



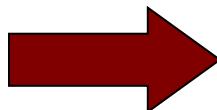
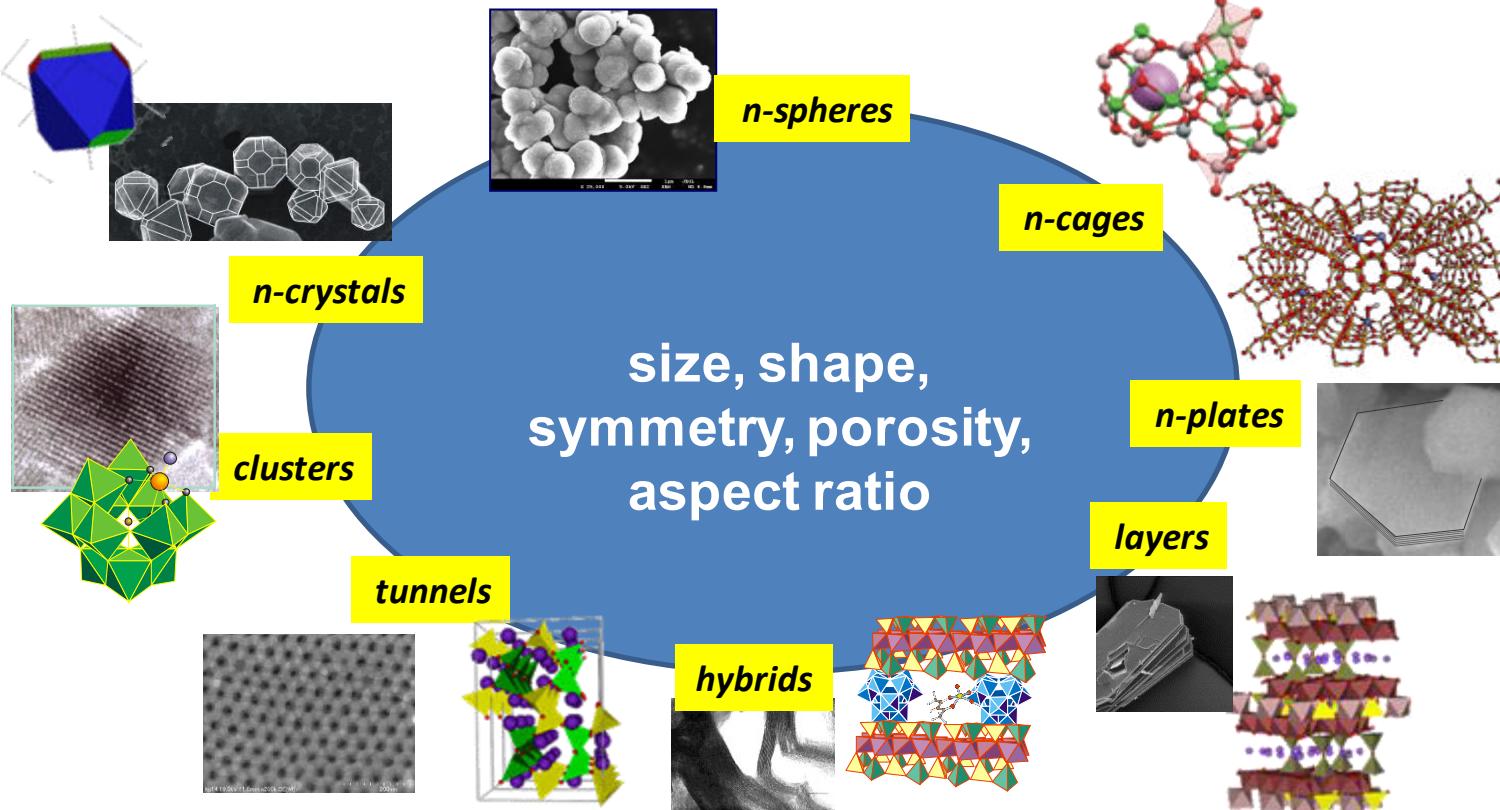
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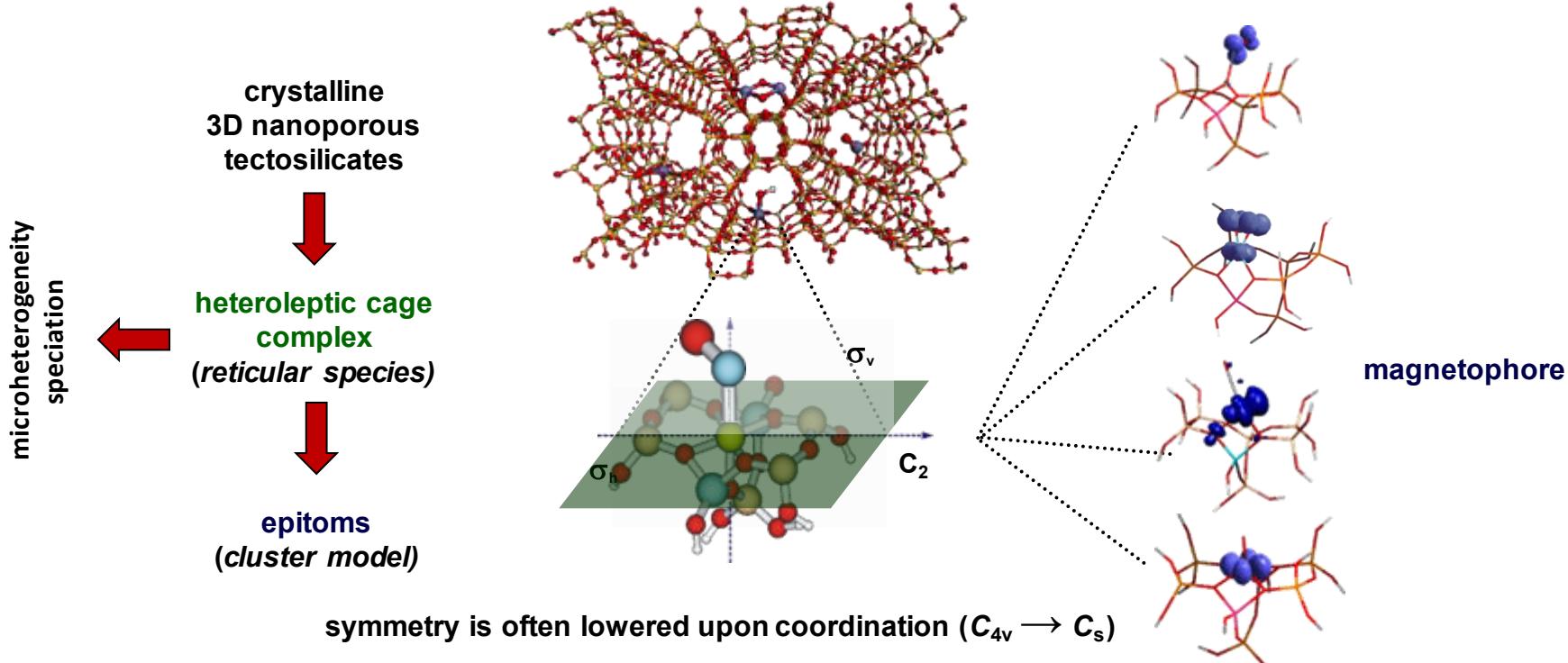
Application of EPR to materials, surfaces, and powders

gallery of heterogeneous materials with reduced dimensionality



chemical and magnetic functionalization by TMI – spin phenomena
at interfaces associated with reactivity

surface complexes – symmetry and speciation



heterogeneity of surface and the presence of heteroleptic ligands gives rise to low symmetry and pronounced speciation (distribution of EPR parameters, strain effects) resulting in complex EPR spectra

chemical species in disordered systems detected with EPR

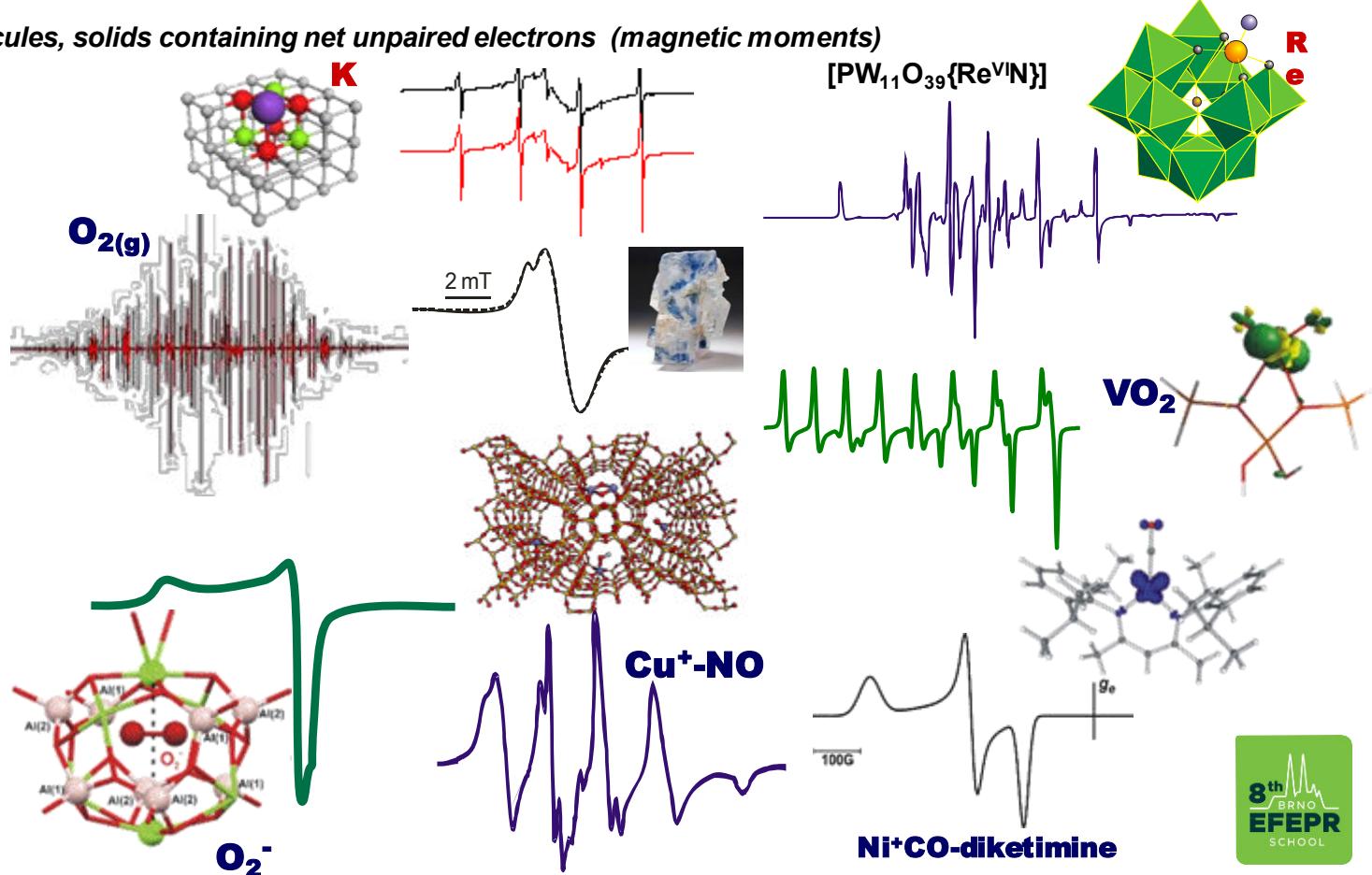
paramagnets = atoms, molecules, solids containing net unpaired electrons (magnetic moments)

some simple adsorbed molecules with unpaired electrons (NO , NO_2 , O_2)

transition-metal ion complexes (molecular and supported)

electronic defects in solids

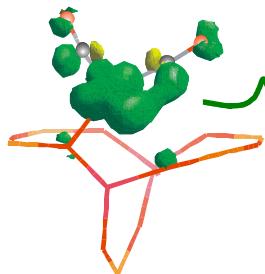
electrons of conducting bands



EPR profits

identification

$$Y(B, \nu) = C \int_{\theta}^{\pi/2} \int_{\varphi}^{2\pi} \sum_i P(i, \theta, \varphi, \nu) f(B - B_0[\nu], \sigma_B) d\cos\theta d\varphi$$



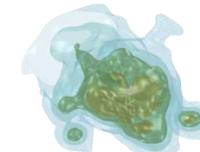
$$\begin{aligned} Y(B) dB &\xrightarrow{B = B_0 + r \cdot \text{grad } B} I(x, y, z) \\ I = \iint Y(B) dB &\xrightarrow{B = \text{const}} I(t) \end{aligned}$$

quantification (analytics)

$$N_x = \frac{g_w^2 [S(S+1)]_w h_w Q_x H_m^w G_w P_w^{0.5}}{g_x^2 [S(S+1)]_x h_x Q_x H_m^x G_x P_x^{0.5}} \left(\frac{A_x}{A_w} N_w \right)$$

spatial distribution (imaging)

$$I(B) = \int_{-\infty}^{+\infty} (S(B - r \cdot \text{grad}_r B) \cdot P(r) \cdot C(r)) dr$$



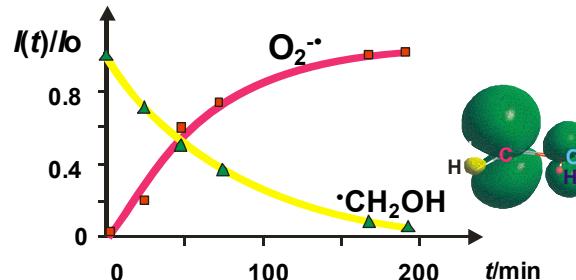
www.novlet.eu



ERI TM600 scanner

dynamic phenomena

rate processes (kinetics)



outline

1. EPR spectra of anisotropic systems

isotropic and anisotropic spectra

powder systems

angular dependency of g factor

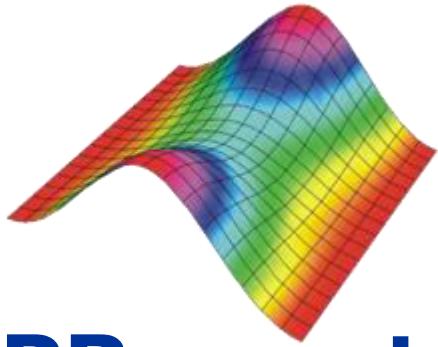
symmetry of EPR spectrum

2. Extra features of powder EPR spectra of anisotropic systems

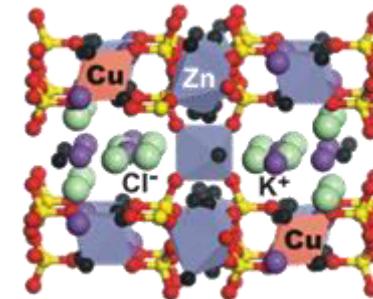
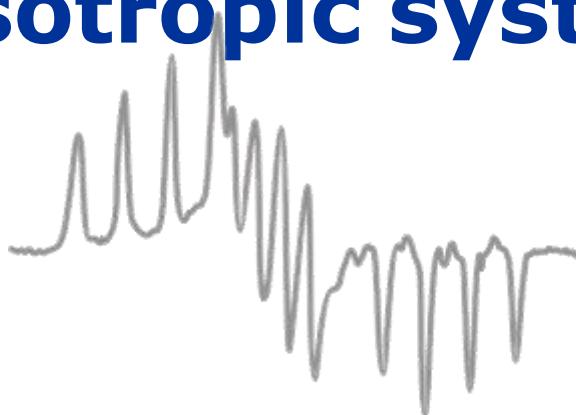
3. Low-symmetry effects

4. Local inhomogeneity – strain effects

5. Local symmetry probes



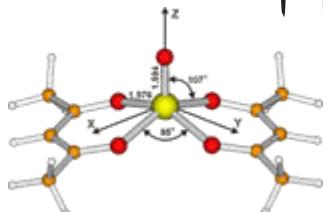
EPR spectra of anisotropic systems



isotropic spectra

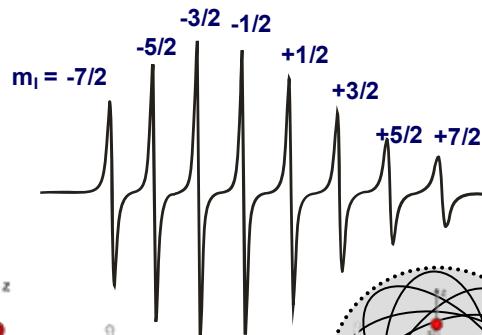
Isotropic = „same in all directions”

- In fluid solution a molecule can tumble rapidly, and presents an „average” to the external magnetic field direction.
- An „average (or isotropic) response is detected,
- provided that the tumbling is fast compared to the frequency of the experiment.



VO(acac)₂

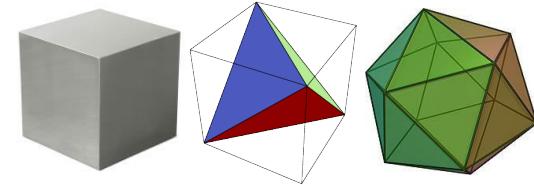
**partially time-averaged spectra-
asymmetric line broadening**



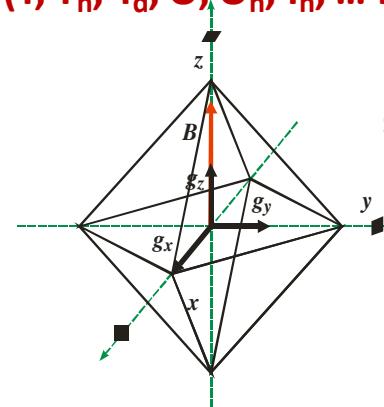
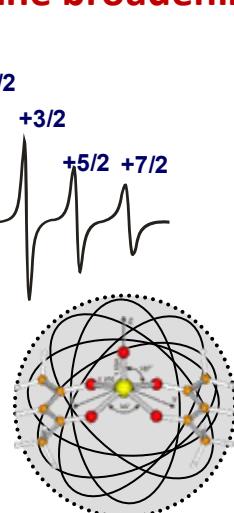
$$\tau_R = \eta V / kT$$

$\overrightarrow{\mu} = -g_{\text{iso}}(\mu_B/\hbar)\overrightarrow{S}$

g is a scalar



**high local symmetry
(T, T_h, T_d, O, O_h, I_h, ... R₃)**



symmetry constraints
 $g_{\text{iso}} = g_{xx} = g_{yy} = g_{zz}$

$$H = \hbar^{-1} g_{\text{iso}} \mu_B B^T \cdot S$$

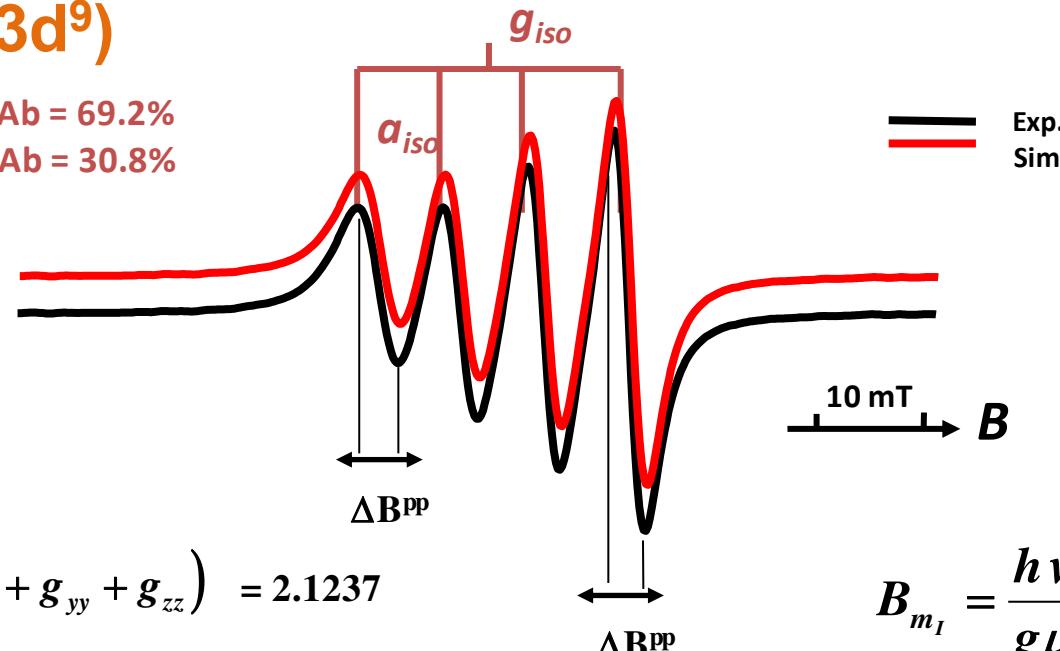
$$H = \hbar^{-1} g \mu_B (B_x S_x + B_y S_y + B_z S_z)$$

Cu(acac)₂ solution spectrum

Cu(acac)₂ (3d⁹)

⁶³Cu $I = 3/2$ $g_n = 1.484$ Ab = 69.2%

⁶⁵Cu $I = 3/2$ $g_n = 1.588$ Ab = 30.8%



$$\langle g \rangle = \frac{1}{3} (g_{xx} + g_{yy} + g_{zz}) = 2.1237$$

$$\langle A \rangle = \frac{1}{3} (A_{xx} + A_{yy} + A_{zz}) = a_{iso} = 7.62 \text{ mT}$$

$$B_{m_I} = \frac{h\nu_0}{g\mu_B} - \frac{a_{iso}m_I}{g\mu_B}$$

note that linewidths are not constant

Cu(acac)₂ solution spectrum

Cu(acac)₂ (3d⁹)

⁶³Cu $I = 3/2$ $g_n = 1.484$ Ab = 69.2%

⁶⁵Cu $I = 3/2$ $g_n = 1.588$ Ab = 30.8%

$$\alpha - \alpha_0 \propto (\Delta g)^2 \tau_R$$

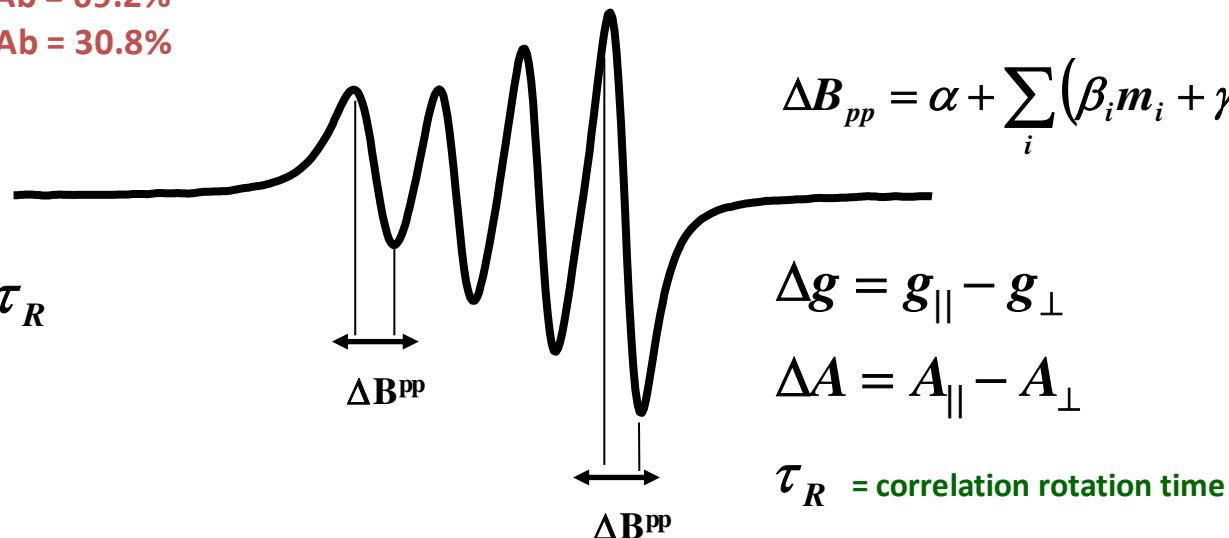
$$\beta_i \propto (\Delta g \Delta A) \tau_R$$

$$\gamma_i \propto (\Delta A)^2 \tau_R$$

for a spherical particle of radius r

$$\tau_R = \frac{4\pi r^3 \eta}{3kT}$$

m_r -dependence of linewidths results from incomplete averaging of g and A tensor anisotropy



$$\Delta B_{pp} = \alpha + \sum_i (\beta_i m_i + \gamma_i m_i^2 + \dots)$$

$$\Delta g = g_{||} - g_{\perp}$$

$$\Delta A = A_{||} - A_{\perp}$$

τ_R = correlation rotation time

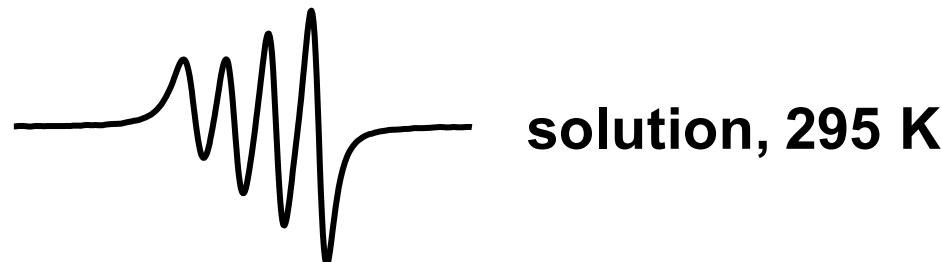
J. Chem. Phys., 33, 1094, (1960),
44, 154, (1966); 44, 169, (1966)

frozen solution „powder” spectrum

Cu(acac)₂ (3d⁹)

