ESR spectroscopy of catalytic systems
- a primer

Thomas Risse

Fritz-Haber-Institute of Max-Planck Society
Department of Chemical Physics
Faradayweg 4-6
14195 Berlin
ESR spectroscopy
Solid vs. solution

Colloidal solution of nanoparticles
(in water at 300 K)

Colloidal solution of nanoparticles
(in ice at 120 K)

- What is the nature of the paramagnetic center?
- Which interactions determine the observed spectra?
- Where does the difference between solution and solid come from?
Outline:

- Introduction
- Magnetic interactions of an unpaired electrons
  - Zeeman interaction
  - interactions with other electron spins (group spins and zero field splitting)
  - hyperfine interaction
- relaxation processes
  - in solution
  - in solids
  - magnetic resonance and dynamics
- experimental aspects
- transition metal ions
  - electronic states and spin orbit coupling
  - ions in crystal or ligand fields
  - some examples ($\text{Ti}^{3+}, \text{VO}^{2+} (d^1), \text{Fe}^{3+} (d^5), \text{Co}^{2+} (d^7), \text{Cu}^{2+} (d^9)$)
- some examples
Introduction

references

ESR spectroscopy


Practical Aspects

Basics of Magnetic Resonance


Introduction
What kind of systems?

**molecules, complexes:**
- (diamagnetic)
- paramagnetic

**metals:**
- (diamagnetic)
- paramagnetic
- ferromagnetic
- antiferromagnetic

**compounds:**
- (diamagnetic)
- paramagnetic
- ferromagnetic
- antiferromagnetic

radicals: NO, O₂, NO₂
reaction intermediates
transition metal complexes

usually ferromagnetic metals e.g. Fe, Co, Ni
conduction band ESR for small particles

e.g. oxides, nitrides defects
ESR spectroscopy
Zeeman interaction

Interaction of an angular momentum with a magnetic field:

classically: \[ E = -\mu B \]

translation to QM

if field is in z-direction: \[ H = \mu_B g J_z B_0 \]

eigenvalues: \[ E = \mu_B g B_0 M_J \]

for \( M_J = \pm 1/2 \): \[ \Delta E = h\nu = \mu_B g B_0 \]
ESR spectroscopy
Zeeman interaction

isotropic case: \[ H = \mu_B g \mathbf{J} \mathbf{B} \]

anisotropic case: \[ H = \mu_B \mathbf{J} g \mathbf{B} \]

\( g \) is a symmetric (3x3) matrix
=> always possible to diagonalize principal components \( g_x, g_y, g_z \)

eigenvalues: \[ E = \mu_B g_{\text{eff}} B_0 m_J \]

with: \[ g_{\text{eff}} = \left[ \sin^2(\theta) \cos^2(\phi) g_x^2 + \sin^2(\theta) \sin^2(\phi) g_y^2 + \cos^2(\theta) g_z^2 \right]^{1/2} \]

\( \theta \) and \( \phi \) describe the orientation of the static magnetic field in the g-matrix coordinate system

\[
\begin{align*}
B \parallel x & \quad g_x = 2.0076 \\
B \parallel y & \quad g_y = 2.0050 \\
B \parallel z & \quad g_z = 2.0023
\end{align*}
\]
ESR spectroscopy
interactions with other electron spins

1. dipole-dipole interaction (important for distance measurements; X-band 12 Å < r < 60 Å)

\[ H_{DD} = \frac{\pi \mu_0}{\hbar} g_j g_i \mu_B^2 \left( \frac{\vec{S}_j \cdot \vec{S}_k}{r_{j,k}^3} - \frac{3(\vec{S}_j \cdot \vec{r}_{j,k})(\vec{S}_k \cdot \vec{r}_{j,k})}{r_{j,k}^5} \right) \]

or in compact form:  \( H_{dd} = \mathbf{S}_1 \mathbf{D SS}_2 \)

results in splitting of the states which depends on the relative orientation of the interspin axis, the g-matrix coordinate systems, and the orientation of the magnetic field

important special case: \( g_j = g_k \approx g_e \) and \( E_{zee} > E_{dip} \)

\[ H_{DD} = \frac{\pi \mu_0}{\hbar} g_j g_i \mu_B^2 \left( \frac{3 \cos^2 \theta - 1}{r_{j,k}^5} \right) \]

average out for integration over a sphere

=> no isotropic contribution

\( \theta = \) angle between inter-spin axis and magnetic field
ESR spectroscopy
interactions with other electron spins

