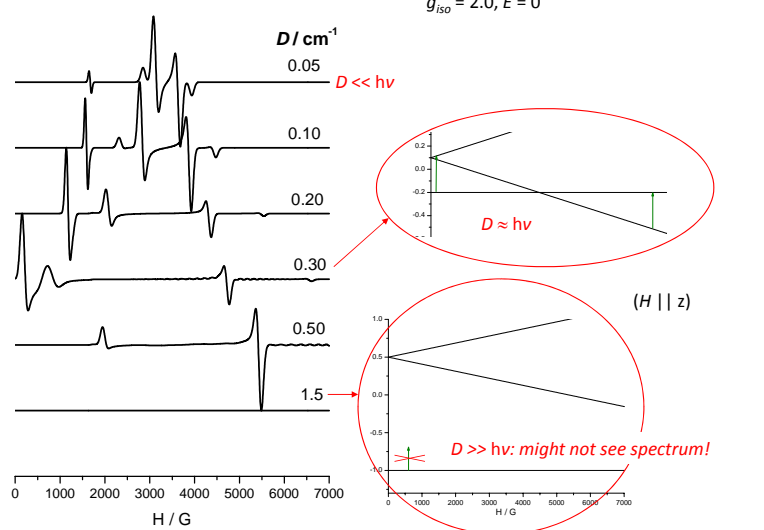
$s = 1$, the "half-field" resonance.

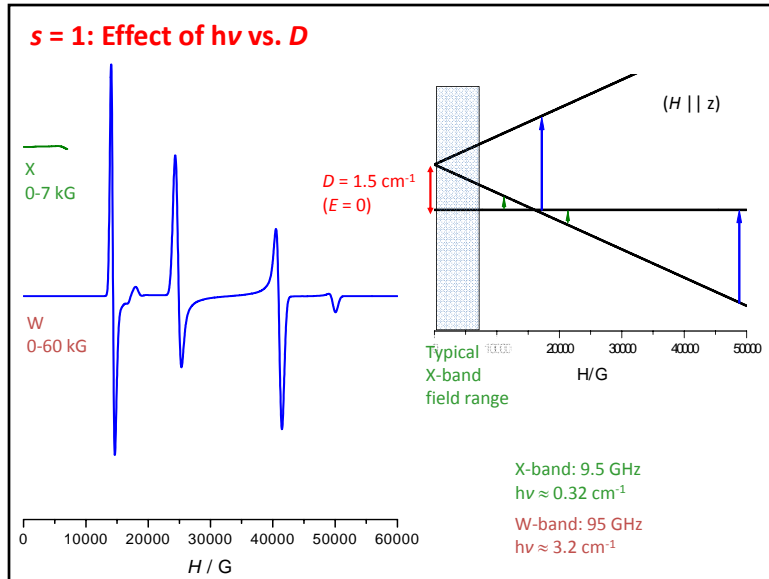


Sign of D from variable temperature behaviour



$s = 1$: Effect of $h\nu$ vs. D





$s = 1$, example: 6-coordinate Ni^{2+} (d^8)

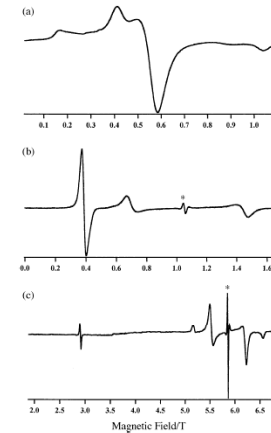
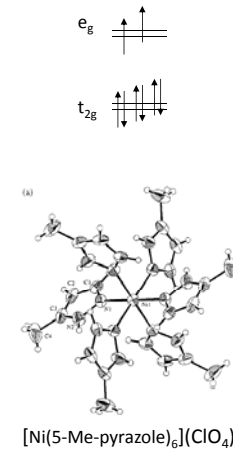


Fig. 4 Frequency dependence of the spectrum of I at 100 K. (a) 9.5, (b) 34, (c) 182 GHz.