^{63}Cu I = 3/2 g_n = 1.484 Ab = 69.2%

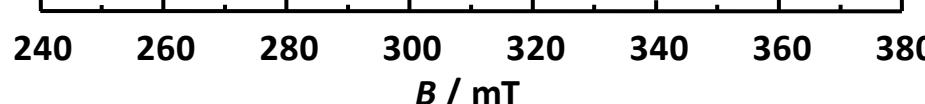
^{65}Cu I = 3/2 g_n = 1.588 Ab = 30.8%



frozen solution, 77 K
toluene

frozen solution, 77 K
toluene + CH₂Cl₂

„glass”



anisotropic spectra

$$\vec{\mu} = -(\mu_B/\hbar) \vec{g} \vec{S}$$

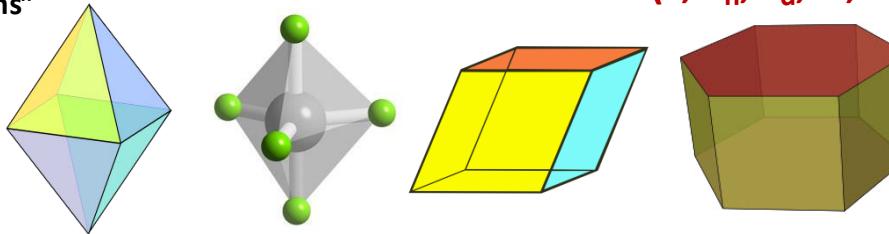
g is a tensor

$$g = \begin{bmatrix} g_{xx} & 0 & 0 \\ 0 & g_{yy} & 0 \\ 0 & 0 & g_{zz} \end{bmatrix}$$

local symmetry lower than
 $(T, T_h, T_d, O, O_h, I_h, \dots R_3)$

Anisotropic = „different in different directions”

- In a solid sample molecular motion is usually restricted,
- often only vibrational motion remains.
- EPR spectra reflect a „sum” of many molecular orientations with respect to the applied magnetic field,
- ideally stochastic distribution is expected.



symmetry constraints

$$g_{xx} = g_{yy} \neq g_{zz}$$

$$g_{xx} \neq g_{yy} \neq g_{zz}$$

$$H = \hbar^{-1} \mu_B \mathbf{B}^T \cdot \mathbf{g} \cdot \mathbf{S}$$

$$H = \hbar^{-1} \mu_B (g_{xx} B_x S_x + g_{yy} B_y S_y + g_{zz} B_z S_z)$$

powder-like systems for EPR measurements

preparation of a sample in a „powder” form

- 1) The paramagnetic must be diluted without being contaminated.
Dilution must be obtained at the **molecular level**.**
- 2) The orientation of paramagnetic particles in space **must be completely stochastic**. The solid phase must be obtained in a form sufficiently fine to avoid the presence of macrocrystalites. In the case of frozen solutions, these must form a glass.**
- 3) The random orientation of the paramagnets must be tested by rotating the sample in EPR cavity of about 20° and repeating the measurement. If the two spectra are identical, the sample can be considered as a powder one.**

powder-like systems for EPR measurements

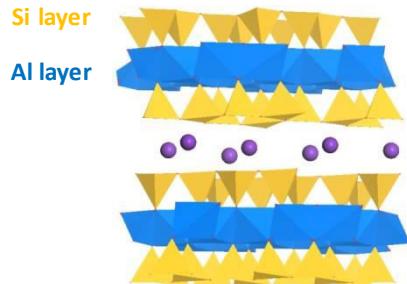
preparation of a sample in the form of glass „powder”

Components	Mixtures	Ratio A:B:C...	Glassing Agents		
			Pure Substance		
hydrocarbon			3-methylpentane	sulfuric acid	sugar (.4 M sucrose)
3-methylpentane/isopentane		1:1	methylcyclopentane	phosphoric acid	triethanolamine
isopentane/methylcyclohexane		1:6	paraffin oil (Nujol)	ethanol	2-methyltetrahydrofuran
methylcyclopentane/methylcyclohexane		1:1	isopentane	isopropanol	di-n-propyl ether
3-methylpentane/isopentane		1:2	methylcyclohexane	1-propanol	decalin
alcohol			isoctane	1-butanol	triacetin
ethanol/methanol		4:1, 5:2, 1:9	boric acid	glycerol	toluene
isopropanol/isopentane		3:7			
ethanol/isopentane/diethyl ether		2:5:5			
isopentane/n-butanol		7:3			
isopentane/isopropanol		8:2			
diethyl ether/isoctane/isopropanol (or ethanol)		3:3:1			
diethyl ether/isopropanol (or ethanol)		3:1			
diethyl ether/toluene/ethanol		2:1:1			
butanol/diethyl ether		2:5			
aromatic					
toluene/methylene chloride		1:1 or excess toluene			
tolueneacetone		1:1 or excess toluene			
toluene/EtOH or MeOH		1:1 or excess toluene			
toluene/acetonitrile		1:1 or excess toluene			
toluene/chloroform		1:1 or excess toluene			
water					
water/propylene glycol		1:1			
water/glycerol		4:1 to 1:4			
water/(poly)ethylene glycol		4:1 to 1:4			

based on R. S. Drago, Physical methods for chemists, 1992

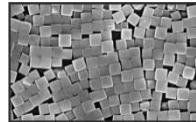
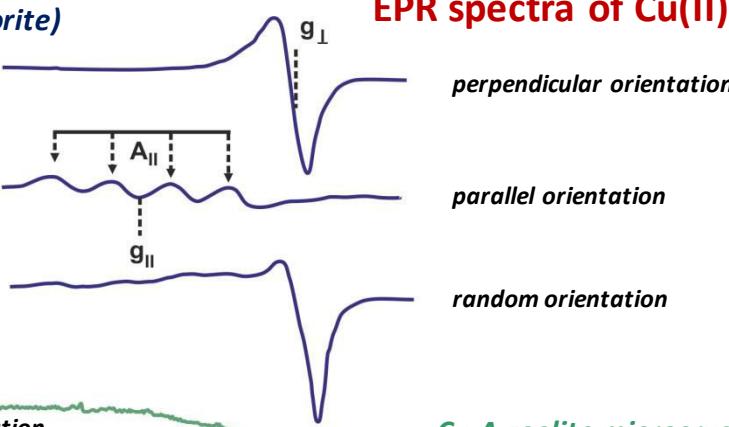
partially-oriented samples

alumina-silicate layered material (hectorite)

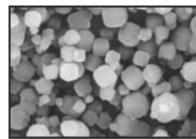


Advanced Techniques for Clay Mineral Analysis, Elsevier, 1981

EPR spectra of Cu(II) probe



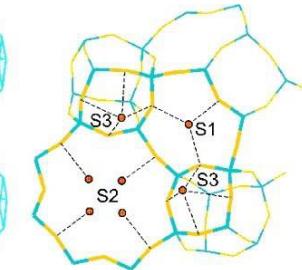
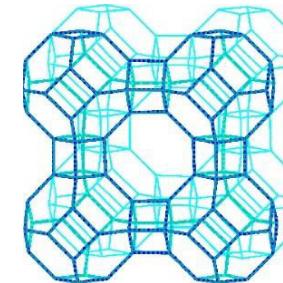
perpendicular orientation
of glass plate



parallel orientation
of glass plate

powder sample

Cu-A zeolite microcrystals deposited on a glass plate



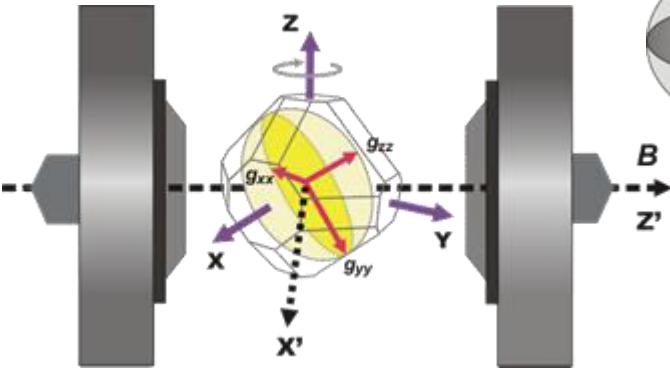
J. Phys. Chem. B, 2003, 107, 8281

260 280 300 320 340
 B / mT

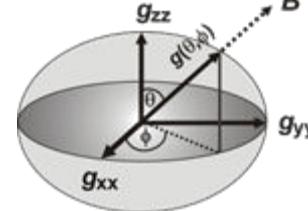
more details on partially oriented powders: F. E. Mabbs, D. Collison, Electron Paramagnetic Resonance of d Transition Metal Compounds, Elsevier, 1992.

orientation-dependent EPR spectrum of monocrystal

reference axis system

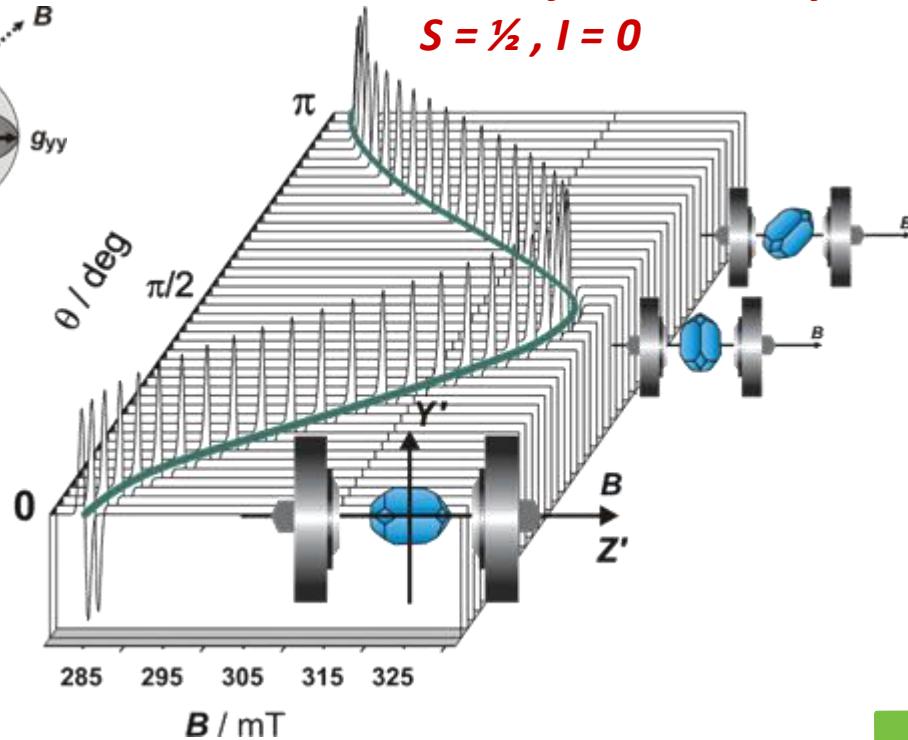


g-tensor ellipsoide



EPR measurements for a monocrystal

$S = \frac{1}{2}$, $I = 0$

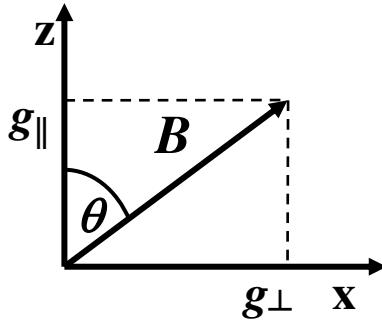


1. measure EPR spectra with respect to rotation about each crystal axe
2. find the relation $B_{\text{rez}}(\theta, \phi)$, ergo $g(\theta, \phi)$
3. fit the experimental $g(\theta, \phi)$ relationship to the theoretical equations

$$g_{\text{eff}}^2 = g_{ii}^2 \cos^2 \theta + g_{jj}^2 \sin^2 \theta + 2g_{ij}^2 \sin \theta \cos \theta$$

4. calculate the principal components of g-tensor (g_{xx} , g_{yy} , g_{zz}) – and orientation of the g-frame with respect to the crystal frame

angular dependency of g factor



example for axial symmetry

$$H = \hbar^{-1} \mu_B [g_{\perp} B_x S_x + g_{\parallel} B_z S_z]$$

$$H = \hbar^{-1} \mu_B B [g_{\perp} S_x \sin \theta + g_{\parallel} S_z \cos \theta]$$

calculation of matrix elements H_{ij}

$$\langle \alpha | H | \alpha \rangle = 1/2 \mu_B B g_{\parallel} \cos \theta$$

$$\langle \alpha | H | \beta \rangle = 1/2 \mu_B B g_{\perp} \sin \theta$$

$$\langle \beta | H | \beta \rangle = -1/2 \mu_B B g_{\parallel} \cos \theta$$

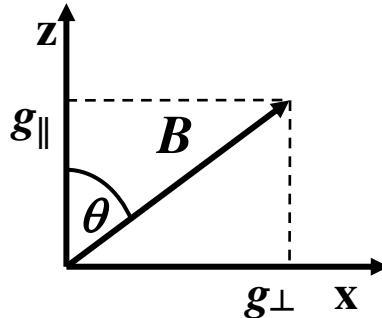
$$\langle \beta | H | \alpha \rangle = 1/2 \mu_B B g_{\perp} \sin \theta$$

calculation of eigenvalues of H_{ij} (E)

$$\begin{array}{cc} \alpha & \beta \\ \begin{pmatrix} 1/2 \mu_B B g_{\parallel} \cos \theta - E & 1/2 \mu_B B g_{\perp} \sin \theta \\ 1/2 \mu_B B g_{\perp} \sin \theta & -1/2 \mu_B B g_{\parallel} \cos \theta - E \end{pmatrix} & S_x |\pm 1/2\rangle = 1/2 |\mp 1/2\rangle \end{array}$$

$$\mathbf{g} = \begin{vmatrix} g_{\perp} & & \\ & \ddots & \\ & & g_{\parallel} \end{vmatrix}$$

angular dependency of g factor



	α	β
α	$1/2\mu_B B g_{\parallel} \cos \theta - E$	$1/2\mu_B B g_{\perp} \sin \theta$
β	$1/2\mu_B B g_{\perp} \sin \theta$	$-1/2\mu_B B g_{\parallel} \cos \theta - E$

$$(1/2\mu_B B g_{\parallel} \cos \theta - E) (-1/2\mu_B B g_{\parallel} \cos \theta - E) - (1/2\mu_B B g_{\perp} \sin \theta)^2 = 0$$

$$E_{1,2} = \pm 1/2\mu_B B (g_{\parallel}^2 \cos^2 \theta + g_{\perp}^2 \sin^2 \theta)^{0.5}$$

$$h\nu = E_2 - E_1 = \mu_B B (g_{\parallel}^2 \cos^2 \theta + g_{\perp}^2 \sin^2 \theta)^{0.5}$$

$$h\nu = \mu_B B g(\theta)$$

$$g(\theta) = (g_{\parallel}^2 \cos^2 \theta + g_{\perp}^2 \sin^2 \theta)^{0.5}$$

for $g_{\parallel} = g_{\perp} = g$ (isotropic system)

$$g(\theta) = g \underbrace{(\cos^2 \theta + \sin^2 \theta)^{0.5}}_{= 1} = g$$

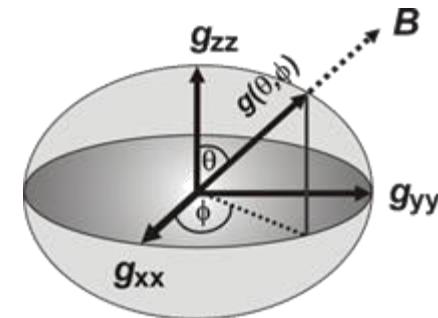
→ angular dependency vanishes

angular dependency of g factor

rhombic symmetry

$$\mathbf{g} = \begin{vmatrix} g_{xx} & & \\ & g_{yy} & \\ & & g_{zz} \end{vmatrix} \quad S = 1/2 \quad I = 0$$

reference frame



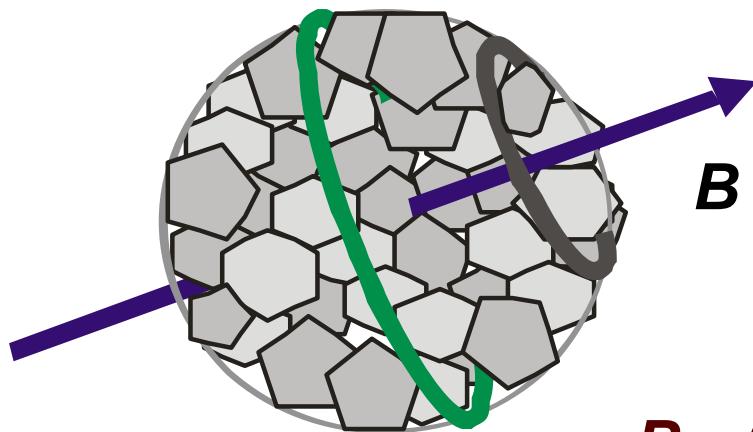
anisotropy of Zeeman interaction

$$B_{res} = \frac{h\nu_0}{g(\theta, \varphi)\mu_B}$$

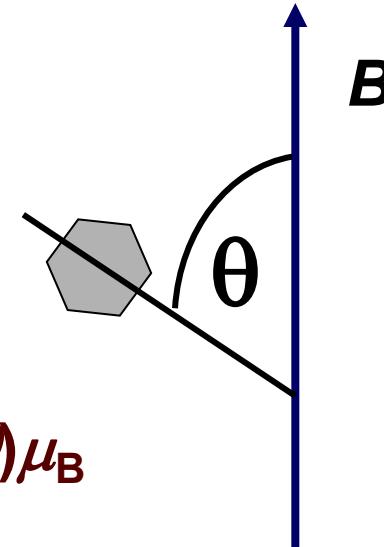
$$g = \left[(g_{xx}^2 \cos^2 \varphi + g_{yy}^2 \sin^2 \varphi) \sin^2 \theta + g_{zz}^2 \cos^2 \theta \right]^{1/2}$$

randomly oriented systems

powder and frozen solution patterns



$$B_{\text{res}}(\theta) = h\nu/g(\theta)\mu_B$$



fraction of crystallites oriented within the solid angle θ and $\theta + d\theta$ with respect to the magnetic field B

randomly oriented systems

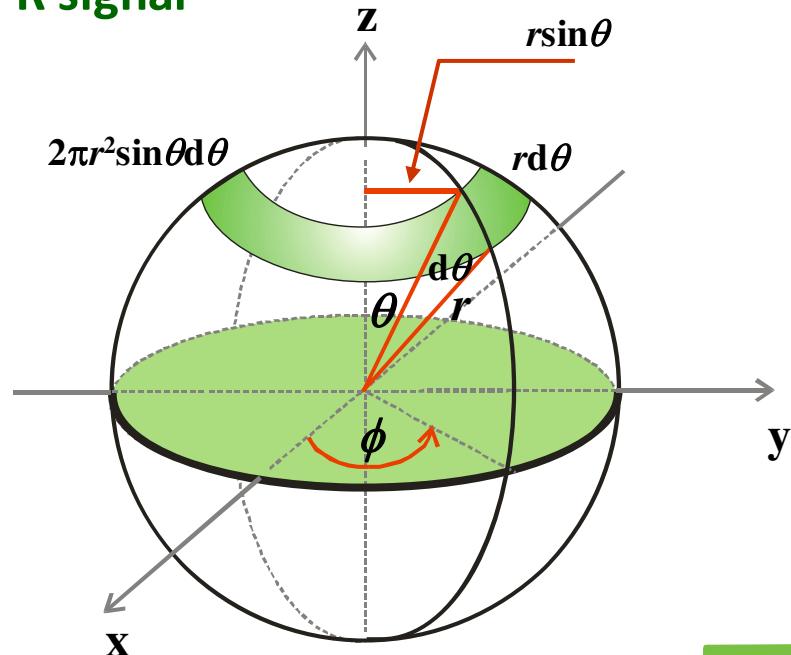
$$B_{res} = \frac{hv_0}{g(\theta, \varphi)\mu_B}$$

g-anisotropy induces angular dependency of EPR signal

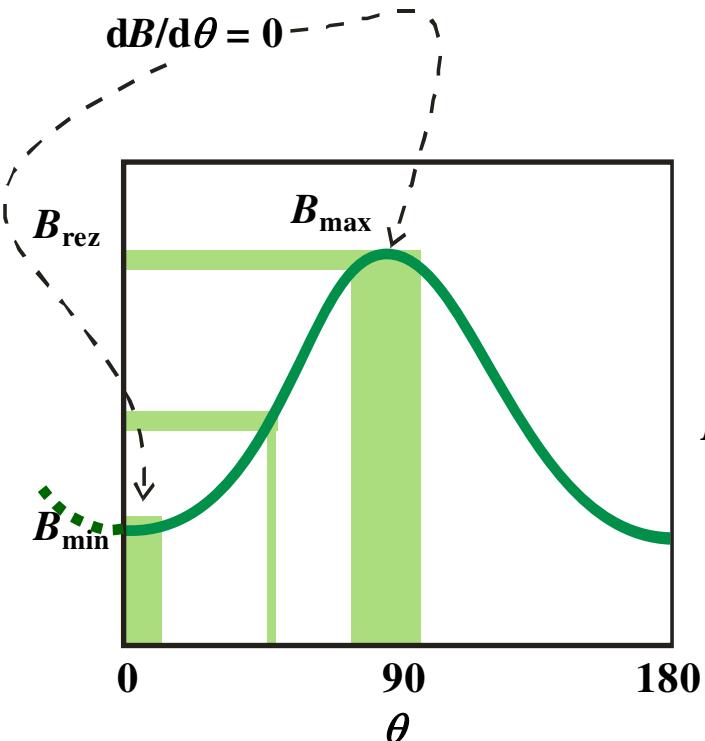
solid angle (Ω)
and
element of area (dA)
on the surface of a sphere

$$\Omega = A/r^2$$

$$d\Omega = \frac{2\pi r^2 \sin\theta d\theta}{r^2} = 2\pi \sin\theta d\theta$$



angular dependency for axial symmetry



$$B = h\nu/g(\theta)\mu_B$$

$$= [g_{\perp}^2 \sin^2 \theta + g_{\parallel}^2 \cos^2 \theta]^{-0.5} h\nu/\mu_B$$

$$= [g_{\perp}^2 - (g_{\perp}^2 - g_{\parallel}^2) \cos^2 \theta]^{-0.5} h\nu/\mu_B$$

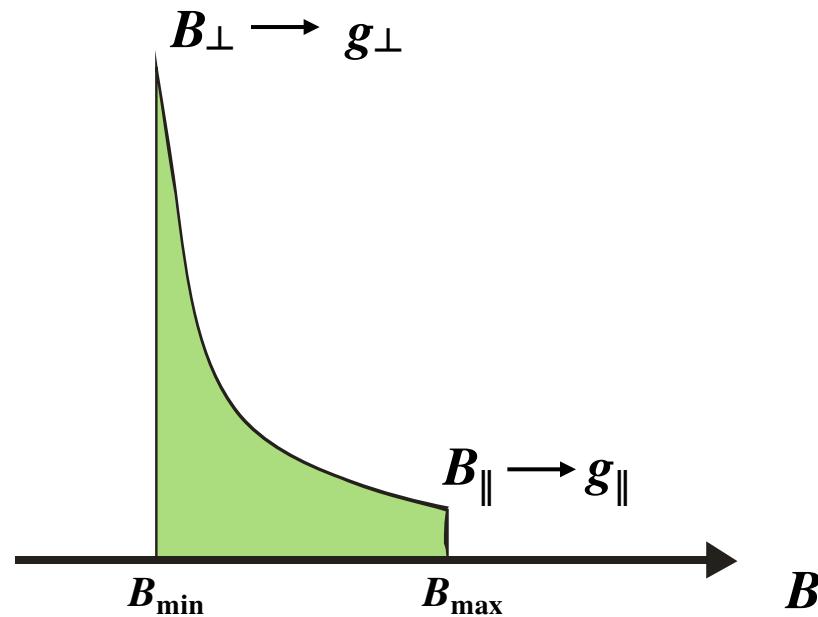
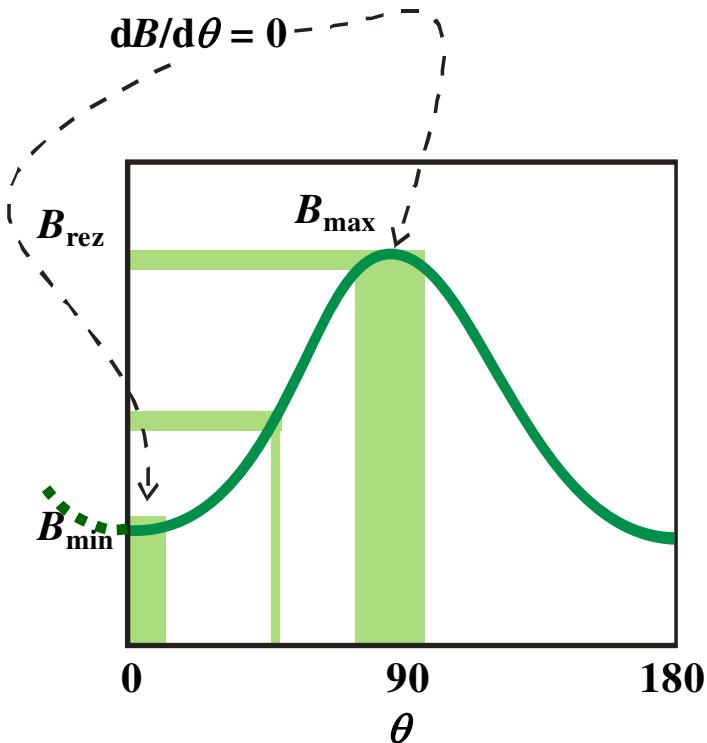
bigger anisotropy - greater span of magnetic resonance field

$$P(\theta)d\theta = d\Omega/4\pi = 1/2\sin\theta d\theta \sim P(B)dB$$

$$P(B) \propto 1/2C \frac{\sin\theta}{dB/d\theta}$$

$$P(B) = C/2(h\nu/\mu_B)^2 \frac{1}{B^3 |(g_{\perp}^2 - g_{\parallel}^2)\cos\theta|}$$