2. exchange coupling (effective for \( r < 10 \text{ Å} \))
   - two electrons have a certain probability to be found in the same orbital
   - extreme case: covalent bond (spin paired \( \Rightarrow \) no signal!)
   - \( \Rightarrow \) ESR is sensitive for weak exchange coupling
   - exchange interaction has an isotropic contribution (most of the times this is the only one which is observed)

\[
H_{\text{exch}} = - J \mathbf{S}_k \cdot \mathbf{S}_j
\]

- \( J \) negative: spins oriented antiparallel
  - antiferromagnetic coupling
- \( J \) positive: spins oriented parallel
  - ferromagnetic coupling
ESR spectroscopy

group spins and zero field splitting

Hund’s rule: more than one energetically degenerate orbital:

first fill one electron in each orbital

\[ S = s_1 + s_2 + s_3 = 3/2 \]

this results in a total spin \( S \), also called group spin

in short this group spin is often called electron spin \( S > \frac{1}{2} \)

there is an important consequence:

These system show an interaction which is mediated by the spin orbit interaction and is formally equivalent to the dipole interaction:

\[ H_{zfs} = S \cdot D \cdot S \]

the interaction is independent of the field. This is also true for the hyperfine interaction, or the dipolar interaction but the zero field splitting is usually the leading term!

size of the effect can vary dramatically: from small for slightly distorted systems to very large such that no ESR signal can be observed
ESR spectroscopy
hyperfine interaction

isotropic case

\[ H = \mu_B g_s \vec{S} \vec{B} \]

\[ m_s = \frac{1}{2} \]

\[ m_s = -\frac{1}{2} \]

\[ \vec{B}_{\text{res}} \]

\[ \vec{B} \ (\text{variable}) \]

reason: hyperfine interaction; \((2I+1)\)-states

DTBN in toluene (300 K)

\[ (^{14}\text{N}) = 1 \]

MnCl₂ in water (300 K)

\[ \text{Mn}^{2+} \ l = 5/2 \]
ESR spectroscopy

hyperfine interaction

What is hyperfine interaction?

interaction of an electron spin with a nuclear spin

isotropic case

\[ H = \mu_B g_S B_0 - \frac{\gamma_n B_0 I_z}{2} + a_{iso} I_z S_z \]

el. Zeeman nuc. Zeeman hyperfine interaction
ESR spectroscopy
hyperfine interaction

in general: two contributions

1. dipole-dipole interaction:

\[ H = \mathbf{S} \mathbf{T} \]

\( \mathbf{T} \) is the anisotropic interaction matrix
traceless => integral over a sphere vanishes

2. Fermi-contact interaction:

\[ H = a_{\text{iso}} \mathbf{S} \]

isotropic, depend on the probability to find an electron at the position nucleus

\[ H_{\text{hfi}} = \mathbf{S} \mathbf{A} \]

with \( \mathbf{A} = \mathbf{T} + a_{\text{iso}} \mathbf{1} \) \( \mathbf{1} \): unit matrix
ESR spectroscopy

effect of rotational motion

rigid limit

free electron

g-tensor
B \parallel x
B \parallel y
B \parallel z

hyperfine interaction
I^{(14N)} = 1

powder spectrum

rigid limit

rotational motion

isotropic rotation

rigid limit

slow motion

fast motion

A_{iso} = 1/3(A_{xx} + A_{yy} + A_{zz})

\tau_c > 50 \text{ ns}

\tau_c \approx 15 \text{ ns}

\tau_c < 1 \text{ ns}

A_{iso} = \frac{1}{3}(g_x + g_y + g_z)

\tau_c \approx 15 \text{ ns}
EPR spectroscopy

relaxation effects

system in thermodynamic equilibrium non equilibrium situation

return to the thermodynamic equilibrium is characterized by two processes:

1. energy relaxation: spin lattice or longitudinal relaxation ($T_1$)
   no spontaneous emission at these frequencies; energy has to be transferred to some partner e.g. the solvent or the lattice in a solid

2. relaxation of the spin coherence: spin-spin or transversal relaxation ($T_2$)
   (entropic term)
ESR spectroscopy
relaxation mechanisms

fluid systems:

for a relaxation of an exited spin state one need fluctuating magnetic field. In particular, the fluctuating field should have a Fourier component at the resonance frequency.

**Where do the fluctuating fields come from?**

in fluids this comes mostly from rotational dynamics of the molecule or of parts of the molecule. This leads to fluctuating fields as long as there are anisotropic interactions.