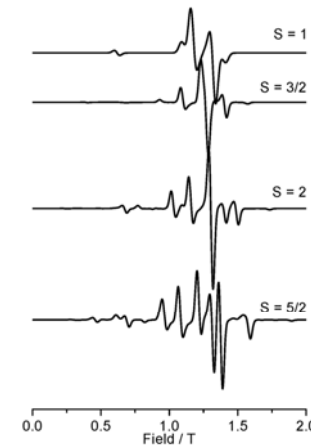
From *JCS Faraday Trans.* 1998, **94**, 3019



Summary and generalising to $s > \frac{1}{2}$:

- Spin s has $2s+1$ degeneracy: $m = +s, +s-1, \dots, -s$.
- Degeneracy lifted in zero-field by ZFS (D and E)
- In **high-field limit** ($D \ll h\nu$ or $g\mu_B H$)
get $2s$ EPR transitions per orientation w.r.t. H
- $H \parallel z$: transitions separated by $2|D|/g\mu_B$ in field units.
- For *axial* systems ($E = 0$),
 $H \parallel x(y)$: transitions separated by $|D|/g\mu_B$ in field units.

Form of $S > \frac{1}{2}$ spectra when $h\nu \gg D$



- **Quantum number S is associated with $2S + 1 M_S$ states**
- **$-S$ to $+S$**
- **$\Delta M_S = \pm 1$**
- **gives $2S$ transitions at any orientation**
- **Number of transitions $\rightarrow S$**
- **Separations $\rightarrow D$**

$s = 3/2$, example: 6-coordinate Cr^{3+} (d^3)

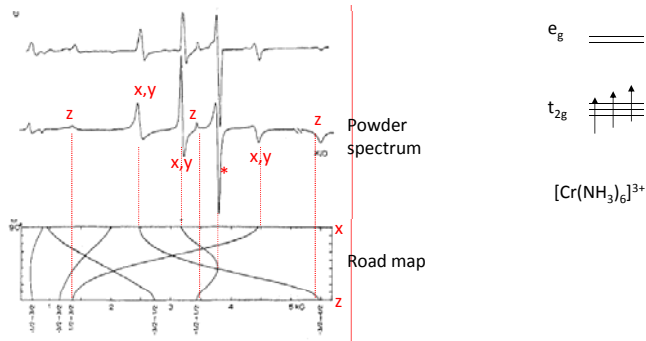


Figure 1.—A comparison of the experimental and simulated epr spectra of $[\text{Cr}(\text{NH}_3)_6][\text{Cl}_6]$. Top: experimental X-band powder spectrum. Bottom: computer-simulated spectrum ($g_x = 1.074, g_y = 1.084, E = 0.0, D = 0.0949 \text{ cm}^{-1}$) with graph showing the angular dependence of the resonance fields. At $\theta = 0^\circ$ the magnetic field is parallel with the z symmetry axis, and at $\theta = 90^\circ$ the magnetic field is in the xy plane.

From *Inorg. Chem.* 1971, 10, 2074

*: intense "off-axis" resonance.
cf. "overshoot" in low frequency Cu^{2+} spectra.

Some special features for half-integer spin

For example: $s = 3/2; m \pm 3/2, \pm 1/2$ (spin quartet)

Zero-field energy matrix ($|m\rangle$ basis):

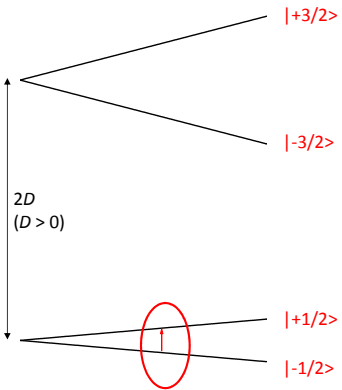
$$\begin{matrix} & | +3/2 \rangle & | -1/2 \rangle & | +1/2 \rangle & | -3/2 \rangle \\ \langle +3/2 | & D & \sqrt{3}E & 0 & 0 \\ \langle -1/2 | & \sqrt{3}E & -D & 0 & 0 \\ \langle +1/2 | & 0 & 0 & -D & \sqrt{3}E \\ \langle -3/2 | & 0 & 0 & \sqrt{3}E & D \end{matrix} \quad \begin{matrix} \text{=====} & +\sqrt{[D^2+3E^2]} \\ \text{=====} & -\sqrt{[D^2+3E^2]} \end{matrix}$$

E mixes $\Delta m \pm 2$, as before

\Rightarrow cannot mix $\pm m$

\Rightarrow two-fold degeneracy retained in zero-field even with $E \neq 0$ (Kramers' theorem)