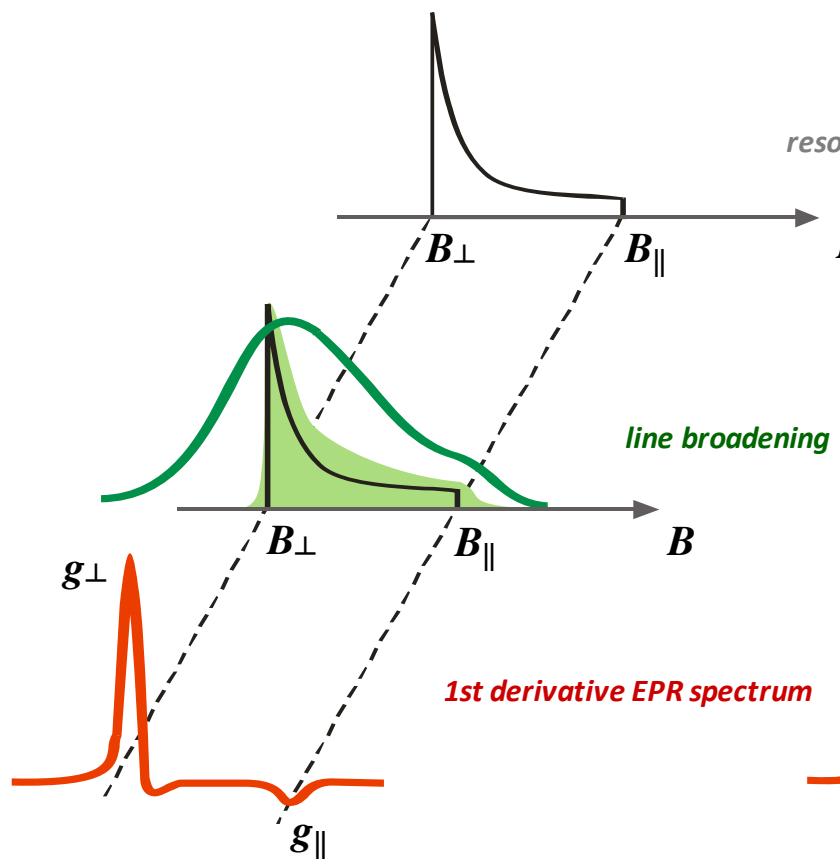
angular dependency for axial symmetry



$$P(B) = C/2(\hbar v/\mu_B)^2 \frac{1}{B^3 |(g_{\perp}^2 - g_{\parallel}^2) \cos \theta|}$$

absorption profiles for axial and rhombic symmetry

axial symmetry

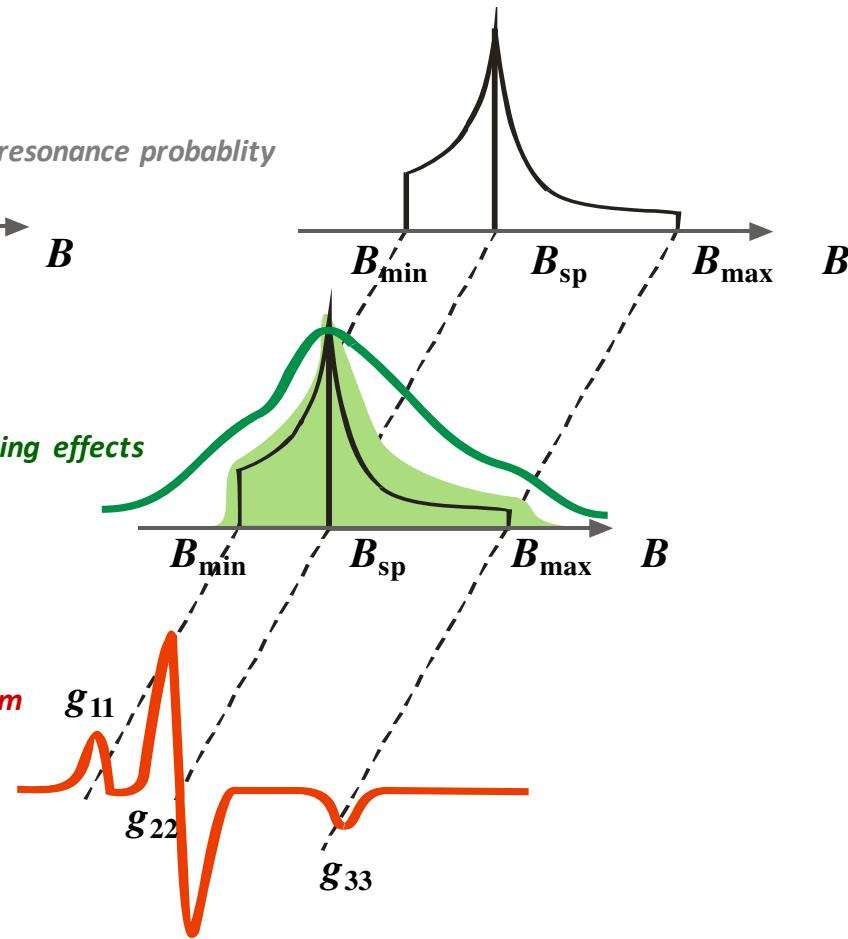


resonance probability

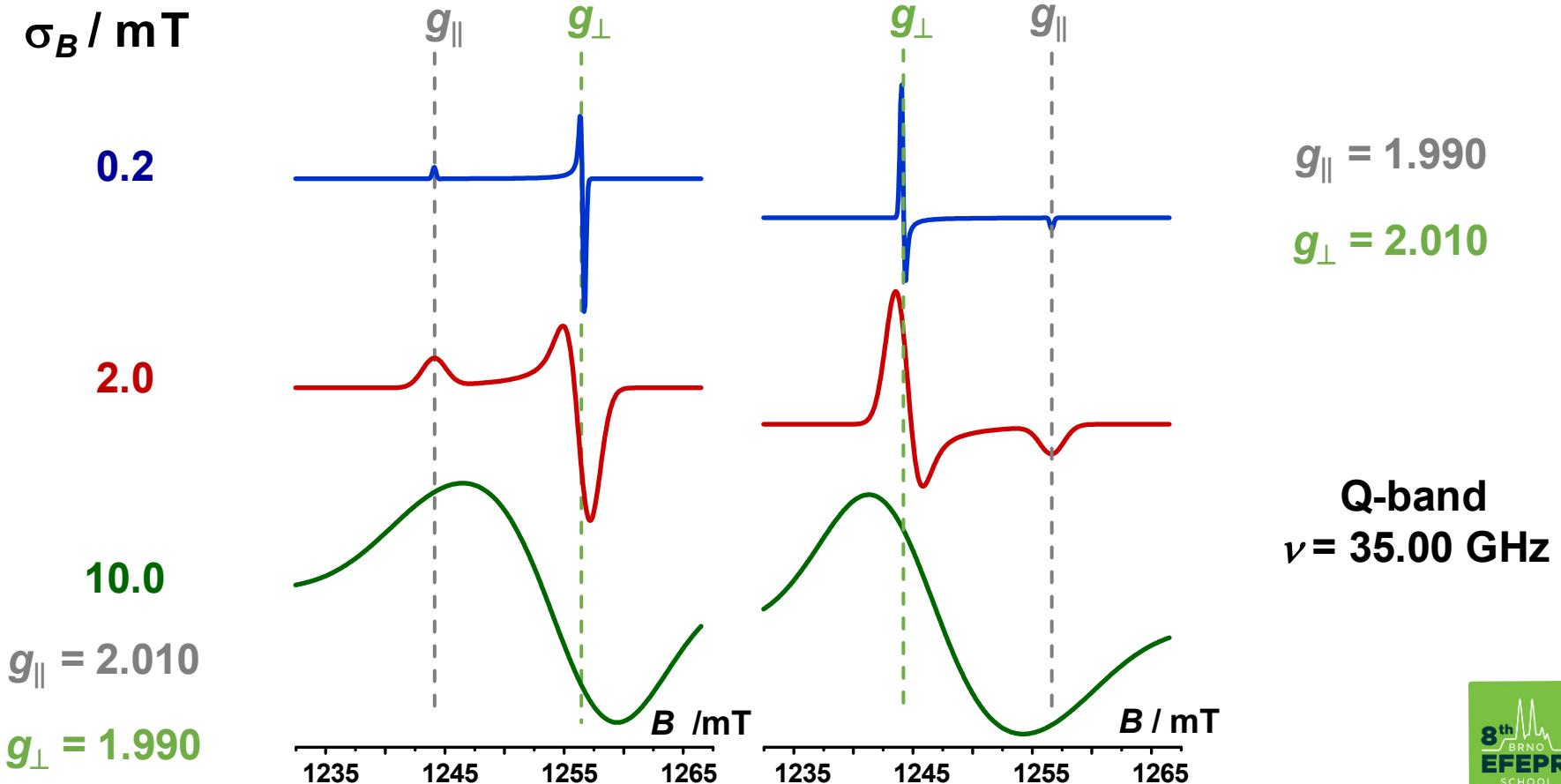
line broadening effects

1st derivative EPR spectrum

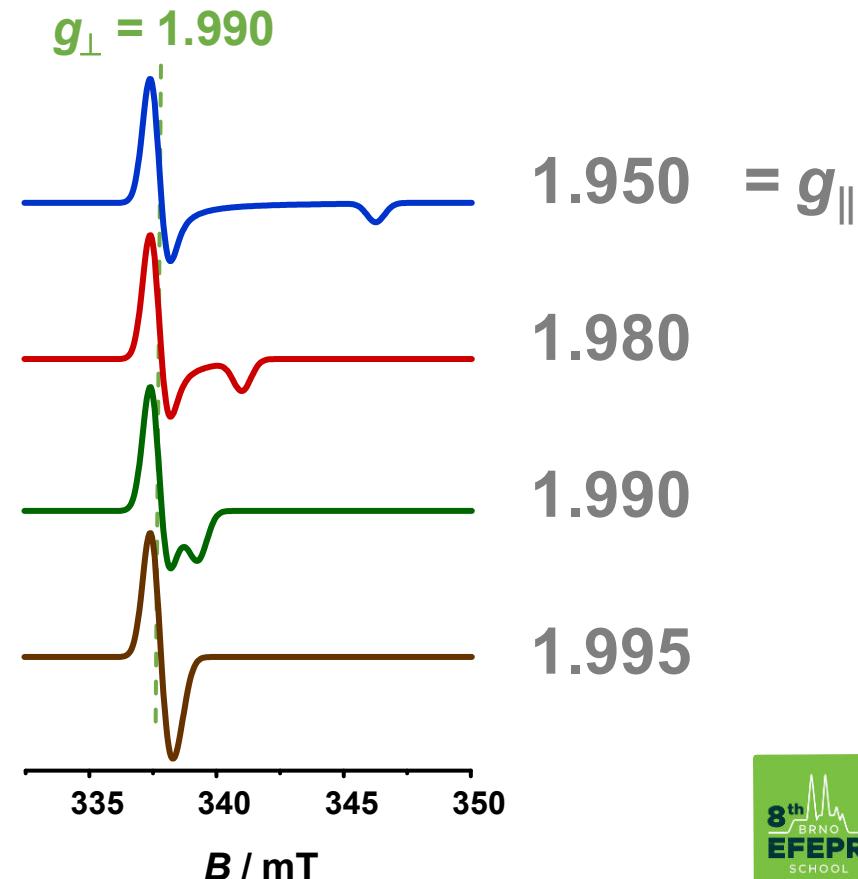
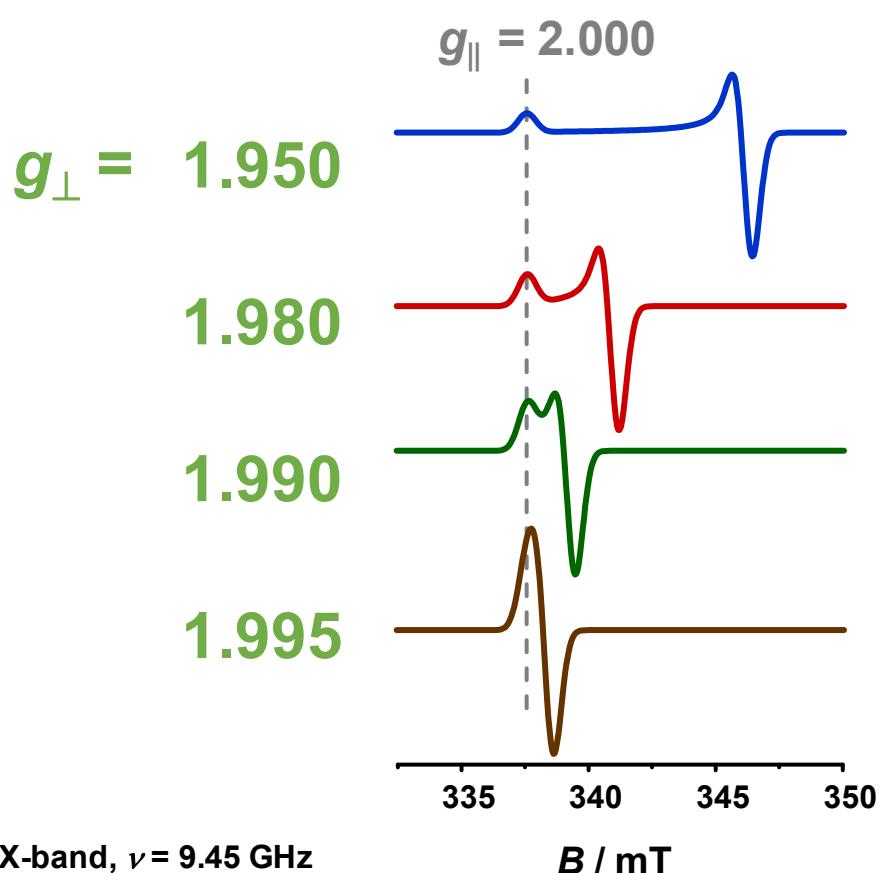
rhombic symmetry



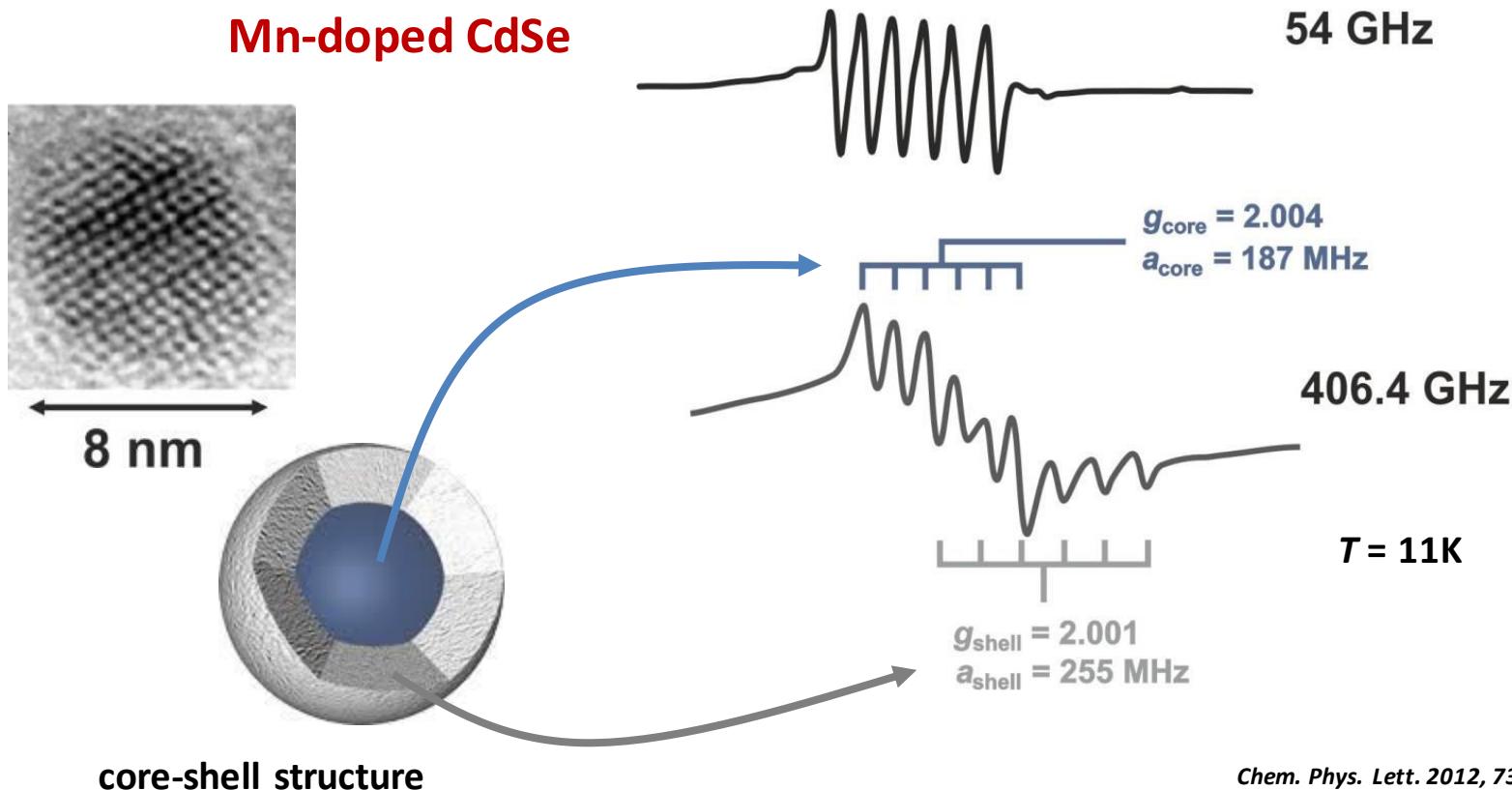
linewidth effects



effect of anisotropy in g -values

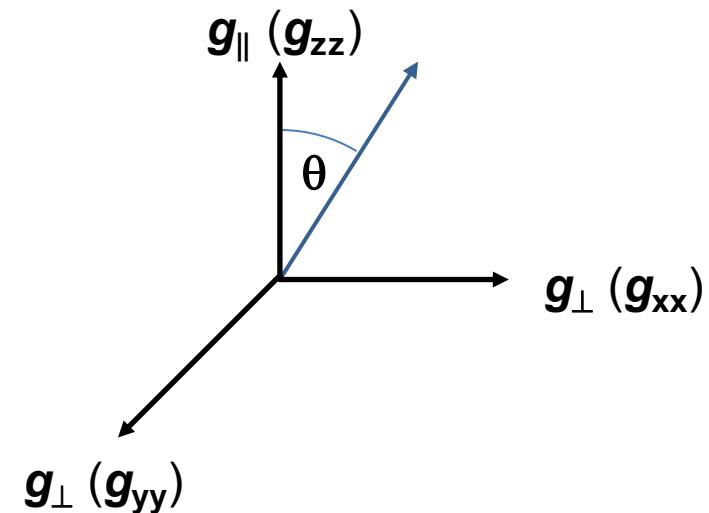
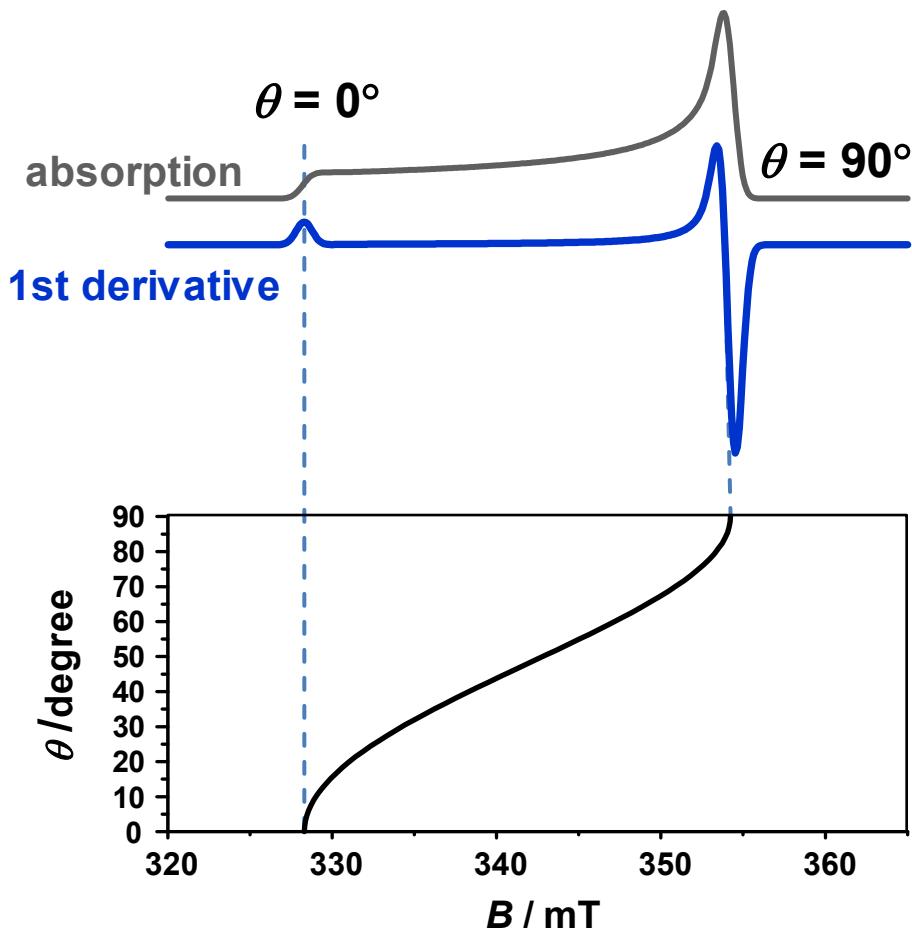


effect of anisotropy in *g*-values



Chem. Phys. Lett. 2012, 73, 524

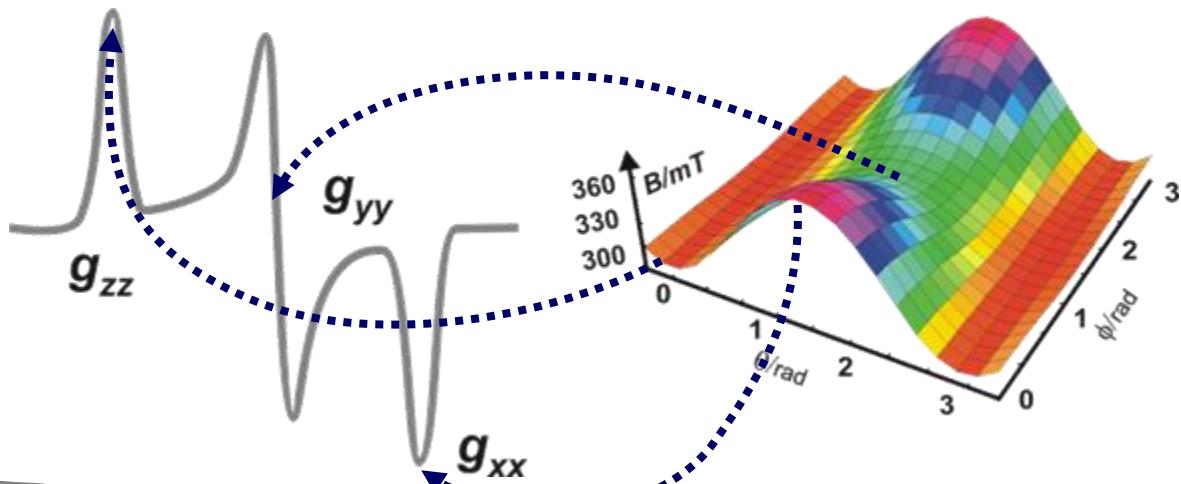
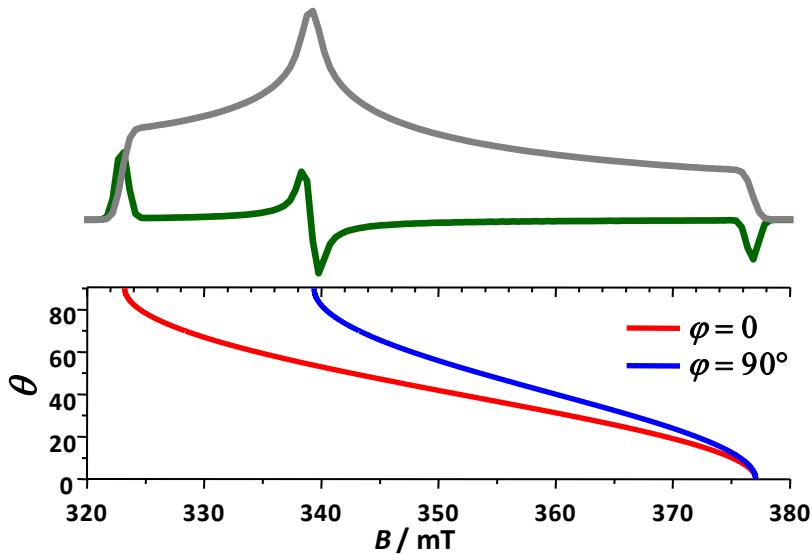
„road maps”



$$\theta = \cos^{-1} \sqrt{\frac{g_{\theta}^2 - g_{\perp}^2}{g_{\parallel}^2 - g_{\perp}^2}}$$

resonant field B_{res} of powder sample

resonance lines in the powder EPR spectrum are coincident with the stationary points of the plot of angular dependency of B