The most efficient channel is usually the one arising form the interaction with the largest anisotropy:

- for systems with $S > \frac{1}{2}$ : dipolar coupling between the spins
  (often this mechanism so fast that these systems cannot be observed in solution at all e.g. Ni$^{2+}$, Co$^{2+}$)
- for $S = \frac{1}{2}$ : for organic radicals often the anisotropic hyperfine
  for transition metal ions often the anisotropic Zeeman interaction

an important channel is spin exchange with a fast relaxing agents (e.g. O$_2$)
(this is widely used and is called ESR oxymetry)
ESR spectroscopy
relaxation mechanisms

solid systems:
relaxation mostly mediated by lattice vibrations (phonons)
(coupling to the phonons via changes in the crystal field and spin orbit interaction)
two processes:
1. direct process (excitation or deexcitation of a phonon)
   longitudinal relaxation
   probability of this process depends on the density of states of the phonon spectrum at the given energy, thus it is temperature dependent
2. indirect process (Raman like process)
   second order process (just the difference between the two photons has to match the energy of the excited spin state)
   The probability of such a process increases dramatically if real states are involved. This is particularly true for higher temperatures.
experimental aspects

cw set-up at 10 GHz
experimental aspects
consequence of lock-in detection

1. lock-in detection gives
   1. derivative of the absorption line

2. holds only true if modulation amplitude is small as compared to line width
field distribution in a microwave resonator

TE_{102}-cavity

helium cryostat

cavity

sample

quartz finger

1 cm

3 cm
experimental aspects
intensity of ESR spectra

What determines the signal intensity?

1. transition probabilities (calculated from quantum mechanics)
2. absorbed microwave power

\[ \mathcal{P} = \frac{1}{2} \omega_0 H_1^2 \chi'' \]

\( \chi'' = \) complex part of the high frequency susceptibility

obeys Curie's law \( \Rightarrow I(\text{ESR Signal}) \sim 1/T \)

\( H_1 = \) oscillating magnetic field (perpendicular to the static magnetic field)

depends on the quality factor Q of the resonator

rectangular cavity:

\[ H_1^2 = \frac{\mu H_0^2 Q_L (1 - |\Gamma_0|^2) P_{inc}}{4\pi\nu_0 \mu''^2} \]

\( \Gamma_0: \) reflection coefficient
\( \mu, \mu': \) mag. perm. waveguide and cavity
experimental aspects

intensity of ESR spectra

What does this mean?

ESR is quantitative, but…

- relative numbers of spins in the sample: easy

- absolute numbers of spins in the sample: difficult
  (one needs a calibration standard which is measured under exactly the same conditions (including sample shape and size, temperature, microwave settings etc.)

- fraction of paramagnetic species as compared to the total number of species: very difficult
  only possible with detailed knowledge of the paramagnetic species (transition probabilities, relaxation properties, coupling situation) and an internal standard of known concentration
transition metal ions
electronic states and spin orbit coupling

We need the electronic ground state:
construction according to Hund’s rules and Pauli principle
example: Co^{2+} (3d^7) for the ground state configuration see literature

\[
\begin{array}{cccccc}
 l &=& +2 & +1 & 0 & -1 & -2 \\
 \uparrow \downarrow & \uparrow \downarrow & \uparrow & \uparrow & \uparrow & \uparrow \\
\end{array}
\]

\[ L = 3, \quad S = 3/2 \text{ (assuming LS coupling)} \]
\[ ^4F \]

no fields: degeneracy: \((2S + 1)(2L + 1) = 28\)
if LS coupling is exactly correct: \(L = \text{const.} \Rightarrow g = g_e\)
spin orbit coupling lifts the degeneracy of states with equal \(L\) and \(S\) but different \(J\)
two contribution: 1. changes the splitting between states \((m_S, m_{S+1})\), shift of \(g_{iso}\)
2. depends on \(m_s^2\) (only important for \(S > 1/2\)) no contribution to \(g_{iso}\)

often neither LS nor jj coupling correct. The correction to the LS case can be made by the so-called Racah coefficients \(B\) and \(C\) which are tabulated
transition metal ions

no fields: degeneracy: \((2S + 1)(2L + 1)\)

degeneracy is lifted partly by external electric fields

the external electric field can due to neighboring ions or ligands

lifting the degeneracy will lead to a partial decoupling of spin and orbit, thus the Racah coefficient are slightly small than in the free ion

drastic effects are observed if \(\Delta > E_{\text{pair}}\)

pure ionic interactions: crystal field theory

including covalency: ligand field, MO theory
transition metal ions
symmetry reduction

spherical

octahedral

e_g

t_2g

tetragonal distortion

tetrahedral

t_2g

e_g

tetragonal distortion

isotropic g, A

axial g, A
transition metal ions

$\text{Ti}^{3+}$, $\text{VO}^{2+}$ ($d^1$)