$s = 3/2, D \gg hv$

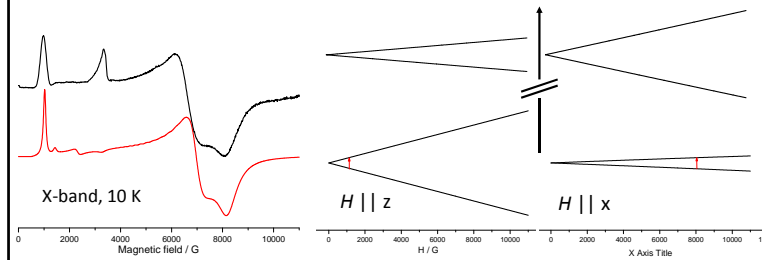
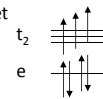


- Can't excite $|\pm 1/2\rangle \rightarrow |\pm 3/2\rangle$
- Can excite $|-1/2\rangle \rightarrow |+1/2\rangle$
- Allowed, $\Delta m = 1$ transition
- \Rightarrow can usually always detect an EPR spectrum from a half-integer spin system.
- transitions all within one doublet
- spectra look like $s = 1/2$ with weird g
- "Effective spin $1/2$ " with g_{eff}

$s = 3/2, D \gg hv$: effective g -values

• g_{eff} are very sensitive to E/D , hence can use them to determine this ratio (including sign) even when you cannot determine D or E !

- If $E \neq 0$ (or $\theta \neq 0$) then mixing can allow transitions within " m " = $\pm 3/2$ doublet
- Example, distorted tetrahedral Co^{2+} compound (high spin d^7)...



$g_{\text{eff}} = 7.4, 1.1, 0.87$

$E/D = -0.16; D < -15 \text{ cm}^{-1}$

• See Pilbrow, *J. Magn. Reson.* 1978, 31, 479 for thorough discussion of g_{eff} for $s = 3/2, 5/2$

Electron Paramagnetic Resonance (EPR) Spectroscopy

(a.k.a. ESR, EMR)

Lecture VIII. The anomalous paramagnetism of copper acetate

Eric McInnes & David Collison, EPSRC UK National EPR Facility & Service
Photon Science Institute, The University of Manchester
eric.mcinnis@manchester.ac.uk david.collison@manchester.ac.uk

“Anomalous paramagnetism and exchange interactions in copper acetate”,

Bleaney and Bowers, *Proc. Roy. Soc. (London)* 1952, 451

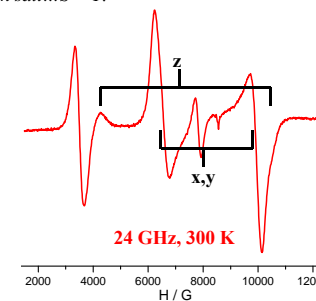
“The paramagnetic resonance spectrum is found to resemble
that of a nickel Tutton salt... $S = 1$.”



$S = 1$

$-2J \approx 300 \text{ cm}^{-1}$

$S = 0$



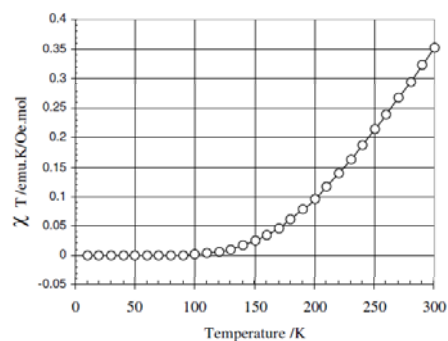
•EPR proved structure was dimeric.

•EPR spectrum due to triplet population

•Intensity decreases with T \Rightarrow antiferromagnetically coupled

• $g_z > g_{x,y}$ (square planar Cu^{2+})

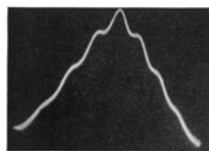
Magnetic properties of copper acetate



Variation of χT vs T for $\text{Cu}_2(\text{OAc})_4 \cdot 2\text{H}_2\text{O}$

Antiferromagnetic coupling

$S = 0$ ground state



Oscillogram showing
hyperfine structure with
magnetic field parallel to z-
axis