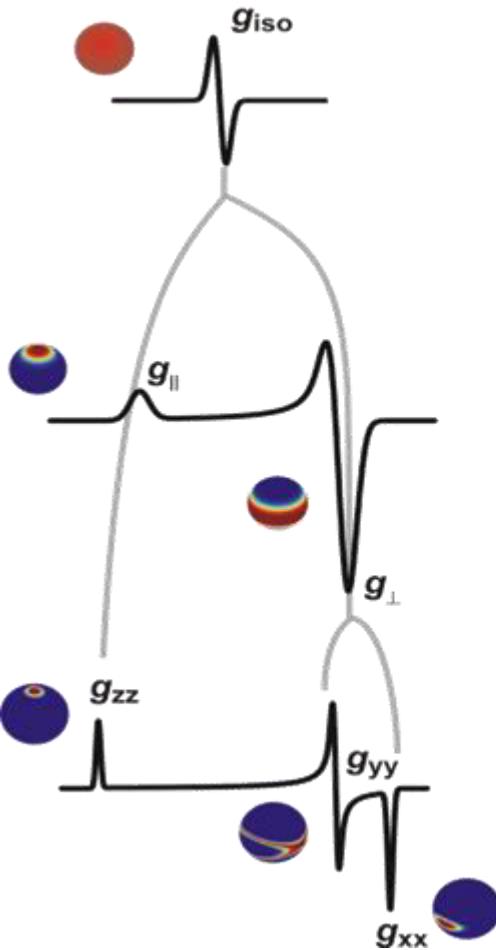


$$\frac{\partial B(\theta, \phi)}{\partial \theta} = 0 \quad \theta = 0 \quad \rightarrow g_{zz}$$
$$\frac{\partial B(\theta, \phi)}{\partial \phi} = 0 \quad \theta = 90^\circ, \phi = 0^\circ \quad \rightarrow g_{xx}$$
$$\frac{\partial B(\theta, \phi)}{\partial \phi} = 0 \quad \theta = \phi = 90^\circ \quad \rightarrow g_{yy}$$

symmetry – EPR spectrum relationship

simplest EPR symmetry

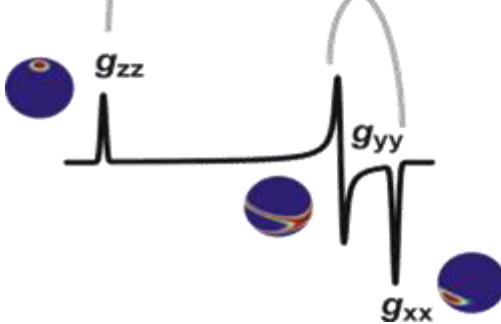
isotropic



axial

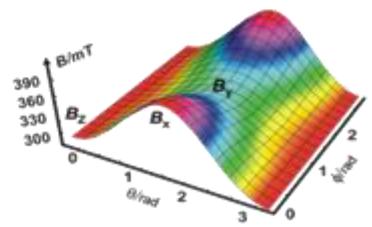
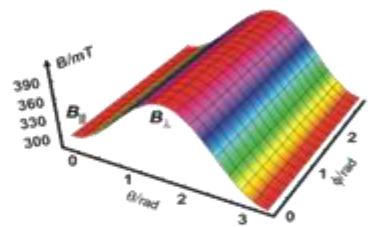
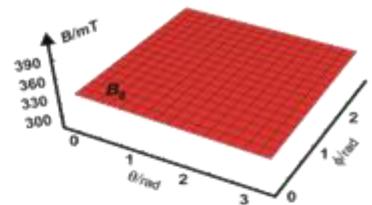


rhombic



resonant magnetic field

$$\mathbf{B}(\theta, \phi)$$

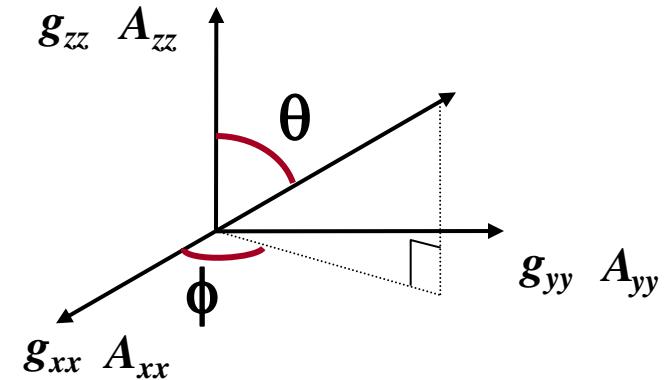


anisotropy of g - and A -tensors

$$g = \begin{vmatrix} g_{xx} & & \\ & g_{yy} & \\ & & g_{zz} \end{vmatrix} \quad A = \begin{vmatrix} A_{xx} & & \\ & A_{yy} & \\ & & A_{zz} \end{vmatrix}$$

anisotropy of hyperfine interaction

$S = 1/2 \quad I \neq 0$



$$B_{res} = \frac{h\nu_0}{g\mu_B} - \frac{Km}{g\mu_B}$$

$$gK = \left[(g_{xx}^2 A_{xx}^2 \cos^2 \phi + g_{yy}^2 A_{yy}^2 \sin^2 \phi) \sin^2 \theta + g_{zz}^2 A_{zz}^2 \cos^2 \theta \right]^{\frac{1}{2}}$$

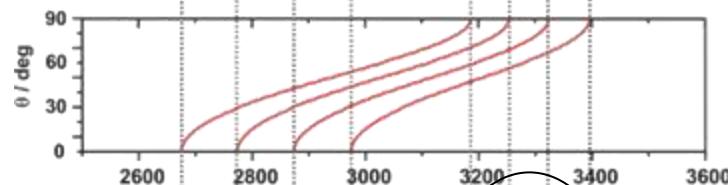
anisotropy of hyperfine interaction



parallel orientation

perpendicular orientation

$S = 1/2, I = 3/2$



changes of the
resonant field with
angle θ

„parallel“ component
 $g_{\parallel}, A_{\parallel}$

polioriented system
„powder spectrum“

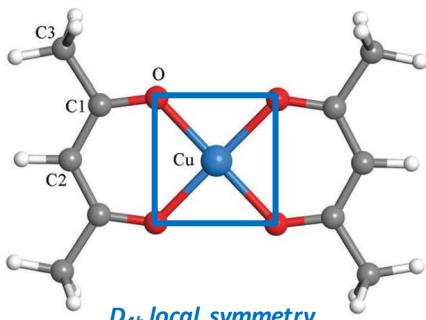
perpendicular component
 g_{\perp}, A_{\perp}

point symmetry vs. EPR symmetry

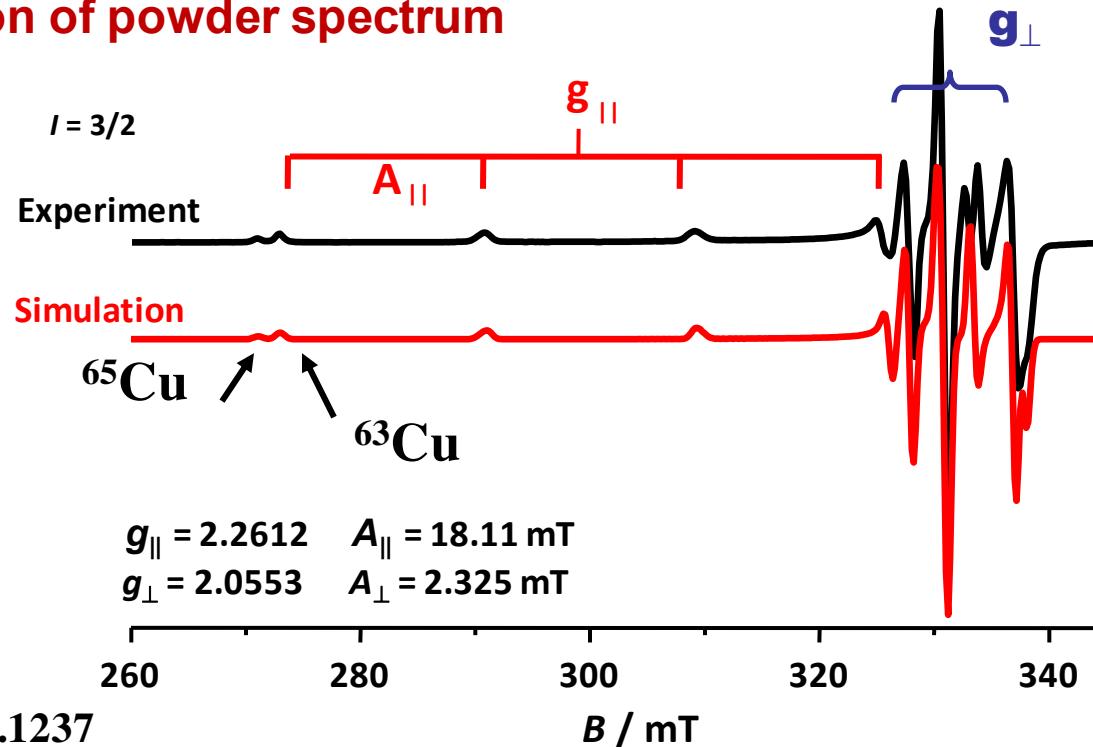
Crystallographic system	Bravais cell	Point symmetry	EPR symmetry	Constraints
Triclinic		C_1, C_i	Triclinic	$g_{ij} \neq 0 \text{ i } g_{xx} \neq g_{yy} \neq g_{zz}; A_{xx} \neq A_{yy} \neq A_{zz}$ $\alpha \neq \beta \neq \gamma \neq 0^\circ$ all non-coincident
Monoclinic		C_2, C_s, C_{2h}	Monoclinic	$g_{xz} = g_{yz} = g_{zx} = g_{zy} = 0 \text{ i } g_{xx} \neq g_{yy} \neq g_{zz}; A_{xx} \neq A_{yy} \neq A_{zz}$ one axis of g and one of A coincident
Trigonal		C_3, S_6	Axial non-collinear	As for $C_2 \text{ i } g_{xx} = g_{yy} \neq g_{zz}, g_{xy} = -g_{yx}; A_{xx} = A_{yy} \neq A_{zz}$ $g_{xy} = g_{yx} = 0 \text{ i } g_{xx} = g_{yy} \neq g_{zz}$ $A_{xx} = A_{yy} \neq A_{zz}$ only g_{zz} and A_{zz} coincident
Tetragonal		C_4, S_4, C_{4h} $D_4, C_{4v}, D_{2d}, \dots$	Axial non-collinear Axial	as for C_3 as for D_3
Hexagonal		C_6, C_{3h}, C_{6h} $D_6, C_{6v}, D_{3h}, D_{6h}$	Axial non-collinear Axial	as for C_3 as for D_3
Orthorombic		D_2, C_{2v}, D_{2h}	Rhombic	As for $C_2 \text{ i } g_{xy} = g_{yx} = 0$ all coincident
Regular		T, T_h, O, T_d, O_h	Isotropic	As for $D_3 \text{ i } g_{xx} = g_{yy} = g_{zz}; A_{xx} = A_{yy} = A_{zz}$ all coincident

EPR symmetry

computer simulation of powder spectrum

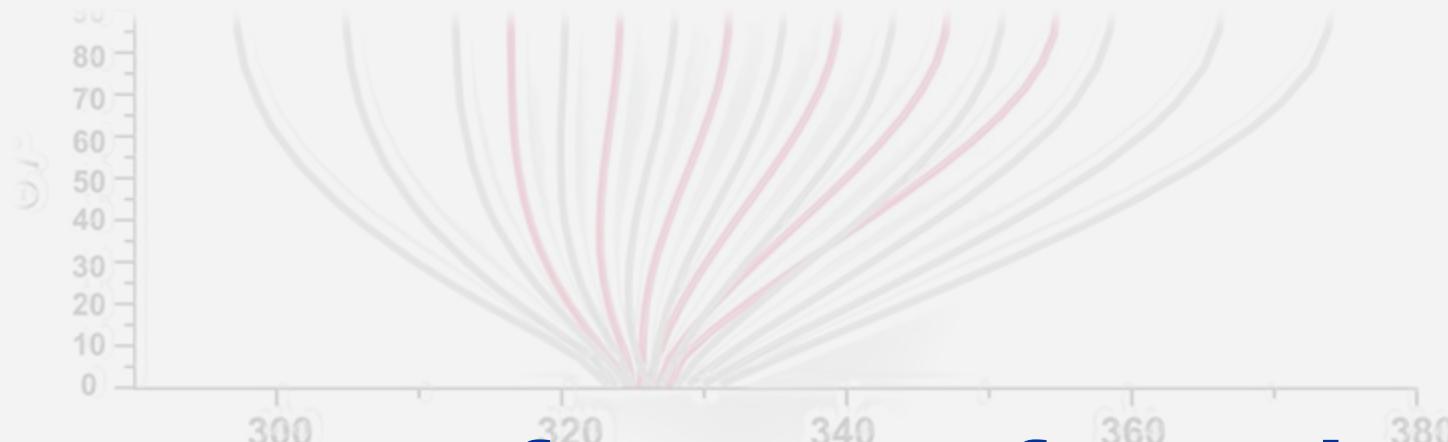


D_{4h} local symmetry



$$\langle g \rangle = \frac{1}{3} (2g_{\perp} + g_{\parallel}) = g_{iso} = 2.1237$$

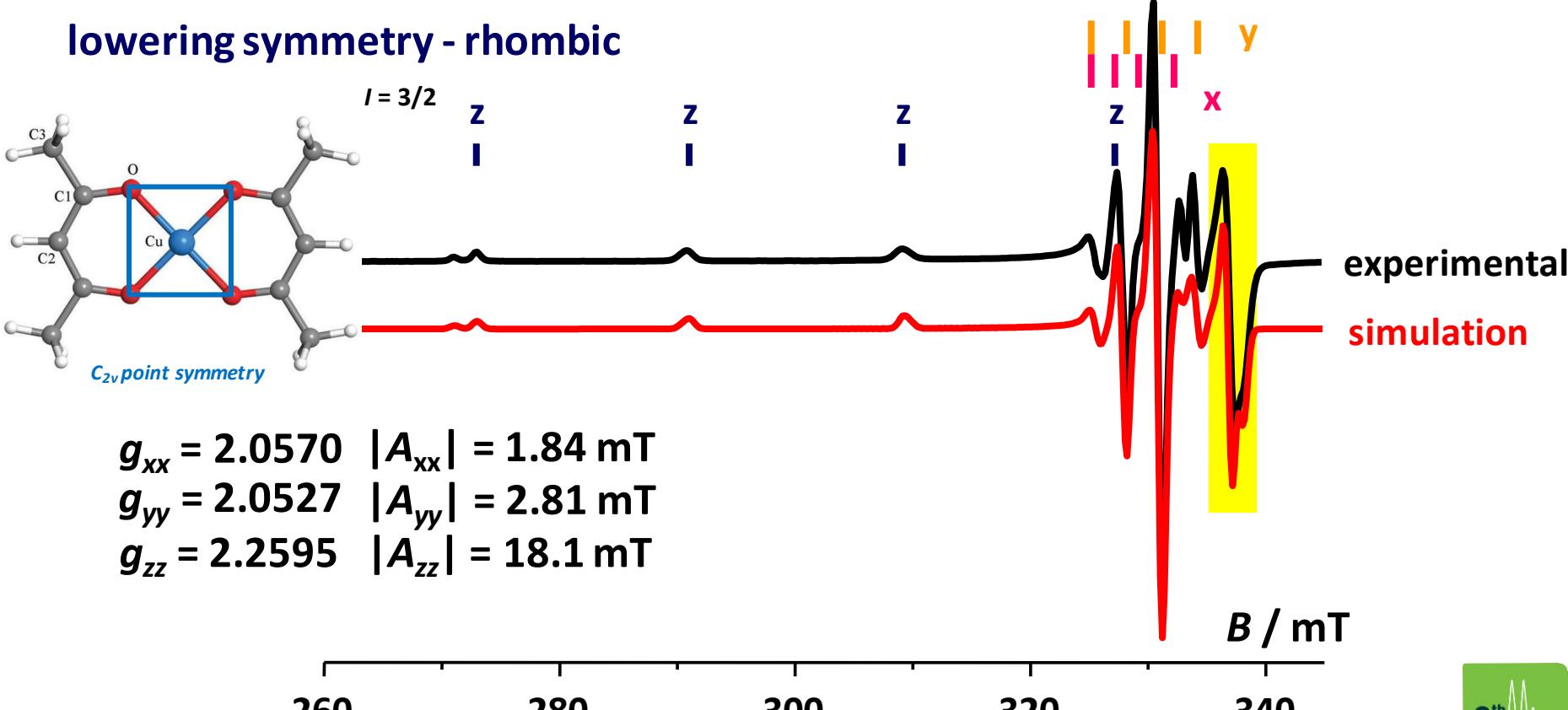
$$\langle A \rangle = \frac{1}{3} (2A_{\perp} + A_{\parallel}) = |a_{iso}| = 7.62 \text{ mT}$$



extra features of powder EPR spectra of anisotropic systems

EPR symmetry

lowering symmetry - rhombic



off-axis turning points

For some combinations of the principal values of g_{ii} and A_{ii} , owing to intricate relationship of $B_{\text{res}}(\theta, \phi)$, stationary points and therefore EPR lines may arise, which do not correspond to field orientations along the principal axes of g and A

$$\left(2A_i^2 - \frac{\hbar v A_i}{m} \right) < \left(\frac{g_i^2 A_i^2 - g_j^2 A_j^2}{g_i^2 - g_j^2} \right) < \left(2A_j^2 - \frac{\hbar v A_j}{m} \right)$$

regular features $\theta = 0$

$\theta = 90^\circ, \varphi = 0^\circ$

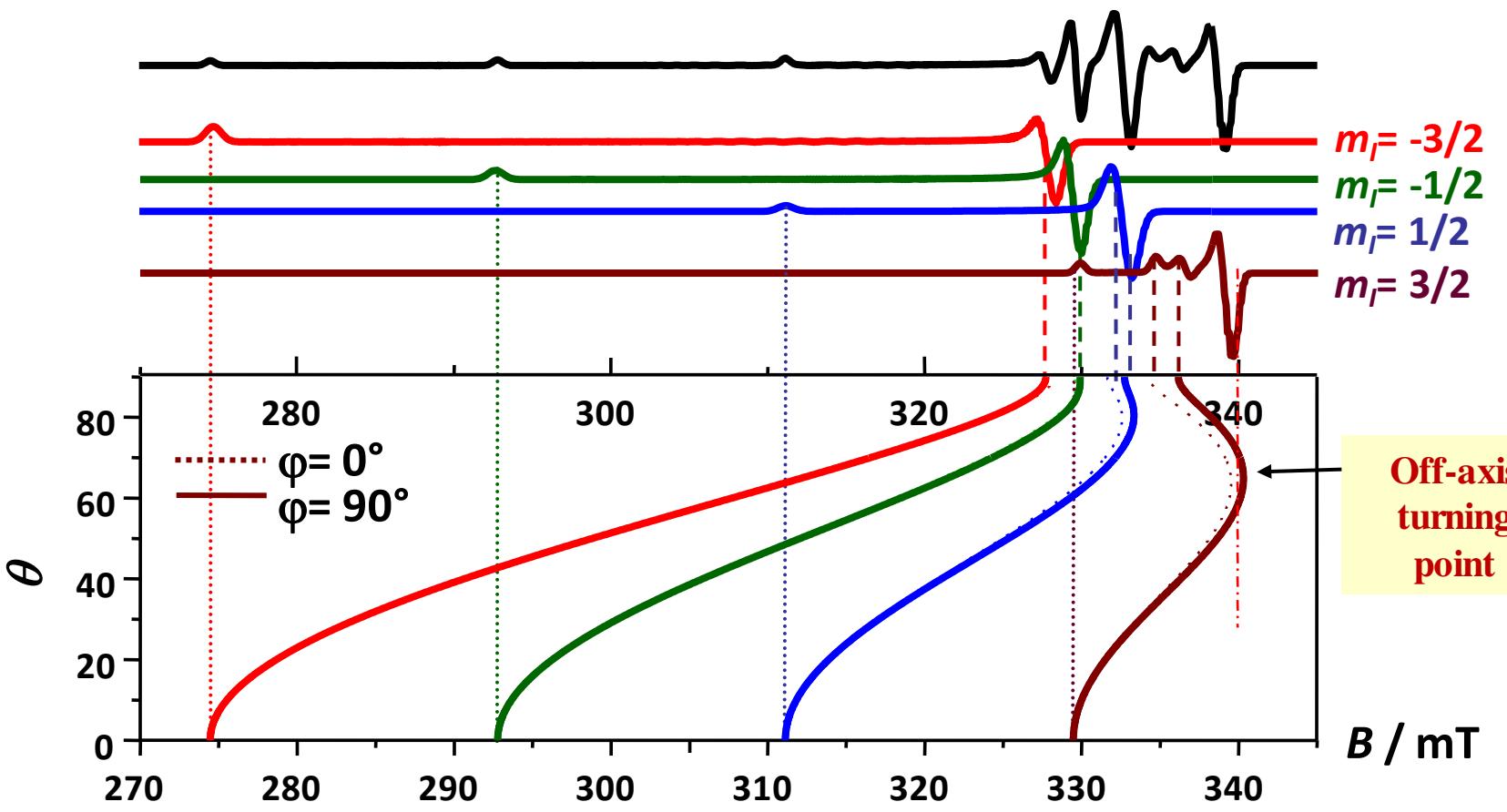
$\theta = \varphi = 90^\circ$

extra, off-axis features $\theta = 90^\circ, \varphi = \varphi_{xy}$

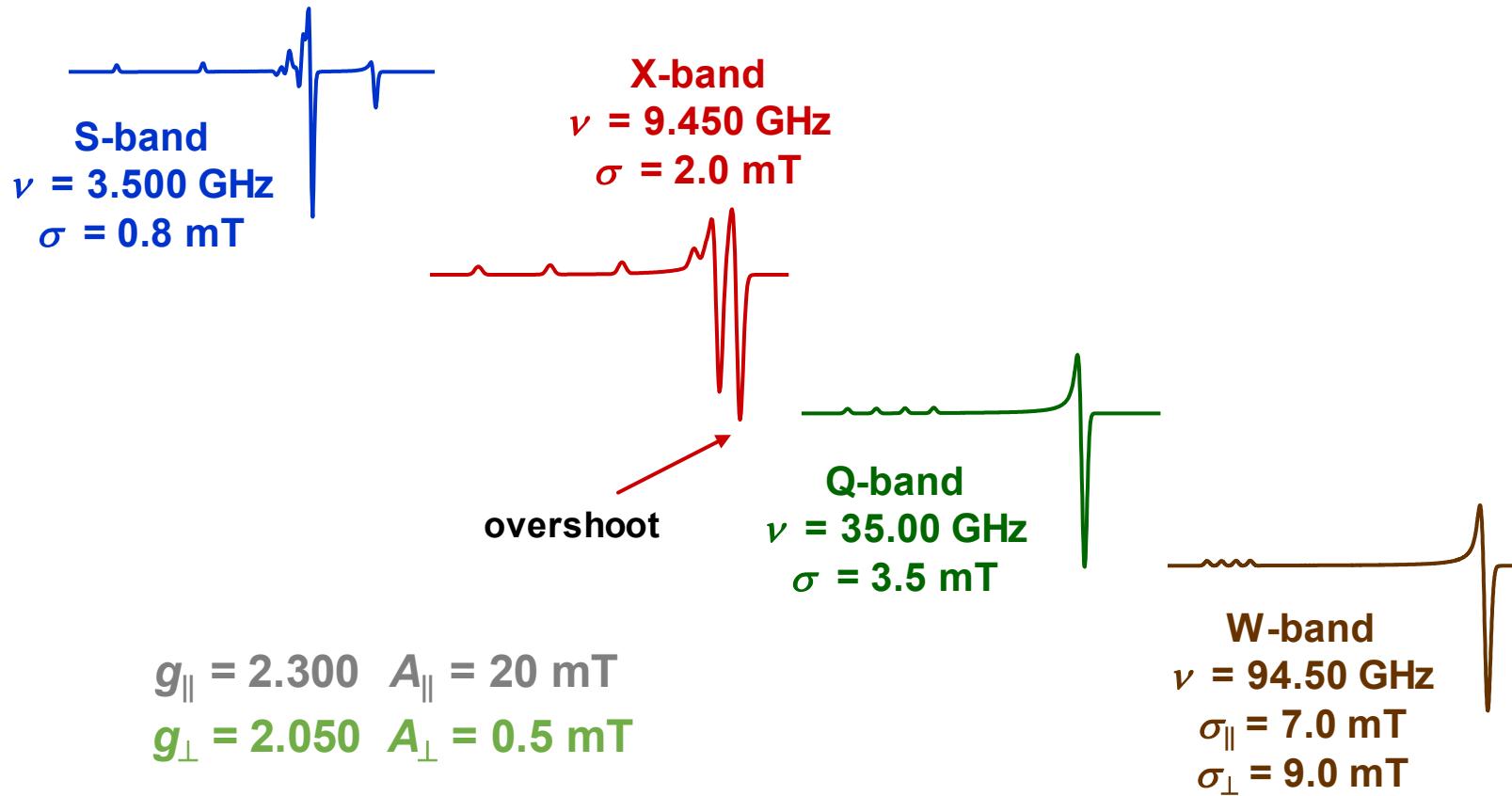
$\theta = \theta_{yz}, \varphi = 90^\circ$