$\text{Ti}^{3+}$: typically 6 fold coordination in distorted octahedral symmetry
often axial symmetric tensor ($g_x = g_y \neq g_z$) $g \approx 1.85 - 2$
87% of the isotopes have no nuclear moment
$^{47}\text{Ti}$ (7.4 %; $I=5/2$) and $^{49}\text{Ti}$ (5.4%; $I =7/2$)
$\Rightarrow$ intense pattern due to $g$-anisotropy just weak satellites
from hf-interaction

$\text{V}^{4+}$, $\text{VO}^{2+}$
isoelectronic to $\text{Ti}^{3+}$, mostly $\text{VO}^{2+}$
typical $g$-values: $g_{\parallel} = 1.94$, $g_{\perp} = 1.98-1.99$
$^{51}\text{V}$ (99.75%; $I =7/2$) $\Rightarrow$ characteristic hyperfine pattern;
usually well resolved because of small $g$-tensor anisotropy
transition metal ions
Fe$^{3+}$, Mn$^{2+}$ (d$^5$)

Fe$^{3+}$: ground state $^6$S, high-spin (S=3/2), low-spin (S=1/2)
in cubic symmetry: $g_{\text{iso}} \approx 2$
low symmetry: large zero-field splitting (only transitions within Kramers-Dubletts) large g-anisotropies $g_{\parallel} = 2$, $g_{\perp} = 6$
97.8% of the isotopes have no nuclear moment => almost no hf-satellites

Mn$^{2+}$ isoelectronic to Fe$^{3+}$; just high spin systems of importance
small g-anisotropy, much smaller zero-field splitting rf. Fe (a few GHz) transition between different Kramers multipletts possible

$^{55}$Mn (100%; I =5/2) => characteristic hyperfine pattern;
usually well resolved because of small g-tensor anisotropy
transition metal ions

Co$^{2+}$ (d$^7$)

Co$^{2+}$: ground state $^4$F, high-spin (S=3/2), low-spin (S=1/2)

octahedral and tetrahedral ligand field are usually distorted

perfect octahedral symmetry: $g_{\text{iso}} = 4.3$

small distortion: $g$ from 1.5 to 7; however, $g_{\text{iso}}$ often close 4.3

in tetrahedral symmetry smaller deviations from $g_e$

low symmetry: large zero-field splitting (usually not possible to observe a spectrum in solution, require low temperatures)

$^{59}$Co (100%; $I = 7/2$) => eight line spectrum
transition metal ions
Cu$^{2+}$ (d$^9$)

Cu$^{2+}$: ground state $^2$D, S=1/2
usually distorted octahedral ligand field (tetragonal symm.)
=> axial symmetric tensor: $g = 2 - 2.2$; usually $g_\parallel < g_\perp$
distorted tetrahedral ligand field (tetragonal symm.)
$g_\parallel > g_\perp$ is usually found

$^{63}$Cu (69.2%; I =3/2); $^{65}$Cu (30.8%; I =3/2);
almost equal gyromagnetic ratio => strongly overlapping
hyperfine multipletts
ESR spectroscopy
transition metal ions

Colloidal solution of nanoparticles (in water at 300 K)

Colloidal solution of nanoparticles (in ice at 120 K)

- moderate hyperfine anisotropy
  \( A_z \approx 20 \text{ mT}, A_x = A_y \approx 8 \text{ mT} \)
  \( a_{iso} \approx 12 \text{ mT} \)
- almost isotropic g-value
  \( \Rightarrow \) no Co;

Ta and V have similar electronic structures however, the spin orbit coupling plays a much bigger role for Ta.

isotropic spectrum consist of 8 lines
\( g = 1.98 \)

\( 25 \text{ mT} \)

\( 25 \text{ mT} \)

\( 25 \text{ mT} \)

\( 25 \text{ mT} \)

\( 25 \text{ mT} \)

\( 25 \text{ mT} \)

\( 25 \text{ mT} \)
Fe in AlPO$_4$-5

two species: 1. $g \approx 2$

2. $g \approx 4.3$

1. species: octahedral coordinated Fe$^{3+}$ on lattice positions

2. species: extra lattice Fe$^{3+}$ in a distorted tetrahedral environment

strong redistribution of sites upon heating. At high temperature minimal 3 different sites occupied by Fe$^{3+}$. Regular lattice sites account for approx. 45% of the sites.

ESR spectroscopy
transition metal ions

Benzene adsorbed to NaPdY(a), NaPtY (c) NaCeY (d) zeolites

b) simulation assuming
g_{iso} \approx 2.0023
coupling to twelve equivalent protons
a_{iso} = 0.312 \text{ mT}

Formation of benzene dimer radical cations
only isotropic values: due to fast motion