$\theta = \theta_{xz}, \varphi = 0^\circ$

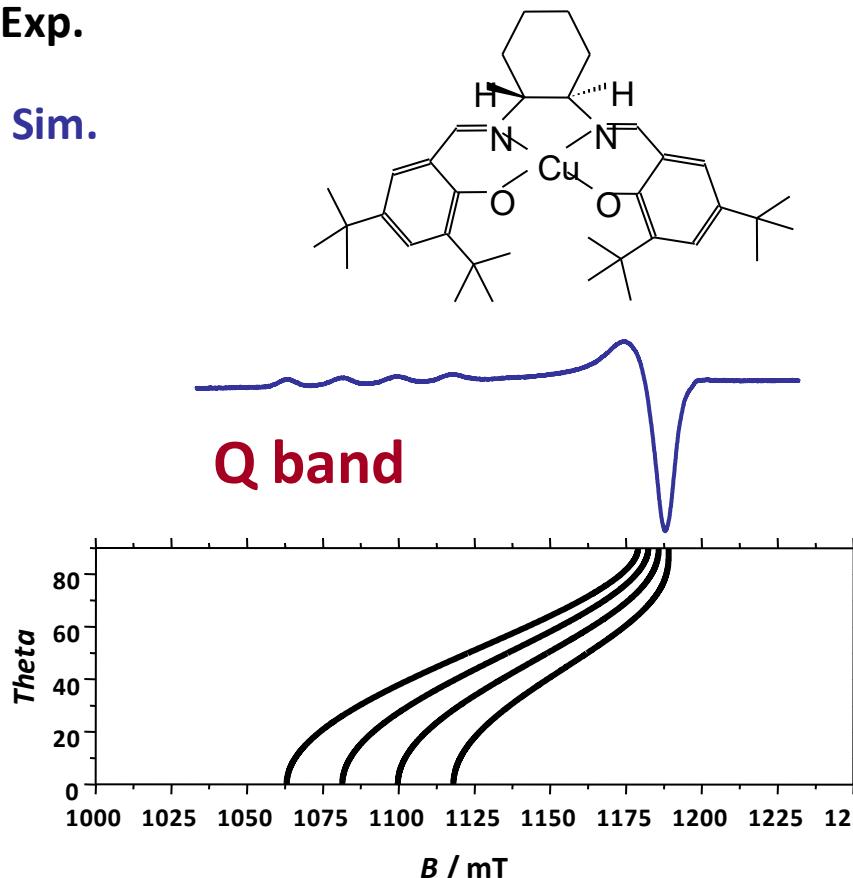
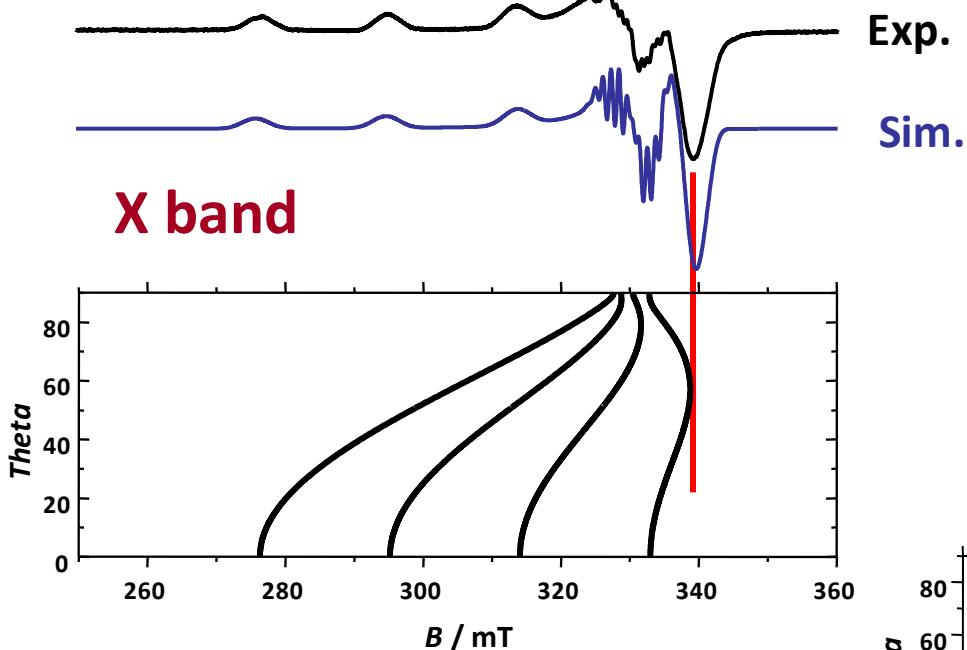
analysis of angular effects



molecular complexes of Cu(II) – glass spectra

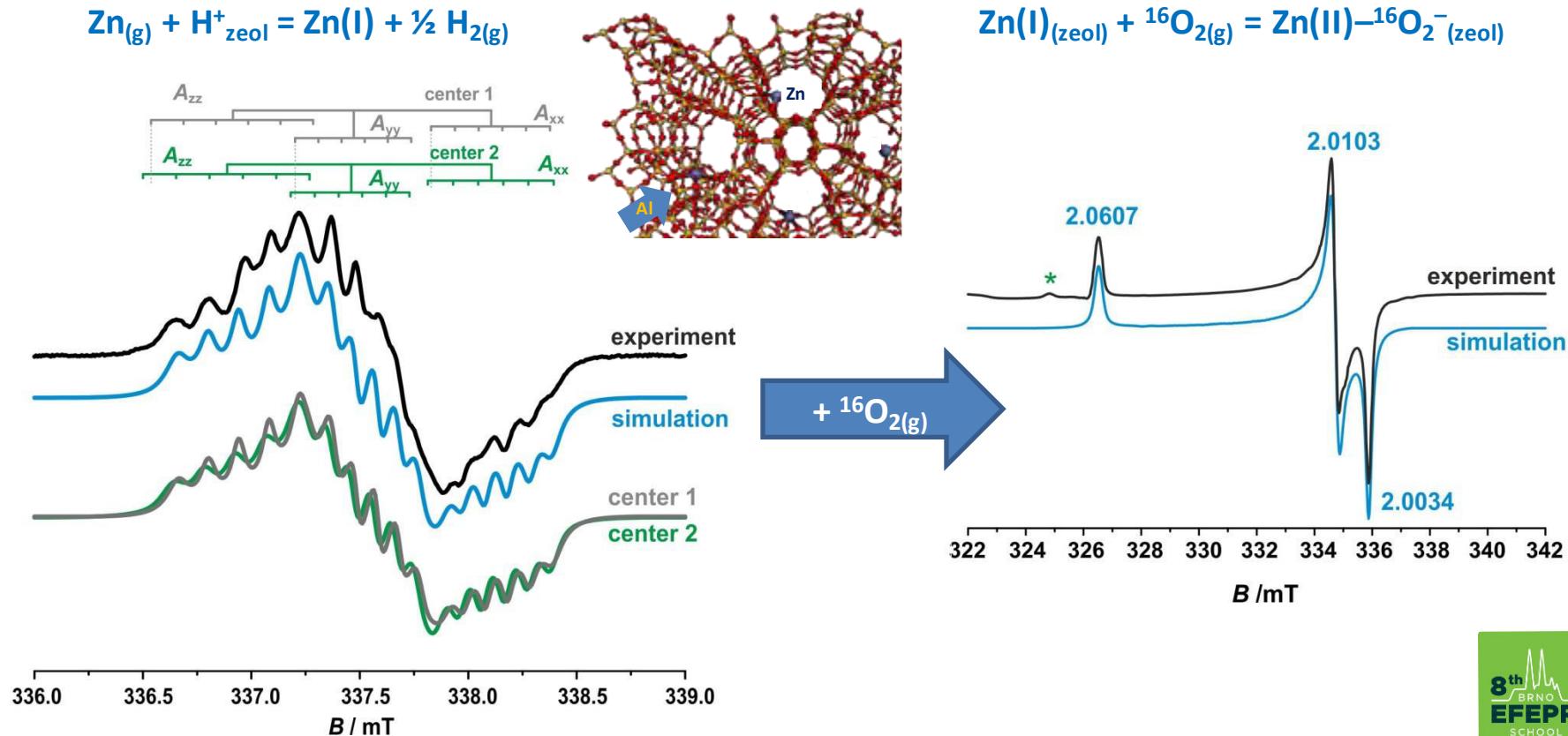


molecular complexes of Cu(II) – glass spectra



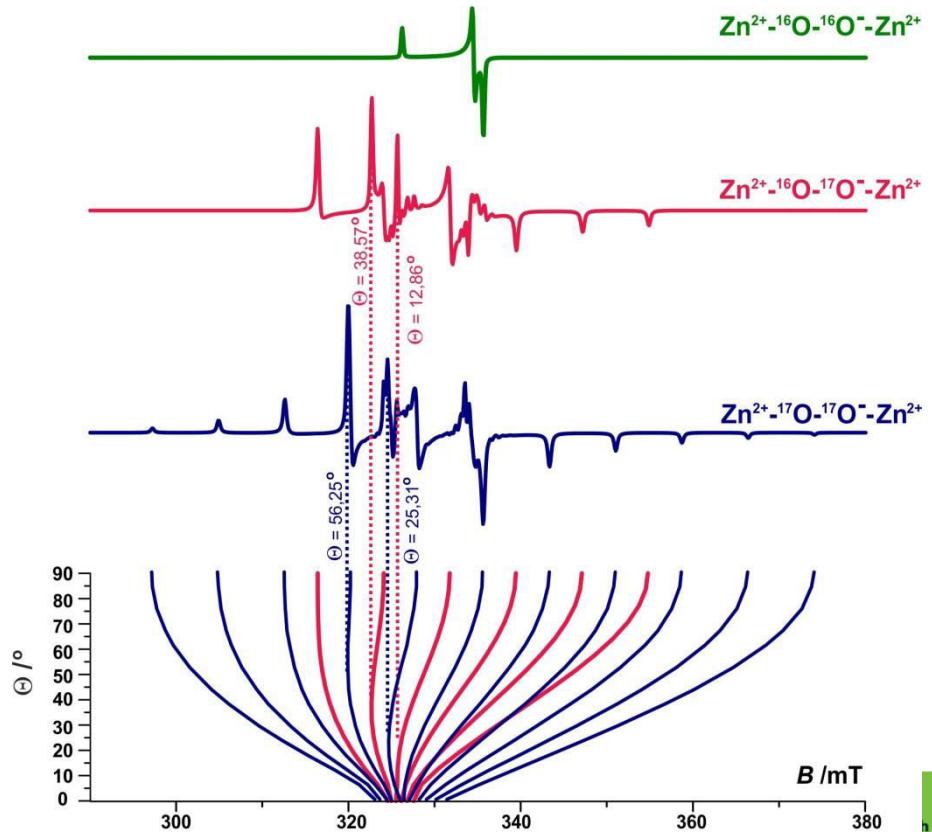
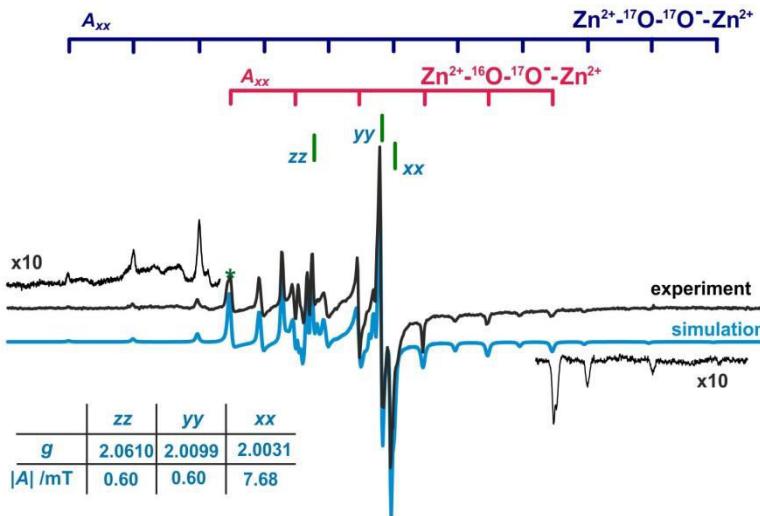
Zn(II)-superoxide species

chemical vapor deposition in zeolite ZSM-5 (Al, I = 5/2)

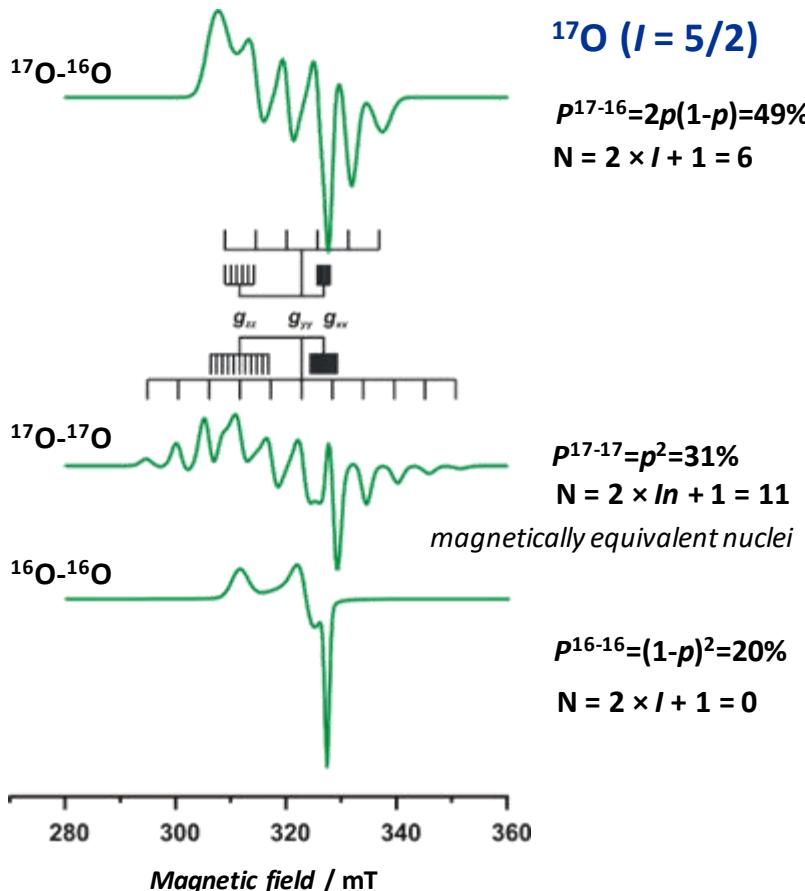


Zn(II)-superoxide species

^{17}O , $I = 5/2$



Zn(II)-superoxide species

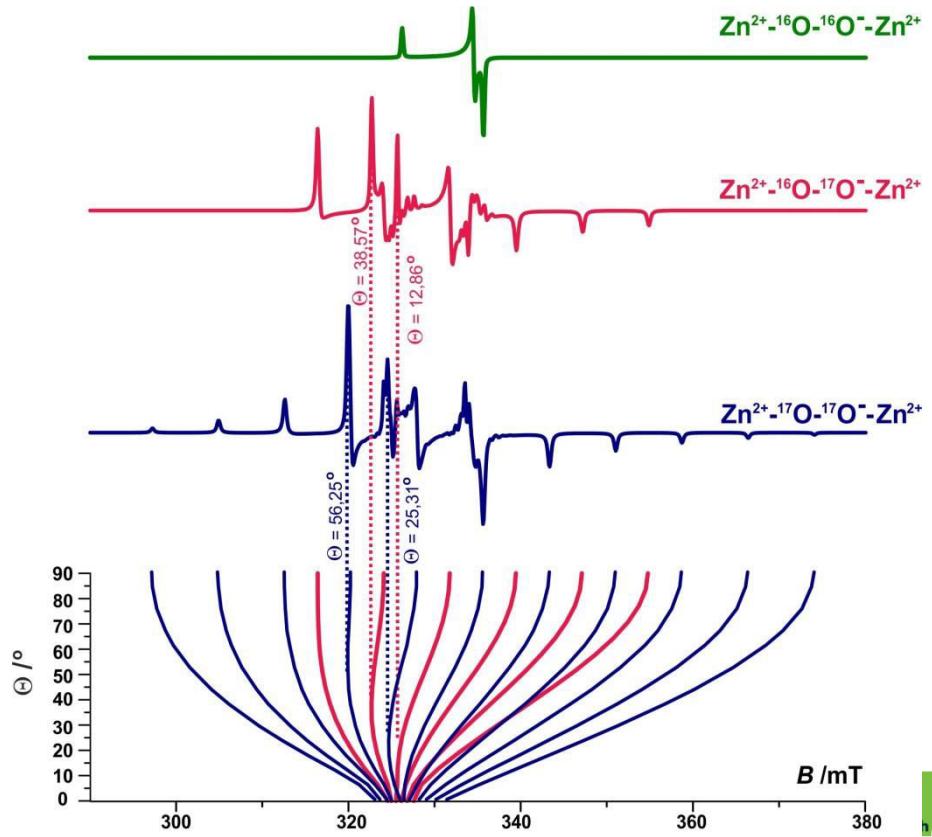
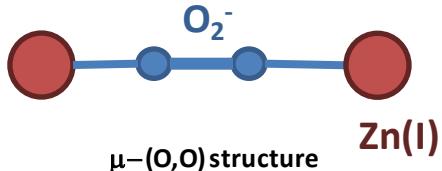
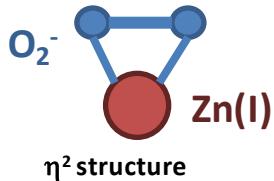
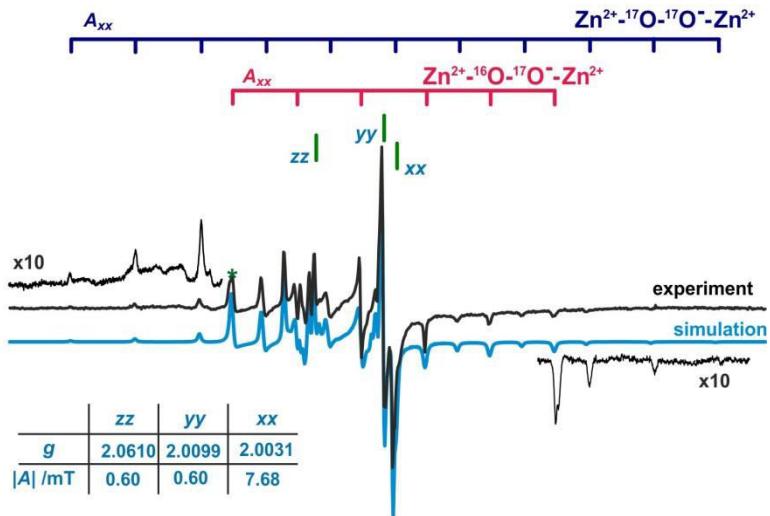


Species	$^{16}\text{O}^{16}\text{O}$	$^{16}\text{O}^{17}\text{O}$ $^{17}\text{O}^{16}\text{O}$	$^{17}\text{O}^{17}\text{O}$
Concentration	$(1 - x)^2$	$2x(1 - x)$	x^2
Number of lines	1	6	11
Distribution of lines			

$x - ^{17}\text{O}$ enhancement level

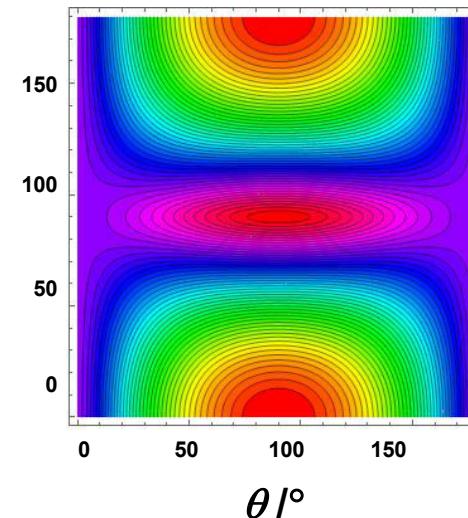
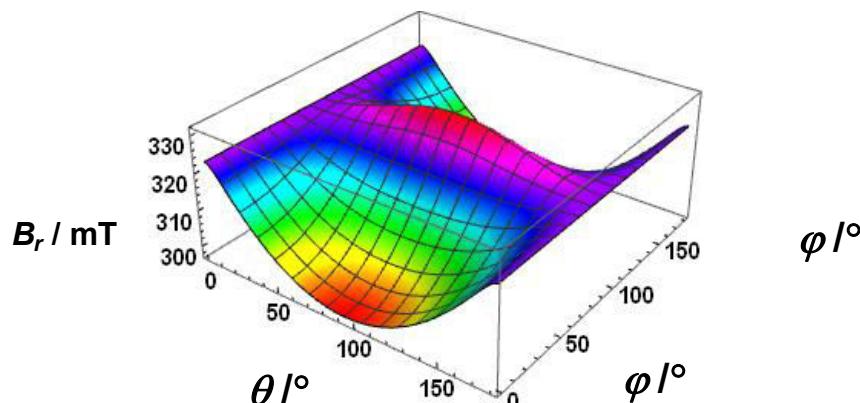
Zn(II)-superoxide species

^{17}O , $I = 5/2$



Zn(II)-superoxide species

$\text{Zn(II)}-\text{^{17}O}^{17}\text{O}^-$ line $m_l = 5$

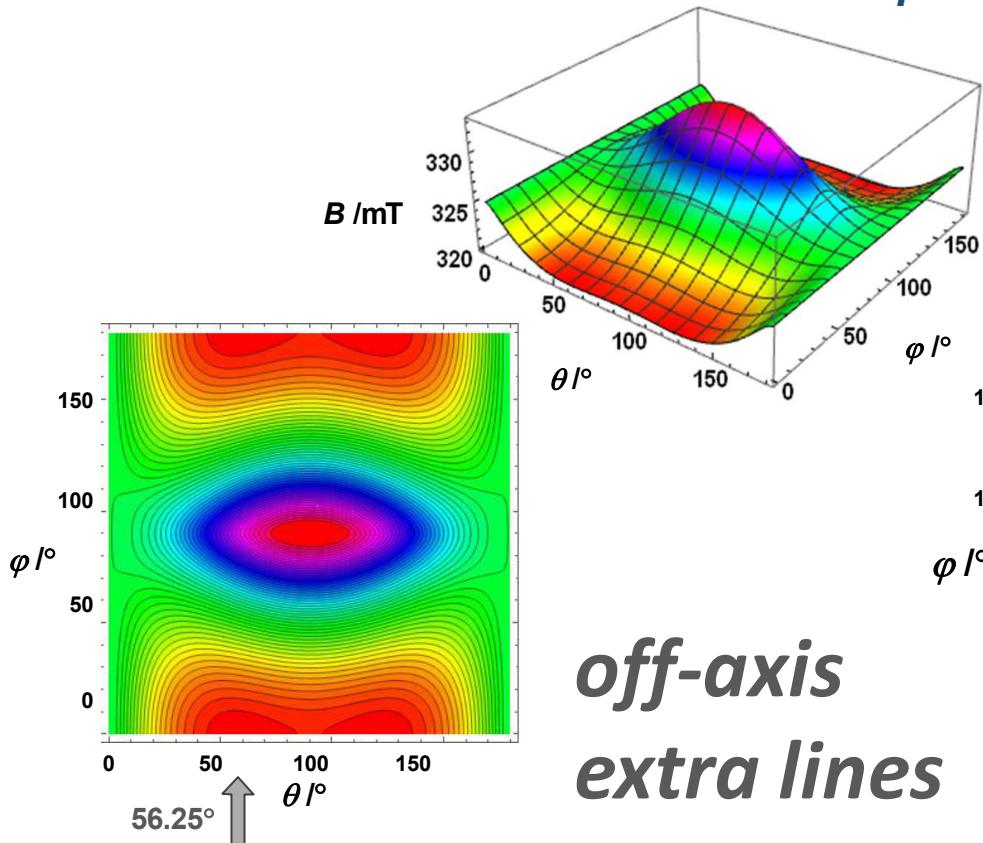


all regular resonances

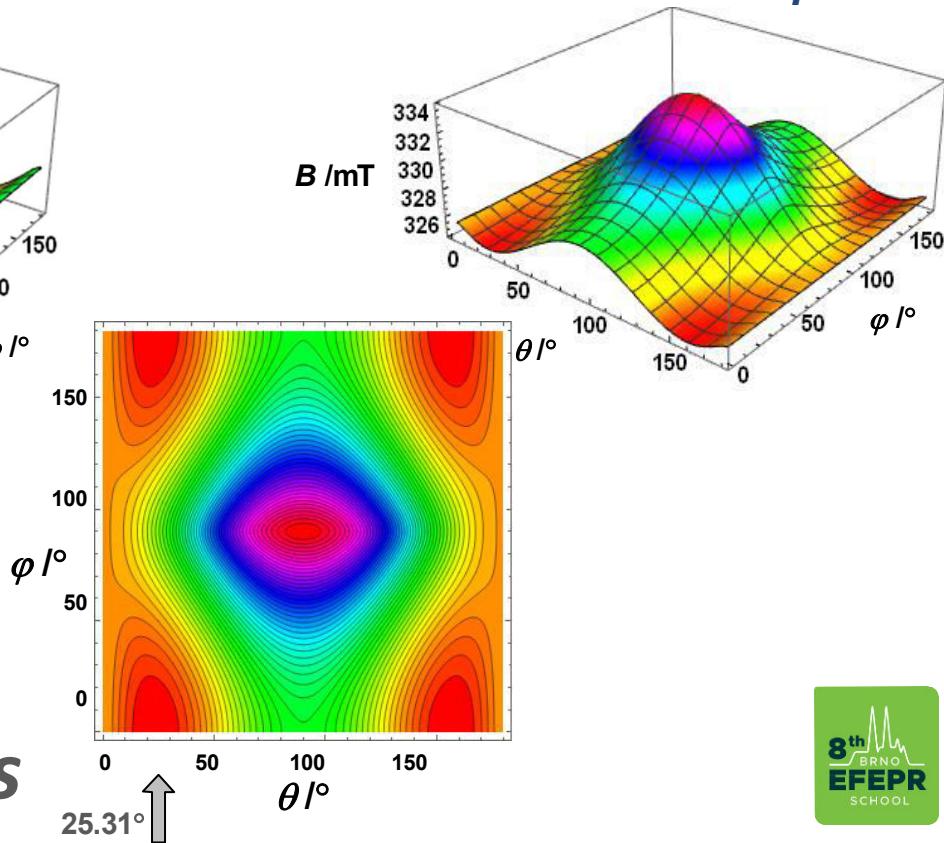
Zn(II)–superoxide species

Zn(II)– $^{17}\text{O}^{17}\text{O}^-$

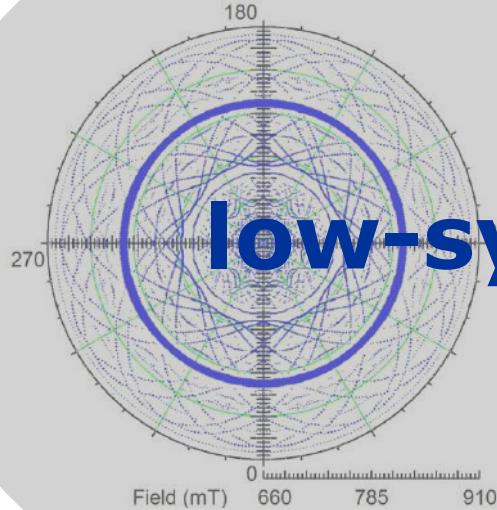
line $m_l = 2$



line $m_l = 1$



*off-axis
extra lines*

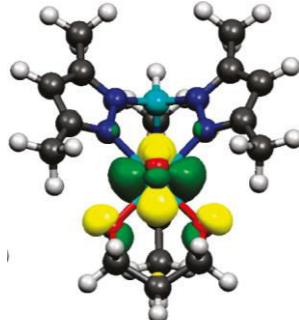
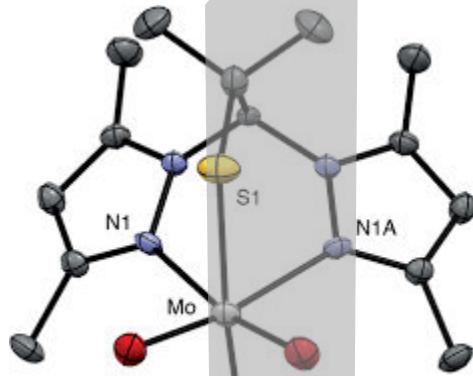


low-symmetry effects in EPR spectra

low symmetry complexes

low symmetry at molybdenum center

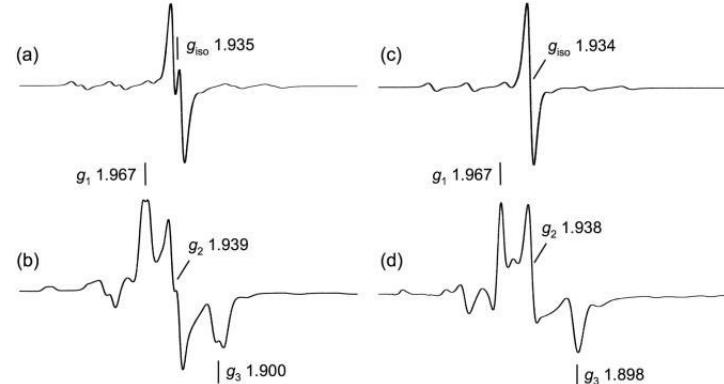
scorpionate complexes – models for molybdenum enzymes



Mo(V) ($^{95,97}\text{Mo}$ $I = 5/2$), 4d^1 , $S = \frac{1}{2}$, C_s point symmetry (or local symmetry)

cis- $[(\text{L3S})\text{MoO}_2\text{Cl}]$

σ

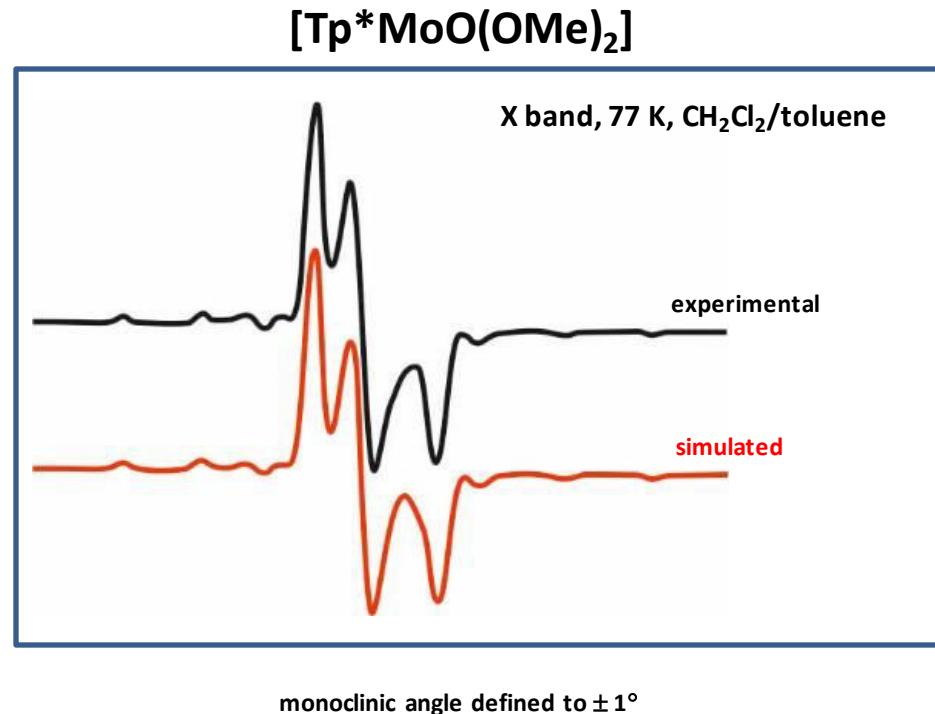
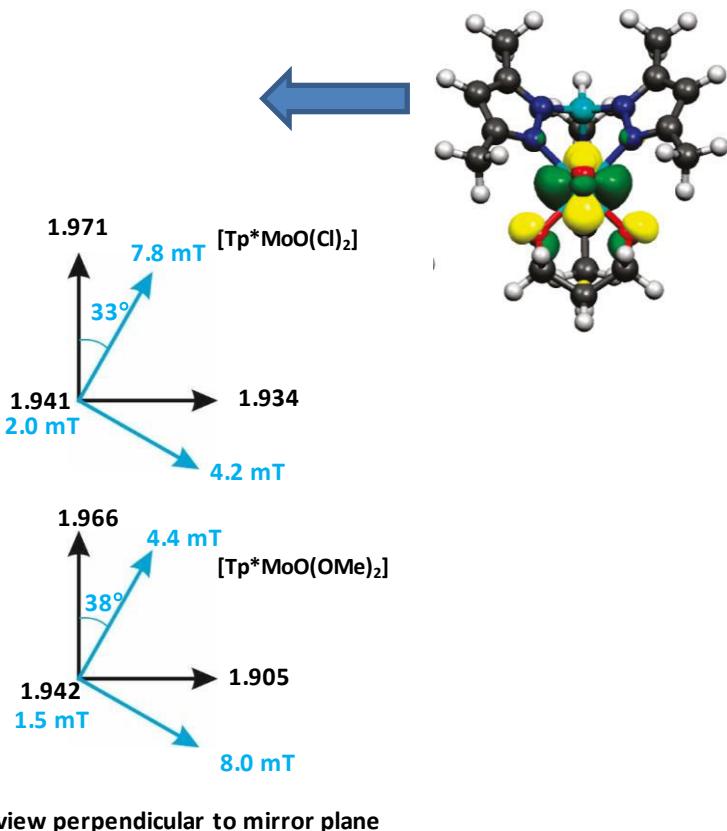


Inorg. Chem. 2010, 49, 9460–9469

C_s	E	σ		
A'	+1	+1	x, y, R_z	x^2, y^2, z^2, xy
A''	+1	-1	z, R_x, R_y	xz, yz

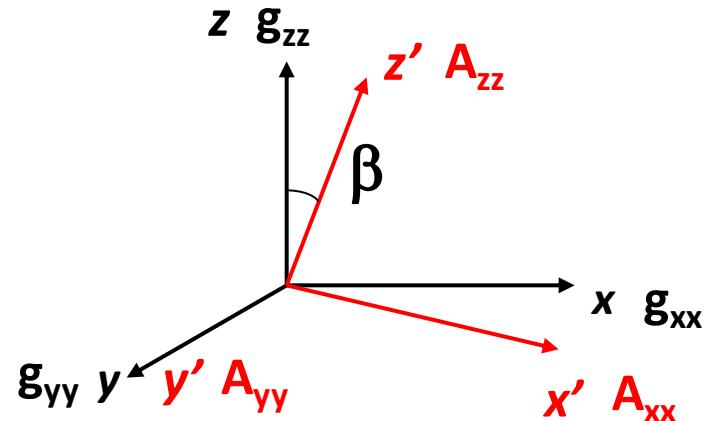
Eur. J. Inorg. Chem. 2016, 2357-2376

measuring low symmetry



non-coincidence of g - and A -tensor principal axes

$$B_{\text{res}} = \frac{hv_0}{g\mu_B} - \frac{Km}{g\mu_B} \quad S = 1/2 \quad I \neq 0$$



$$g = \left[(g_{xx}^2 \cos^2 \varphi + g_{yy}^2 \sin^2 \varphi) \sin^2 \vartheta + g_{zz}^2 \cos^2 \vartheta \right]^{\frac{1}{2}}$$

$$gK = \left[(g_{xx}^2 A_{xx}^2 \cos^2 \phi + g_{yy}^2 A_{yy}^2 \sin^2 \phi) \sin^2 \vartheta + g_{zz}^2 A_{zz}^2 \cos^2 \vartheta \right]^{\frac{1}{2}}$$

$$K \approx [A_x^2 \sin^2(\theta - \beta) + A_z^2 \cos^2(\theta - \beta)]^{\frac{1}{2}}$$

consider transition in the xz plane

non-coincidence of g - and A -tensor principal axes

$$K \approx [A_{xx}^2 \sin^2(\vartheta - \beta) + A_{zz}^2 \cos^2(\vartheta - \beta)]^{1/2}$$

$$\frac{\partial B(\vartheta, \varphi)}{\partial \vartheta} = 0 \quad \text{for } \theta \text{ given by}$$

$$\tan 2\vartheta = \frac{\sin 2\beta}{F + \cos 2\beta} \quad F = \left(\frac{g\mu_B B}{mK} \right) \left(\frac{g_{xx}^2 - g_{zz}^2}{A_{xx}^2 - A_{zz}^2} \right) \left(\frac{K^2}{g^2} \right)$$

when $\beta = 0$
or $\Delta g \gg \Delta A$

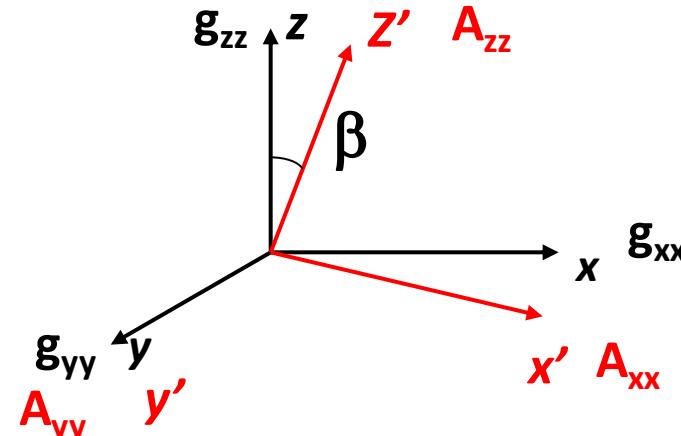
$$F \gg 1 \rightarrow \tan 2\vartheta = 0 \rightarrow \text{spectral features at } \theta = 0^\circ \text{ and } 90^\circ \text{ (along } g \text{ principal axes)}$$

when $\Delta A \gg \Delta g \rightarrow \tan 2\vartheta = \tan 2\beta$ features appear along
A principal axes ($\theta = 0^\circ$ and β)

J. Am. Chem. Soc. 102, 156, 1980;
106, 7000, 1984.

for $F = 1$ the resonant field becomes a function of g_{xx} , g_{zz} , A_{xx} , A_{zz} , and β

the non-coincidence effects on an EPR powder spectrum become obvious if two (or more) tensors have relevant and comparable anisotropies between them



non-coincidence of g - and A -tensor principal axes

Effects of non-coincidence of tensors g and A on a powder spectrum:

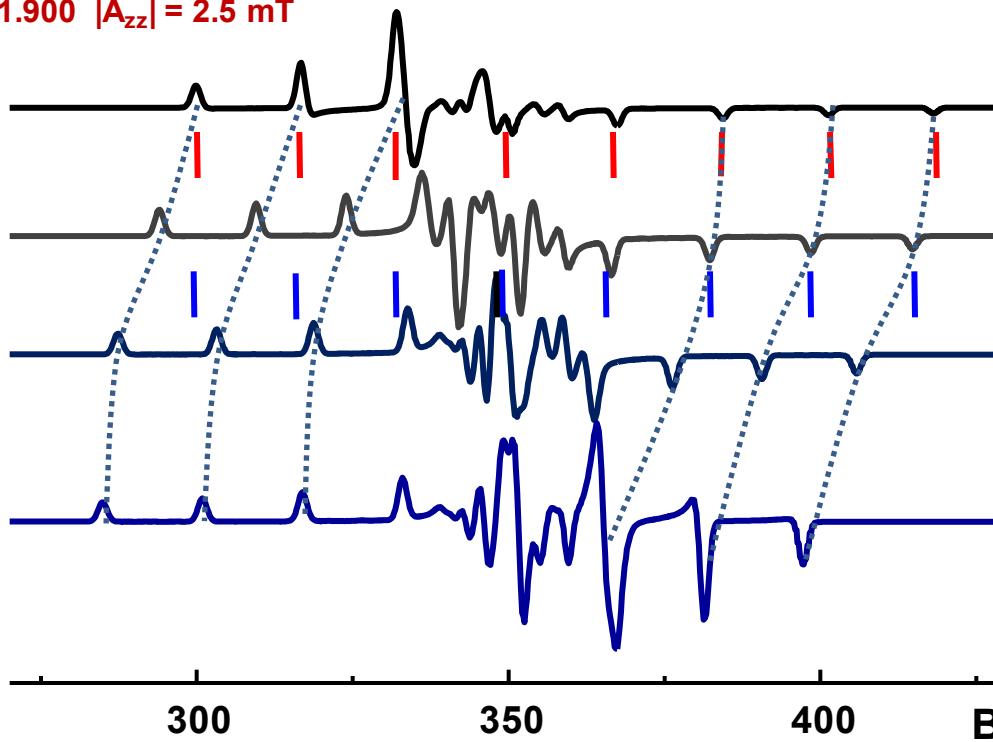
- 1) the spectrum contains „too many lines”**
- 2) the intensity and position of the spectral lines
is not that expected on the basis of simple
considerations**
- 3) it is not possible to simulate the spectrum
assuming rhombic or axial symmetry**

non-coincidence of g - and A -tensor principal axes

$g_{xx} = 2.000$ $|A_{xx}| = 15$ mT

$g_{yy} = 1.950$ $|A_{yy}| = 2.5$ mT

$g_{zz} = 1.900$ $|A_{zz}| = 2.5$ mT



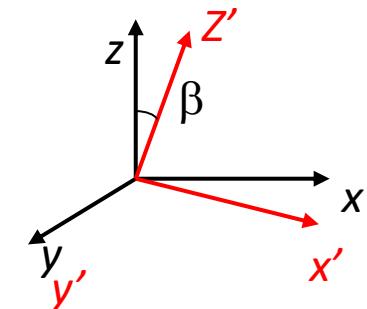
$I = 7/2$

$\beta = 0^\circ$

$\beta = 30^\circ$

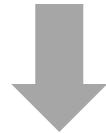
$\beta = 60^\circ$

$\beta = 90^\circ$



low-symmetry features

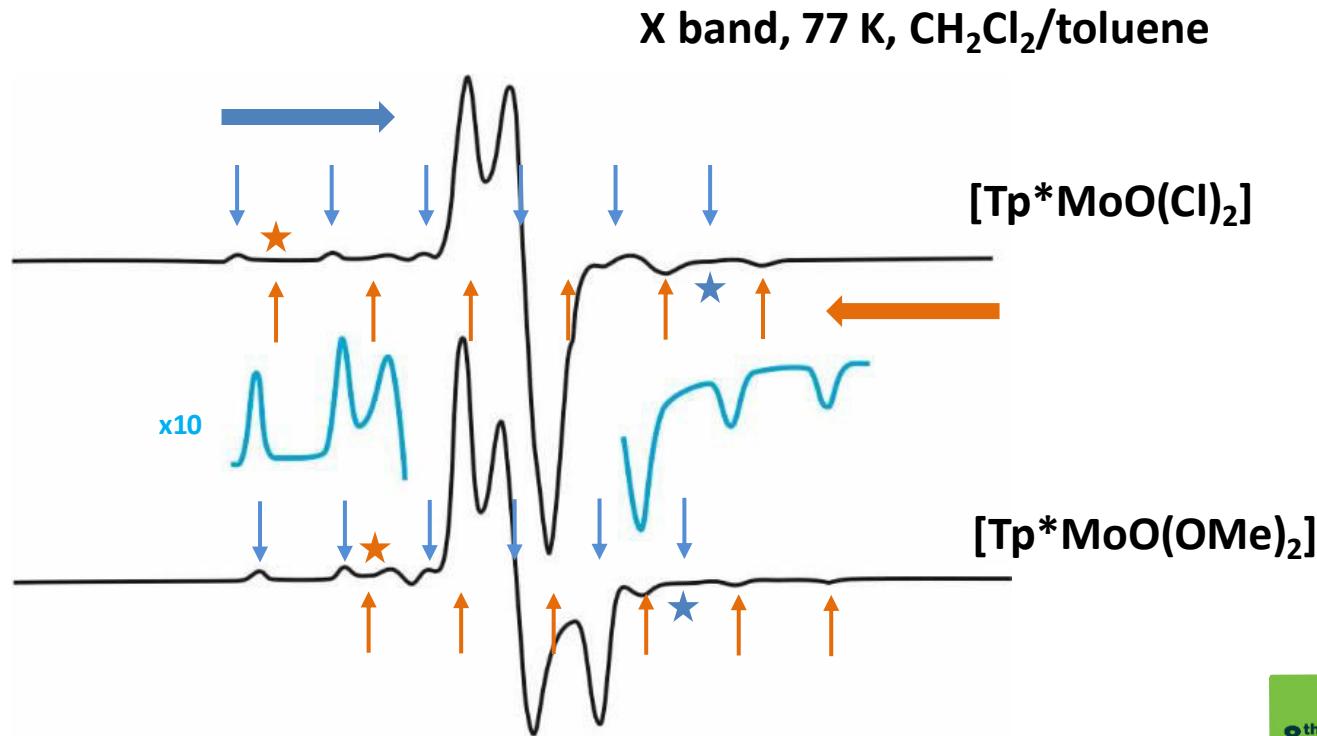
low symmetry

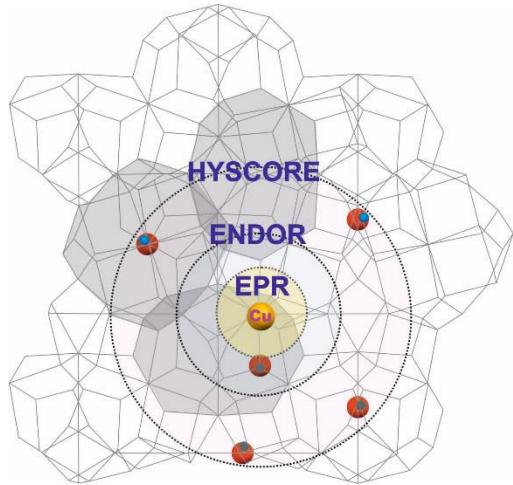


non-coincidence
of g - and A - axes



irregular hyperfine
separation

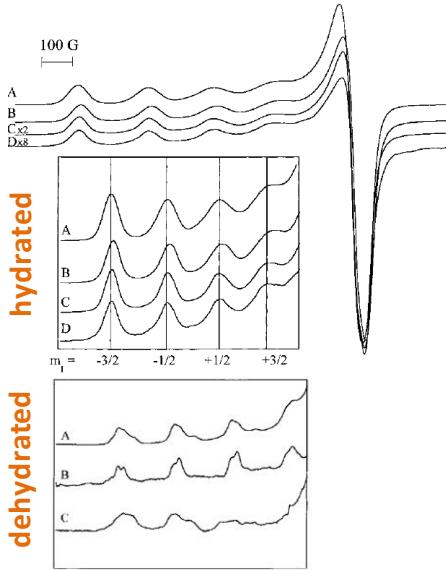




Local inhomogeneity and local symmetry probes

strain broadening and smearing of EPR features

Cu-ZSM-5 zeolite



J. Phys. Chem. B 2000, 104, 6568-6575

g-strain

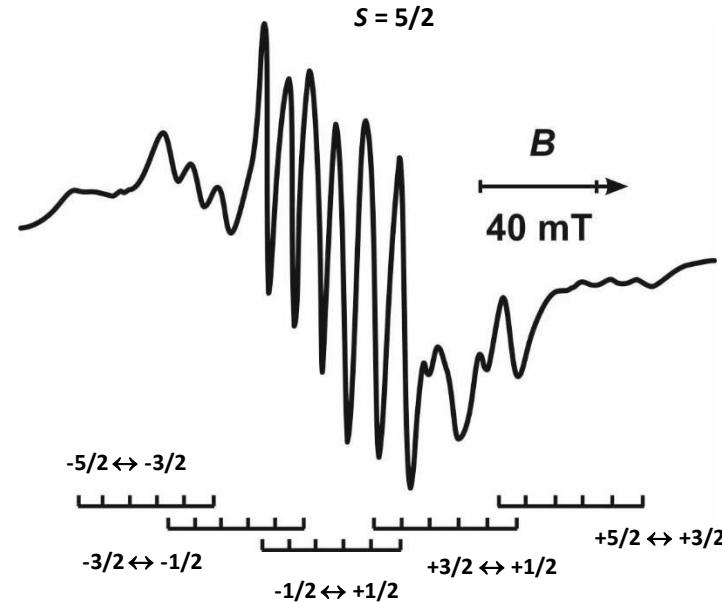
Powder samples come with a distribution of local surroundings (conformations) of the paramagnetic centers

For EPR this means that a paramagnetic center, which has a slightly different structural surrounding, exhibits a slightly different *g*-value.

This structural inhomogeneity is a source of the so called *g-strain*, and is reflected in the spectroscopy in the form of an inhomogeneous line shape.

This normally results in a change from a *Lorentzian* to *Gaussian* line shape. An important consequence of this *g*-strain effect is that the line width is in general, also anisotropic.

hydrated MnK-A zeolite (0.1 wt.% Mn)



J. Am. Chem. Soc., 1996, 118, 9615-9622.

strain broadening and smearing of EPR features

g-strain

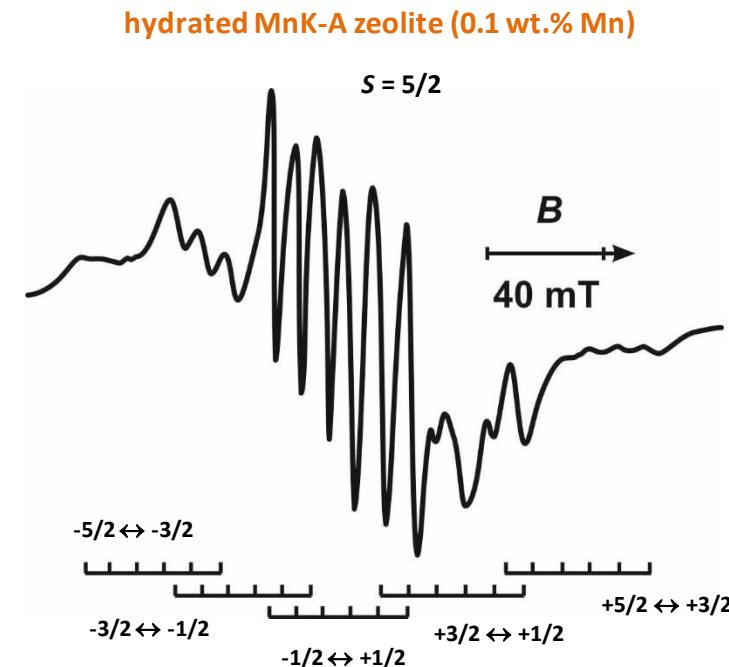
In magnetically diluted systems *g*-strain (but also *A*- and *D*-strains) leads to apparent m_I and frequency dependence of the hyperfine (and fine) linewidths (σ):

$$\sigma_v^2 = \left(\sum_{i=x,y,z} \left\{ \sigma_{R_i}^2 \left[\frac{\Delta g_i}{g_i} \nu_0(B) + \Delta A_i m_I \right]^2 \right\} g_i^2 l_i^2 \right) / g^2$$

σ_{R_i} are the residual linewidths due to unresolved metal and (or) ligand hyperfine splitting, homogeneous broadening and other sources;

Δg_i and ΔA_i are the widths of the Gaussian distributions of the *g* and *A* values

J. Magn. Reson. 1991, 93, 12

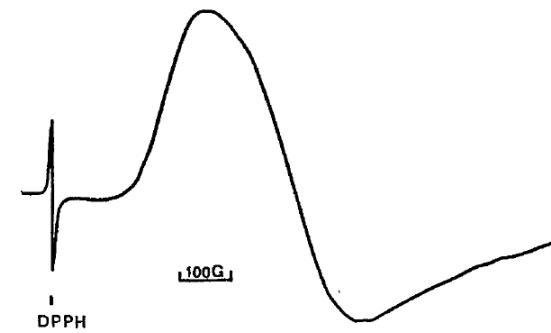
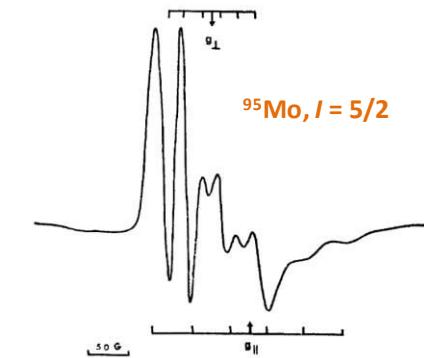
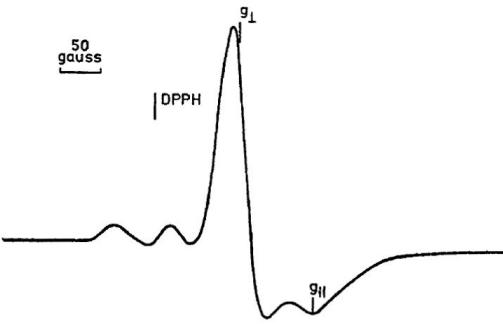


J. Am. Chem. Soc., 1996, 118, 9615–9622.

strain broadening and smearing of EPR features

MoO_x/SiO₂ catalysts

J. Chem. Soc., Faraday Trans. 1, 1978, 74, 2378-2384

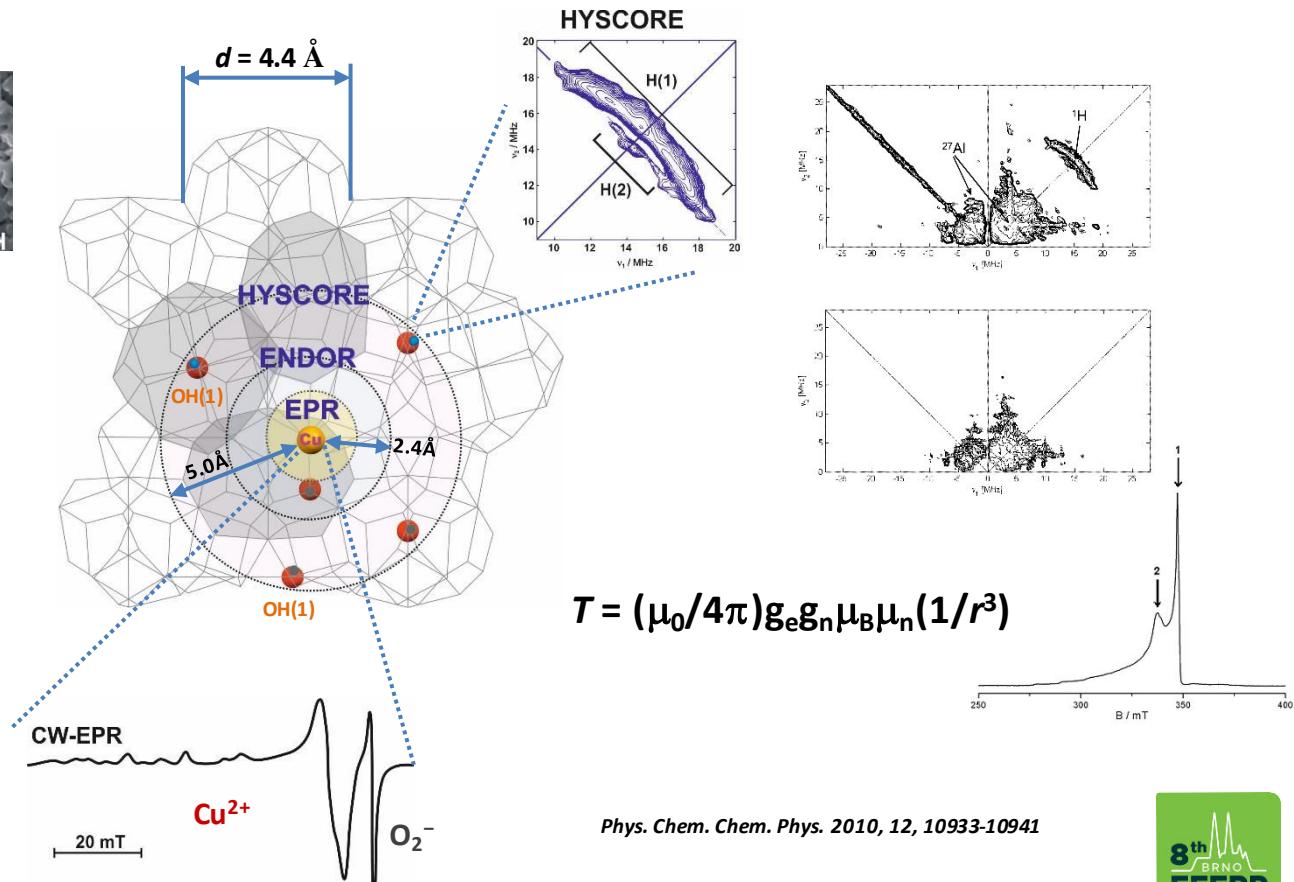
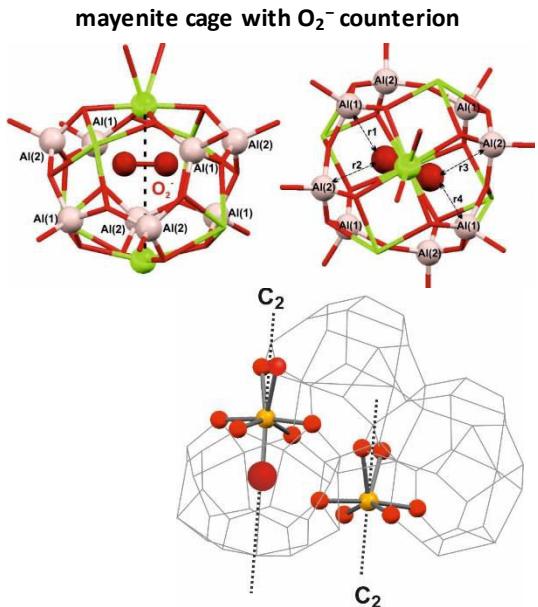
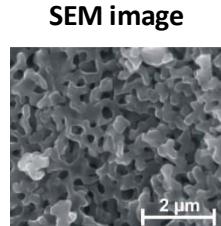


g-strain refers to anisotropic broadening of the linewidths owing to distribution of g-values caused by small local inhomogeneity (slight variations in the orientation of the Mo(V) surface centers, heteroleptic various surface ligands, geometric strains, surface strains). Also, broadening of the g-values depends on the microwave frequency. If the line broadening were determined only by e.g. unresolved hyperfine coupling (which are field-independent), then the line widths would also be field independent, but they often are not.

use of local paramagnetic probes

Mayenite

$12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$
unit cell = 12 cages
charge of unit cell = +4



Phys. Chem. Chem. Phys. 2010, 12, 10933-10941

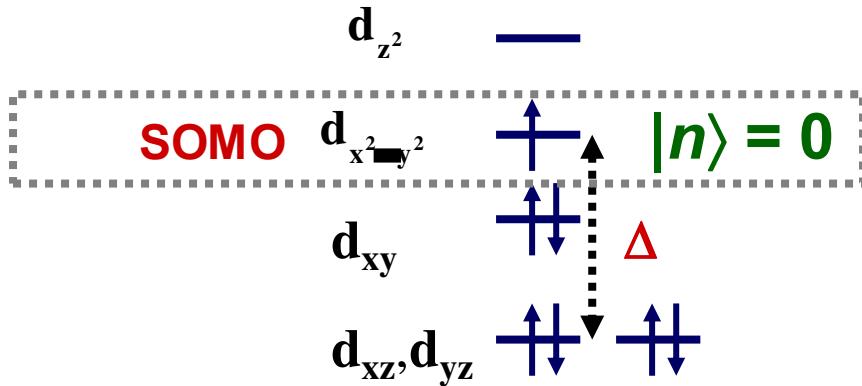
local symmetry probe (g tensor)

$$g_{ij} = g_e \delta_{ij} - 2\lambda \Delta_{ij}$$

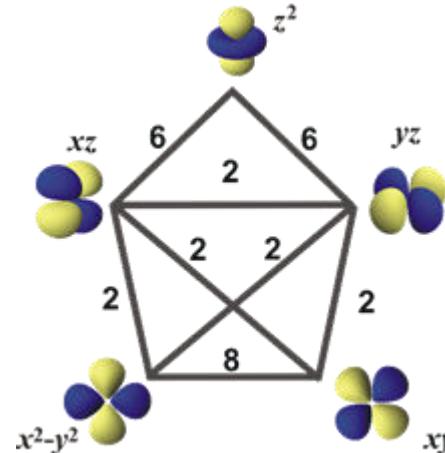
$$\Delta_{ij} \Delta_{ji} \xrightarrow{\hbar^2 \frac{\langle 0 | L_i | n \rangle \langle n | L_j | 0 \rangle}{E_n - E_0}}$$

λ – stała sprzężenia spinowo-orbitalnego

→ $\Gamma_0 \times \Gamma_L \times \Gamma_n \subset$ totally symmetric representation Γ_A

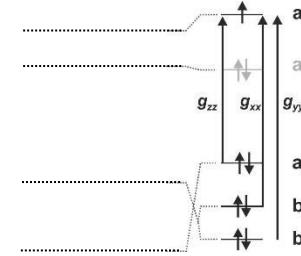
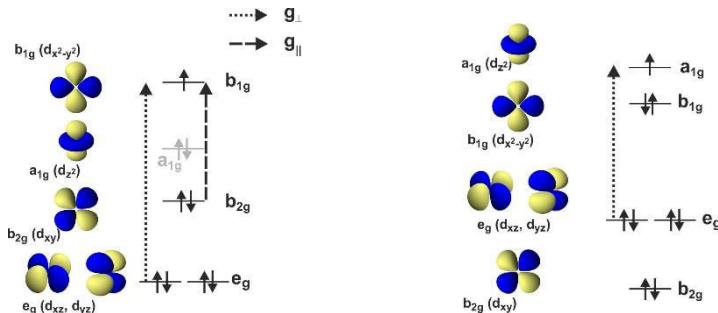
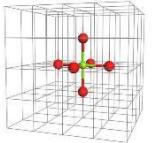


$$g = 2.0023 \pm n\lambda/\Delta$$

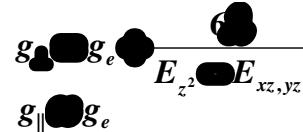
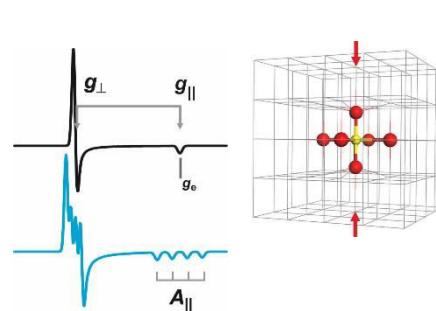
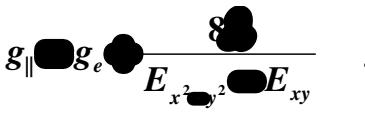
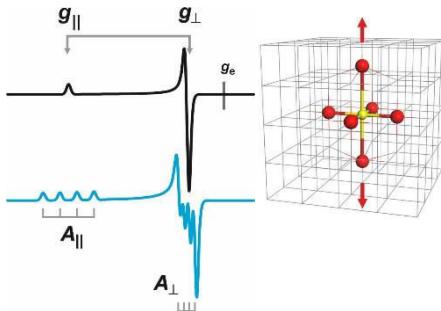


local symmetry probe

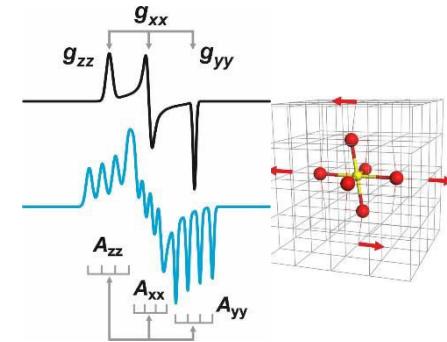
isotropic center



axial distortion

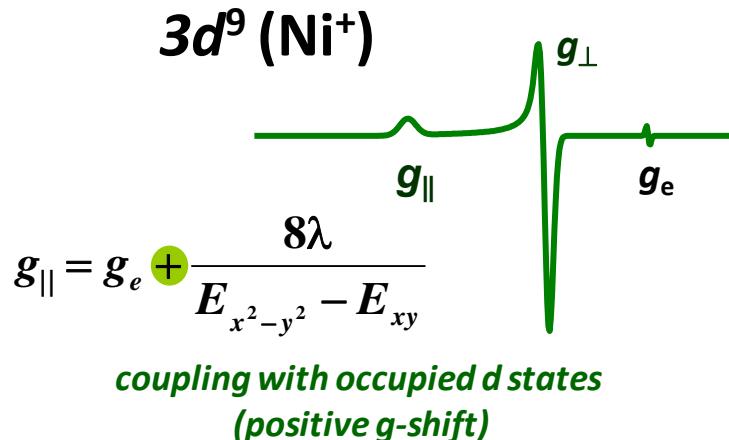
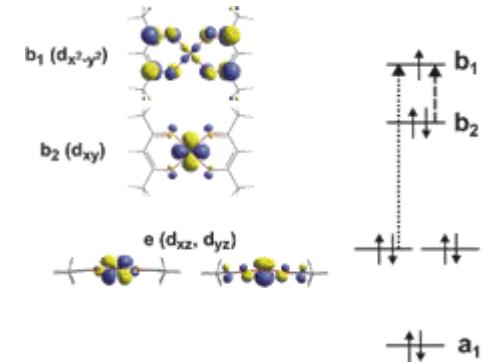
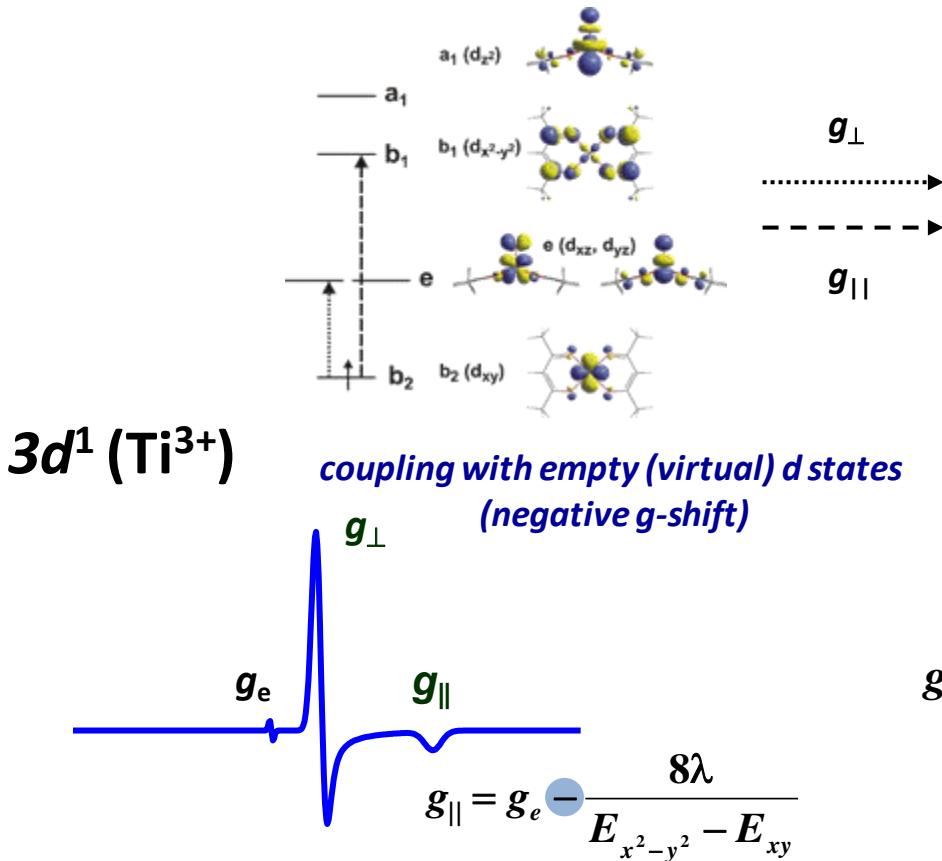


rhombic distortion



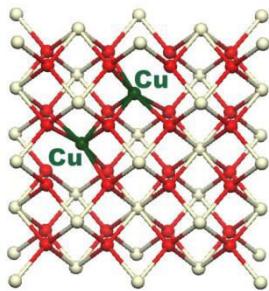
local symmetry probe

differentiation between d^1 and d^9 configurations



local symmetry probe

CeO₂ matrix

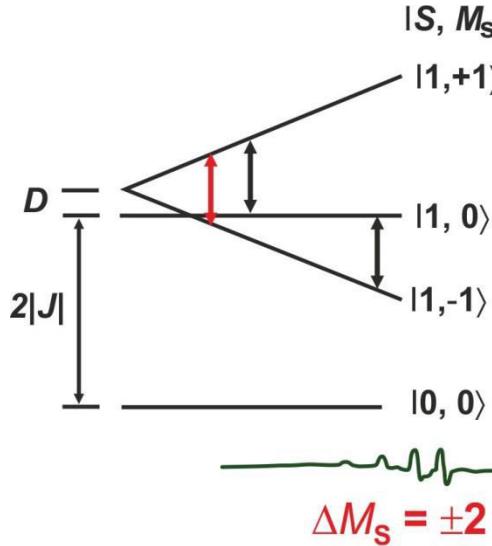


Cu(II)-(O²⁻)₂-Cu(II)

Axial symmetry

2 nearly equivalent Cu(II) centers

Antiferromagnetic coupling



$$g_{\parallel} = 2.2079, g_{\perp} = 2.0403$$

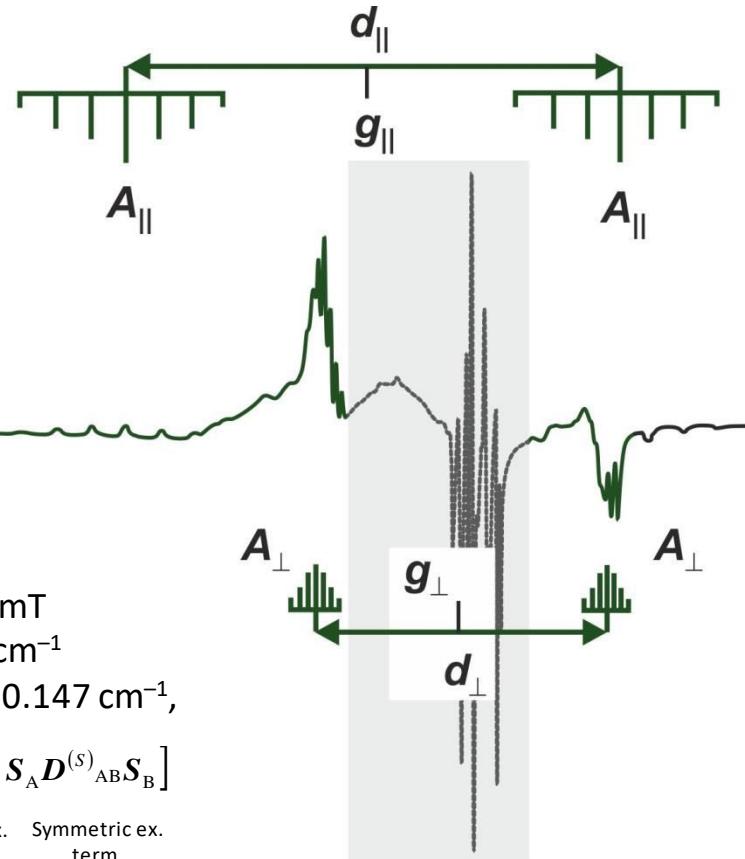
$$|A_{\parallel}| = 8.5 \text{ mT}, |A_{\perp}| = 1.35 \text{ mT}$$

$$D = 0.066 \text{ cm}^{-1}, J = -52.5 \text{ cm}^{-1}$$

$$d_{\text{Cu-Cu}} = -0.081 \text{ cm}^{-1}, D^{(S)} = 0.147 \text{ cm}^{-1},$$

$$H_{EX} = \hbar^{-2} \sum_{AB} \left[-JS_A S_B + d_{AB}(S_A \times S_B) + S_A D^{(S)}_{AB} S_B \right]$$

Isotropic exchange term Antisymmetric ex. term (D.-M.) Symmetric ex. term



Conclusions

Analysis of EPR spectra of powder samples requires:

- 1. computer simulations**
- 2. accounting for EPR parameters strains**
- 3. accounting for low-symmetry effects**
- 4. checking for presence of off-axis extra features**

Useful experiments and procedures
adsorption of probe molecules
isotopic substitution
multifrequency measurements
use of hyperfine techniques

References and further reading

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11. A. Kreiter, J. Hatermann, *J. Magn. Reson.* 1991, 93, 12-26



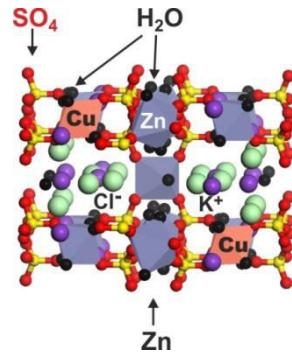
Thanks for your attention!



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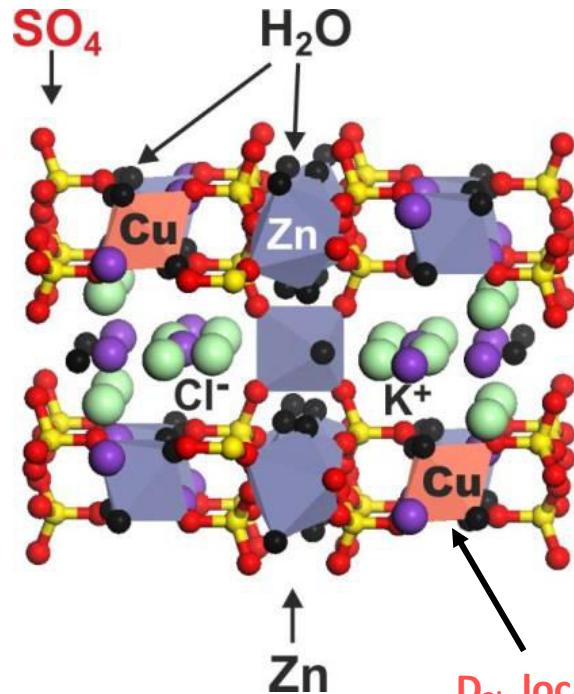
Case study 1

LCAO analysis of g - and A - tensors
Cu(II)-doped $\text{KZnClSO}_4 \times 3\text{H}_2\text{O}$

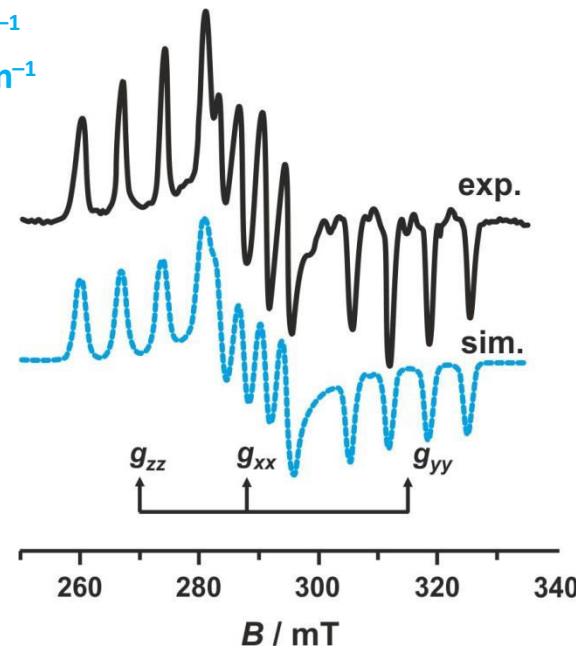


local symmetry probe – case study

Cu(II)-doped KZnClSO₄×3H₂O
(kainite structure)



$$g_{xx} = 2.1535, g_{yy} = 2.0331, g_{zz} = 2.4247$$
$$A_{xx}/10^{-4} = (-)31 \text{ cm}^{-1}$$
$$A_{yy}/10^{-4} = (+)63 \text{ cm}^{-1}$$
$$A_{zz}/10^{-4} = (-)103 \text{ cm}^{-1}$$



J. Magn. Reson. 2010, 205, 293

local symmetry probe – case study

For the D_{2h} local point group symmetry of the hosting site (Figure 11b) the copper $3d$ orbitals can be mixed with $4s$ orbital and ligand-based L orbitals, resulting in the following molecular orbitals responsible for the observed SH parameters:

$$\Psi(A_g) = \alpha(ad_{x^2-y^2} + bd_{z^2} + c_s s) - \alpha' L_1 \quad a^2 + b^2 + c_s^2 = 1$$

$$\Psi(A_g') = \alpha_1(ad_{z^2} - bd_{x^2-y^2} + c_s s) - \alpha_1' L_2$$

$$\Psi(B_{1g}) = \beta_1 d_{xy} - \beta_1' L_3$$

$$\Psi(B_{2g}) = \beta d_{xz} - \beta' L_4$$

$$\Psi(B_{3g}) = \beta' d_{yz} - \beta'' L_5$$

For the A_g ground state symmetry the principal \mathbf{g} and \mathbf{A} values are given by:

$$g_{zz} = g_e - 8\alpha^2\beta_1^2 a^2 \frac{\lambda}{E_{xy}}$$

$$g_{yy} = g_e - 2\alpha^2\beta^2(a - \sqrt{3}b)^2 \frac{\lambda}{E_{xz}}$$

$$g_{xx} = g_e - 2\alpha^2\beta^2(a + \sqrt{3}b)^2 \frac{\lambda}{E_{yz}}$$

$$A_{zz} = \alpha^2 c_s^2 A_{4s} + P \left[-\alpha^2 \kappa + \Delta g_{zz} - \frac{4}{7} \alpha^2 (a^2 - b^2) + \frac{1}{14} \frac{3a + \sqrt{3}b}{a - \sqrt{3}b} \Delta g_{yy} + \frac{1}{14} \frac{3a - \sqrt{3}b}{a + \sqrt{3}b} \Delta g_{xx} \right]$$

$$A_{yy} = \alpha^2 c_s^2 A_{4s} + P \left[-\alpha^2 \kappa + \Delta g_{yy} + \frac{2}{7} \alpha^2 (a^2 - b^2 + 2\sqrt{3}ab) - \frac{\sqrt{3}}{14} \frac{b}{a} \Delta g_{zz} - \frac{1}{14} \frac{3a - \sqrt{3}b}{a + \sqrt{3}b} \Delta g_{xx} \right]$$

$$A_{xx} = \alpha^2 c_s^2 A_{4s} + P \left[-\alpha^2 \kappa + \Delta g_{xx} + \frac{2}{7} \alpha^2 (a^2 - b^2 - 2\sqrt{3}ab) + \frac{\sqrt{3}}{14} \frac{b}{a} \Delta g_{zz} - \frac{1}{14} \frac{3a + \sqrt{3}b}{a - \sqrt{3}b} \Delta g_{yy} \right]$$

Input data

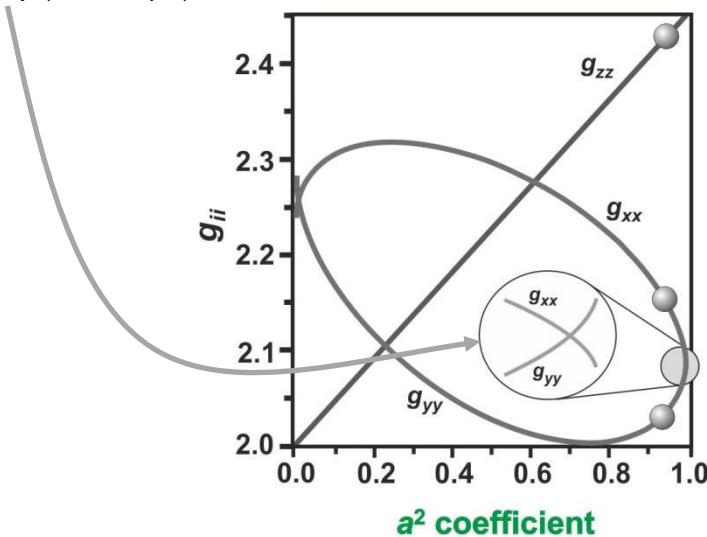
$\lambda = -829 \text{ cm}^{-1}$ is the SOC constant, $P = 0.036 \text{ cm}^{-1}$ and $\kappa = 0.43$ is the Fermi contact parameter of the free Cu^{2+} ion, E_i represents energy separation between A_g ground state and the $3d$ levels ($E_{xy} = 11\ 000 \text{ cm}^{-1}$, $E_{xz} = 11\ 700 \text{ cm}^{-1}$, $E_{yz} = 13\ 100 \text{ cm}^{-1}$) whereas the $a^2 c_s^2 A_{4s}$ term gives direct contribution of the $4s$ orbital to the isotropic hyperfine coupling.

local symmetry probe – case study

Calculation results

$$a^2 = 0.947, \alpha^2 = 0.93 \text{ and } \kappa = 0.284$$
$$\beta_1^2 = 0.80, \beta^2 = 0.80 \text{ and } \beta'^2 = 0.67$$

$$|\text{SOMO}\rangle = 0.96(0.97|x^2-y^2\rangle + 0.03|z^2\rangle),$$

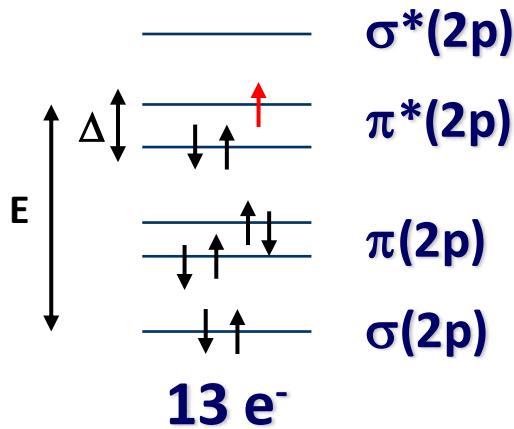
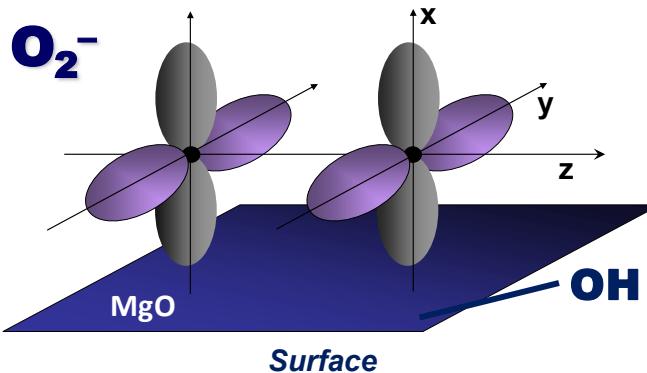


influence of the $|x^2-y^2\rangle/|z^2\rangle$ hybridization degree on the \mathbf{g} tensor values

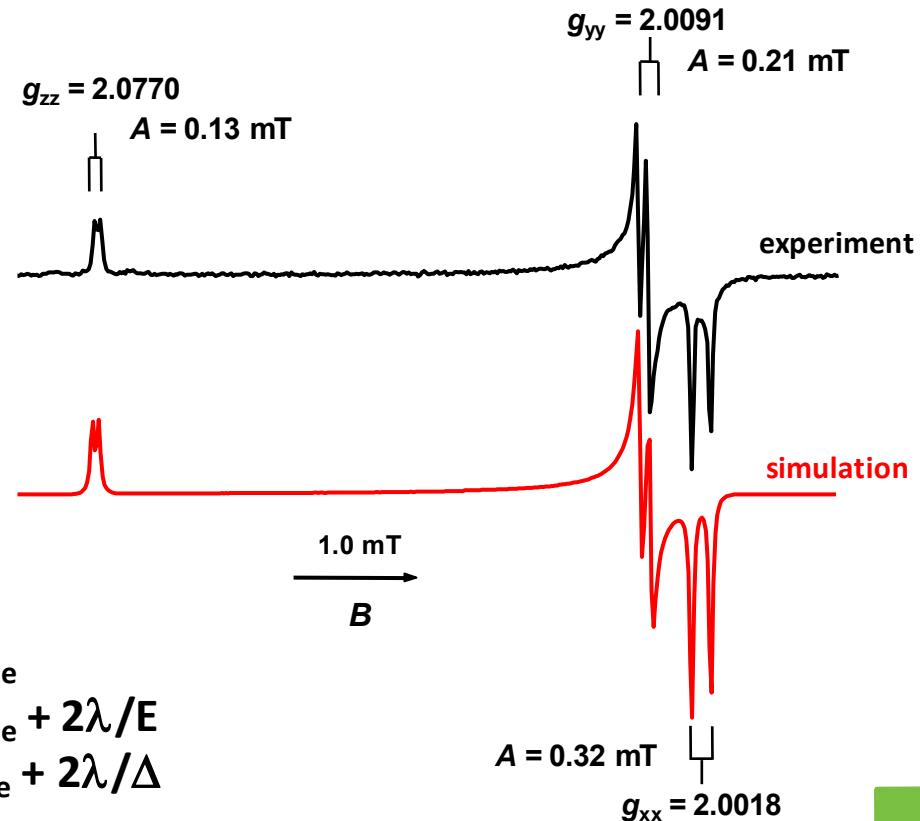
Case study 2

MgO supported superoxide radicals
H superhyperfine structure and extra lines

MgO superoxide surface species

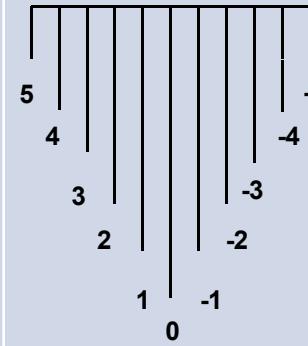


$$\begin{aligned} g_{xx} &\approx g_e \\ g_{yy} &= g_e + 2\lambda/E \\ g_{zz} &= g_e + 2\lambda/\Delta \end{aligned}$$



^{16}O and ^{17}O isotopomers of O_2^-

Isotopomers of O_2^- for two equivalent ^{17}O nuclei ($I = 5/2$)

Species	$^{16}\text{O}^{16}\text{O}$	$^{16}\text{O}^{17}\text{O}$ $^{17}\text{O}^{16}\text{O}$	$^{17}\text{O}^{17}\text{O}$
Concentration	$(1 - x)^2$	$2x(1 - x)$	x^2
Number of lines	1	6	11
Distribution of lines		 5/2 3/2 1/2 -1/2 -3/2 -5/2	 5 4 3 2 1 0 -1 -2 -3 -4 -5

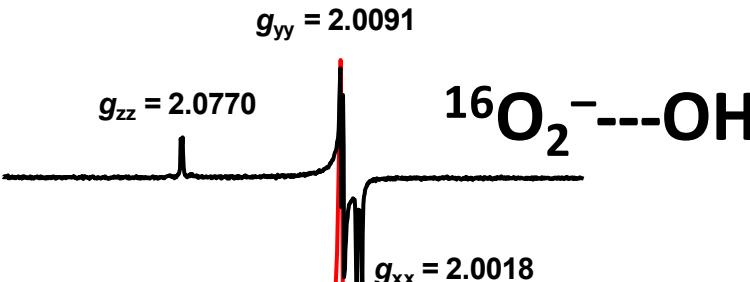
x – ^{17}O enhancement level

^{16}O and ^{17}O isotopomers of O_2^-

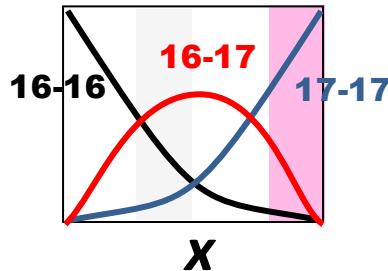
variable enrichment approach for controlling the isotopomer composition

Isotopomers of O_2^-

$^{16}\text{O}-^{16}\text{O}$



$^{16}\text{O}-^{17}\text{O}$



$^{17}\text{O}-^{16}\text{O}$

($^{17}\text{O}, x = 28\%$)

$^{16}\text{O}-^{17}\text{O}$

($^{17}\text{O}, x = 63\%$)

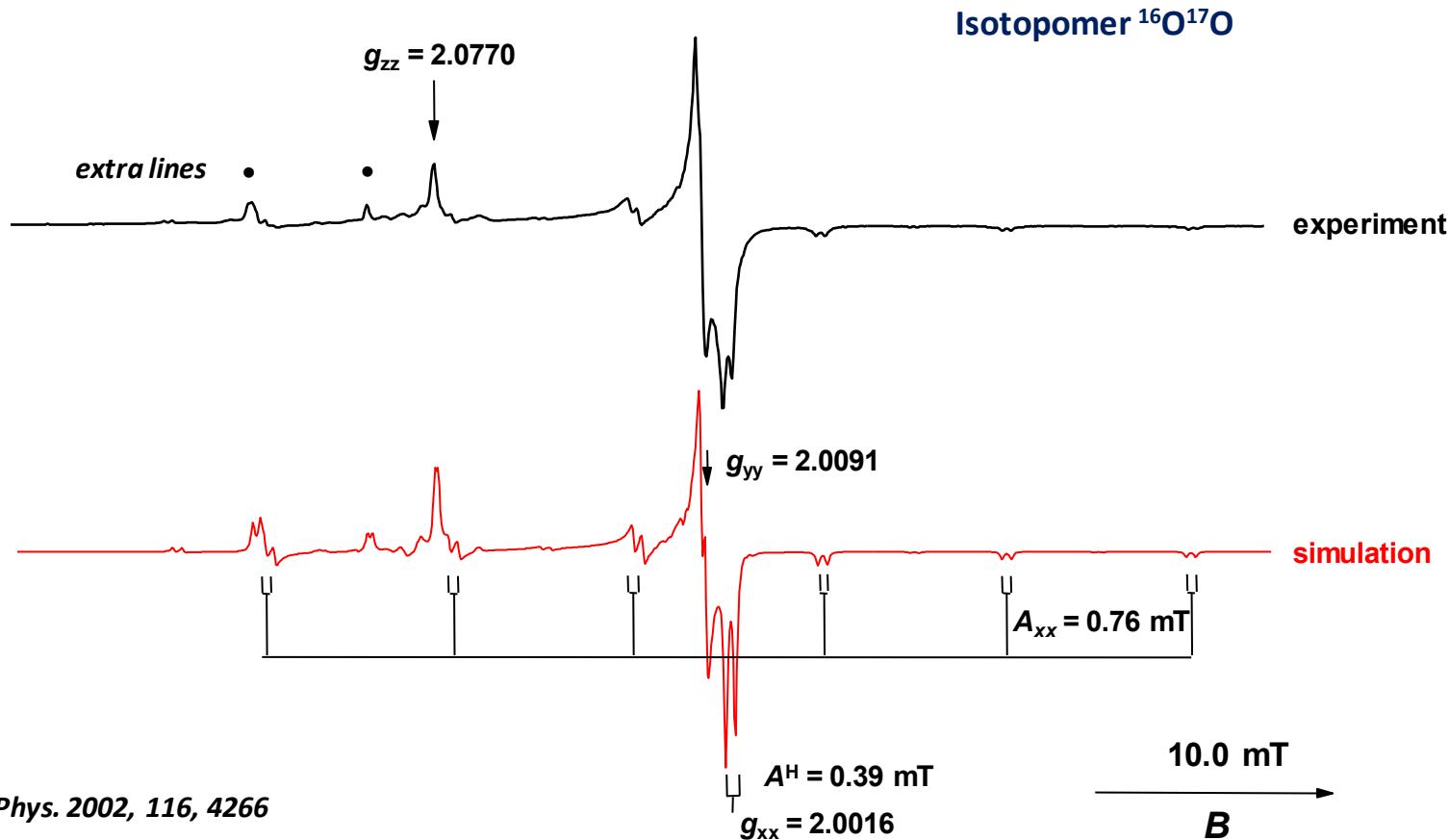
$^{17}\text{O}-^{16}\text{O}$

$^{17}\text{O}-^{17}\text{O}$



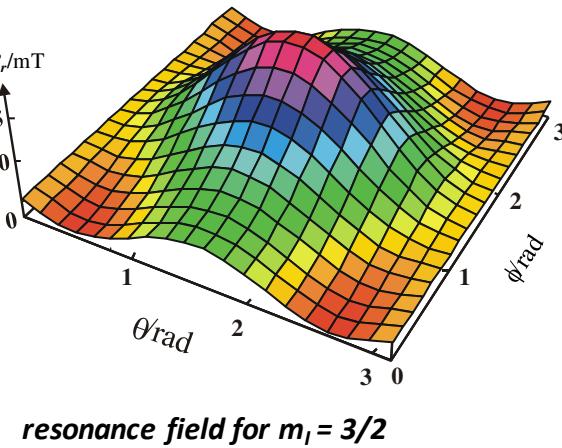
simplification of the spectra through suppression of the speciation and controlled enrichment

$^{16}\text{O}^{17}\text{O}^-$ isotopomer



identification of extra features

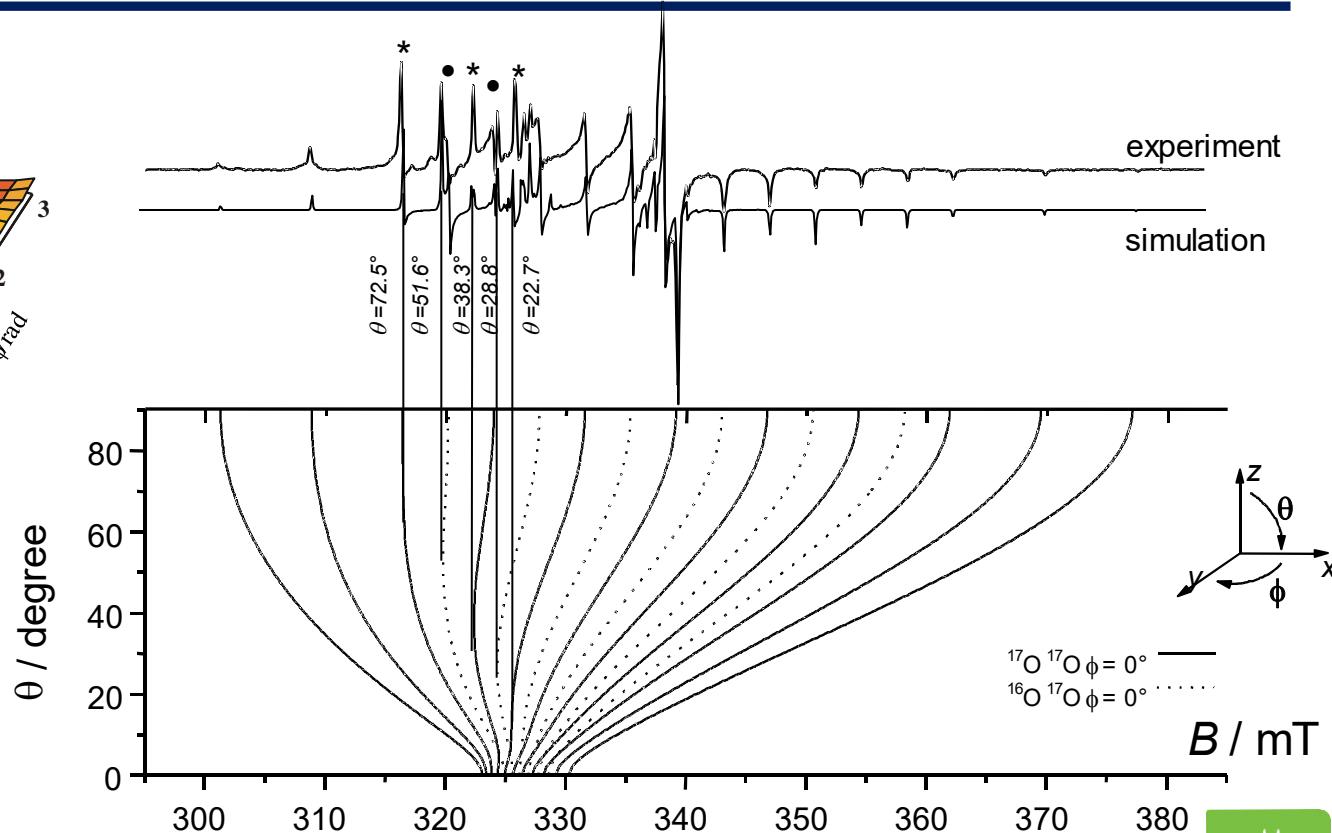
J. Chem. Phys. 2002, 116, 4266



resonance field for $m_I = 3/2$

$$\frac{\partial B(\theta, \phi)}{\partial \theta} = 0$$

$\theta = 28.8^\circ; \theta = 0^\circ;$



5 extra lines corresponding to additional extremes in $B_r(\theta, \phi)$ for $m_I = 3, 5/2, 2, 3/2, 1$

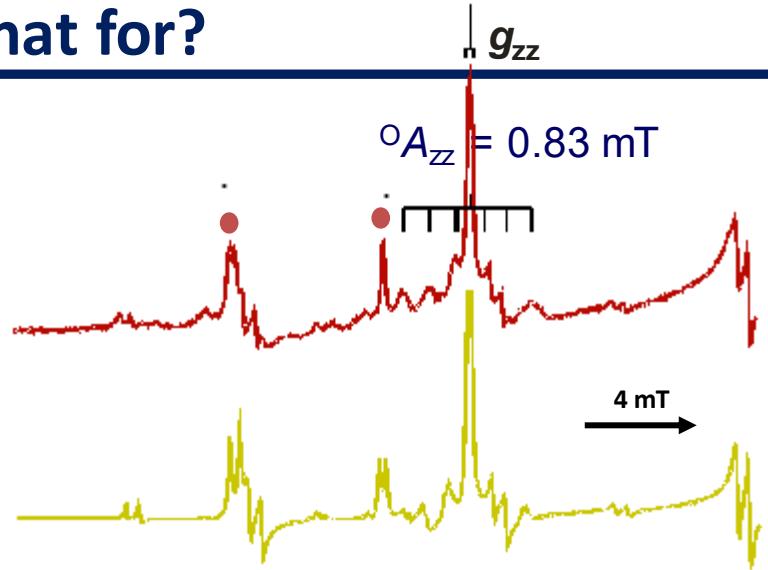
extra lines – what for?

using extra lines to pin down the ${}^0A_{zz}$ value

extra lines ${}^0A_{zz} = 0.83 \pm 0.20$ mT



simulation ${}^0A_{zz} = 0.73$ mT

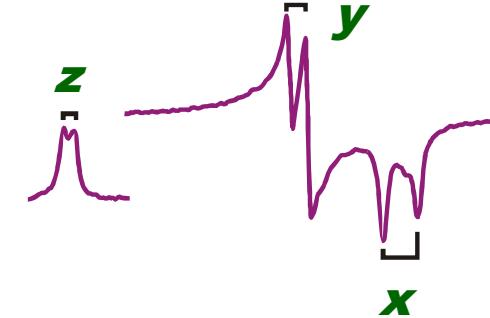
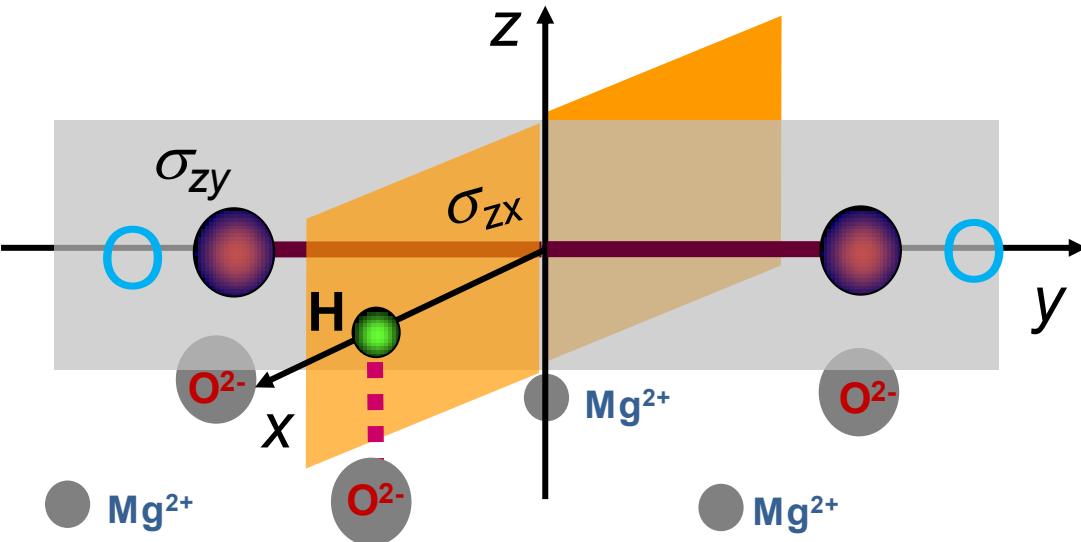


$$B_{zx}(m_I) = \frac{h\nu}{g_{zx}\beta_e} \left[1 - m_I K_{zx} - \frac{[I(I+1) - m_I^2](A'_{yy} + A'_{zz} A'_{xx})}{K_{zx}^2 / 4} - \frac{m_I^2(K_{zx}^2 - A'_{zz}^2)(A'_{xx}^2 - K_{zx}^2)}{2K_{zx}^2} \right]$$

$$K_{zx} = \frac{1}{4m_I} [1 - (1 + m_I^2 \Delta_{zx})^{1/2}] \quad \Delta_{zx} = \frac{g_{zz}^2 A'_{zz}^2 - g_{xx}^2 A'_{xx}^2}{(g_{zz}^2 - g_{xx}^2)} \quad A'_{ij} = A_{ij} / h\nu$$

$$g_{zx} = \frac{g_{zz}^2 g_{xx}^2 (A'_{zz}^2 - A'_{xx}^2)}{(g_{zz}^2 - g_{xx}^2)(\Delta_{zx} - K_{zx}^2)}$$

superhyperfine and hyperfine structure $^{17}\text{O}_2^-/\text{H}^+$ on MgO



$$\begin{array}{ll} {}^{\text{H}}\text{A} = & \boxed{0.39} \\ & \boxed{0.22} \quad {}^{\text{H}}\text{A}_{yz} \\ & \boxed{{}^{\text{H}}\text{A}_{zy}} \quad \boxed{0.13} \end{array} / \text{mT}$$

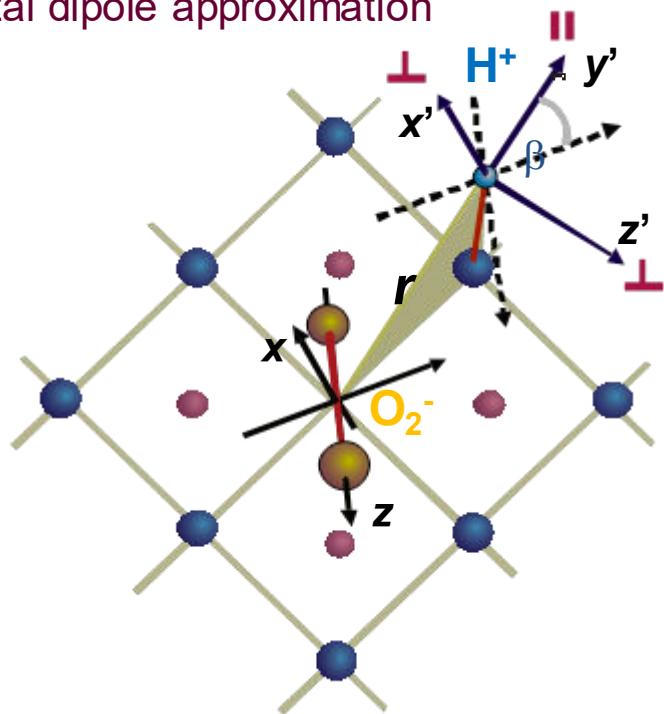
$C_{2v} \rightarrow$ orthorhombic symmetry $\rightarrow \mathbf{g}$ and ${}^0\mathbf{A}$ axes coincident

$C_s \rightarrow$ monocyclic symmetry $\rightarrow \mathbf{g}$ and ${}^{\text{H}}\mathbf{A}$ axes noncoincident

→ the local point symmetry at the given nucleus determines whether or not any of the principal axes of the \mathbf{g} and \mathbf{A} tensors are required to be coincident or not

accounting for the H-shf

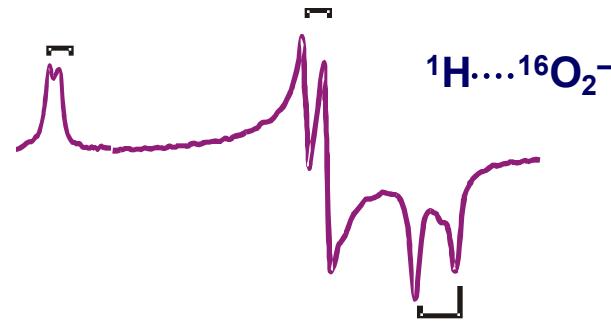
distal dipole approximation



$$A_D = {}^H A_{\parallel} - a_{\text{iso}} = g_e \mu_B g_H \mu_H (3 \cos^2 \phi - 1) / r^3$$

$$r = 0.36 \text{ nm}$$

$$r_{\text{calc.}} = 0.38 \text{ nm}$$



rotation formula of Hoffman (J. Mag. Res. 1984)

$${}^H A_{x'} = {}^H A_x$$

$${}^H A_{y'} = \left(\frac{{}^H A_y^2 - ({}^H A_y^2 + {}^H A_z^2) \sin^2 \beta}{1 - 2 \sin^2 \beta} \right)^{1/2} \quad {}^H A_{z'} = \left(\frac{{}^H A_z^2 - ({}^H A_y^2 + {}^H A_z^2) \sin^2 \beta}{1 - 2 \sin^2 \beta} \right)^{1/2}$$

$$\beta = \arcsin \left(\frac{{}^H A_z^2 - {}^H A_x^2}{{}^H A_y^2 + {}^H A_z^2 - 2 {}^H A_x^2} \right)^{1/2}$$

$$\beta = 39^\circ, {}^H A_{\parallel} = 3.2 \text{ MHz}, {}^H A_{\perp} = -1.98 \text{ MHz}$$