NMR Spectroscopy of Organic Compounds

Lesson 10:
EPR

NMR SPECTROSCOPY
RESEARCH-SERVICE GROUP
IOCB PRAGUE

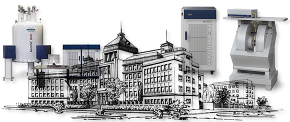
Ján Tarábek

Basic Principles & Applications of Electron Paramagnetic (Spin) Resonance, EPR (ESR).

NMR Analogy

Ján Tarábek

Institute of Organic Chemistry
and Biochemistry (IOCB) of the CAS



NMR Spectroscopy Group

Presentation link: https://nmr.group.uochb.cz/en/nmr-organic-compounds

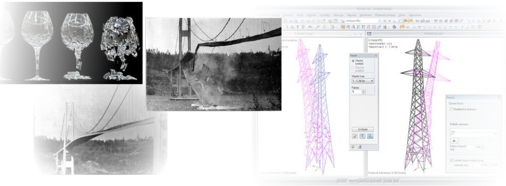
LaTeX 2ε Beamer

Table of Contents

Mechanical Resonances in Physics

Resonance

Physical phenomenon ⇒ Vibration/Oscillation amplitude of a pendulum/oscillator is getting higher in comparison to its natural ground state. It occurs if the frequency ν_{applied} of the periodically applied force equals to the natural one ν_{own}. The applied stimulus may not be necessarily strong.


[1]

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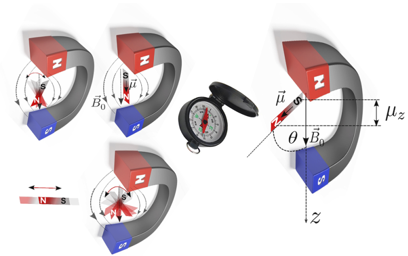
[1] Diverse web resources, mainly 🔗 `https://www.vsb.cz/en`

Resonance of Magnetic Needle in Magnetic Field



Energy ($\varepsilon(\theta)$) of tiny magnet ($\vec{\mu}$) in magnetic field[2] ($\vec{B}_0$):

$$\boxed{\varepsilon(\theta) = -\vec{\mu}\vec{B}_0 = -\mu B_0 \cos(\theta) = -\mu_z B_0} \qquad \text{(I)}$$

$$\varepsilon(0^\circ) = -\mu B_0 \quad \varepsilon(180^\circ) = \mu B_0$$

$$\Delta\varepsilon = \varepsilon(180^\circ) - \varepsilon(0^\circ) = 2\mu B_0 = 2\mu_z B_0$$

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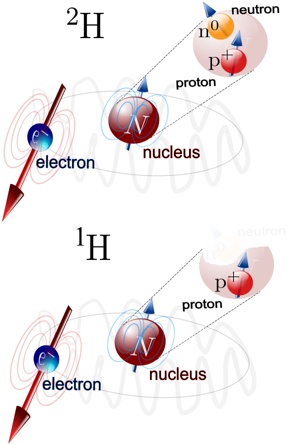
[2] ⚠ $B \equiv$ Magnetic Flux Density $[B] = \mathrm{G}\ (\mathbf{mT})$

Electrons & Nuclei like Tiny Magnets?

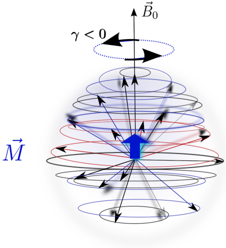
Schematic View of Deuterium & Protium



Proton (p) & Electron (e) Precession in Magnetic Field $\vec{B}_0$

$$\nu_{\mathrm{p}} = -\frac{1}{2\pi}\gamma^*_{\mathrm{p}} B_0(\mathrm{p}) \qquad \text{(II)}$$

$$\nu_{\mathrm{e}} = -\frac{1}{2\pi}\gamma^*_{\mathrm{e}} B_0(\mathrm{e}) \qquad \text{(III)}$$



* $\gamma \equiv$ magnetogyric ratio

$\vec{M} = (1/V)\sum \vec{\mu} \equiv$ magnetization

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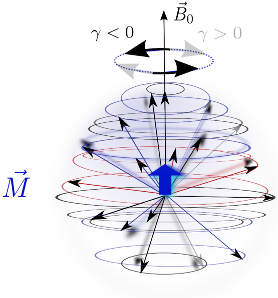
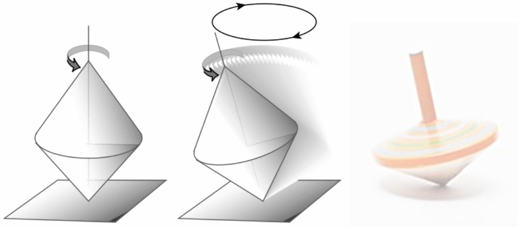
Precession

Ensemble of Magnetic Moments in Magnetic Field $\vec{B}_0$:



Gyroscope in Gravitational Field 🌐:



Electrons & Nuclei like Tiny Magnets?

Examples of Magnetic (non-magnetic) Nuclei & Electron:

Nucleus	$\gamma^{*}/10^{6}$ rad s^{-1} T^{-1}	**Nat. Abund. / %**	$\nu_{\mathrm{N(e)}}$/MHz **at** 11.74 T
^{1}H	267.522	99.985	−500.000
^{12}C	NA**	98.930	NA
^{13}C	67.283	1.070	−125.725
^{14}N	19.338	99.636	−36.132
^{15}N	−27.126	0.364	50.684
^{16}O	NA	99.962	NA
^{17}O	−36.281	0.038	67.782
^{31}P	108.394	100.000	−202.606
e^{-}	−176085.971	NA	329016.005

⇓

Free electron is ≈ 650-time stronger 🧲 than proton

* $\gamma \equiv$ magnetogyric ratio ⚛

** **N**ot **A**vailable

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$\Downarrow$

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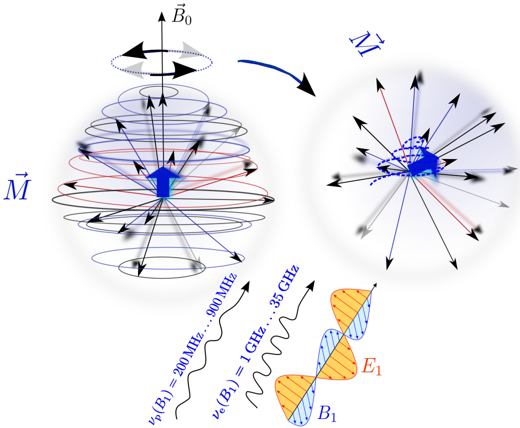
Magnetic Resonance of Protons & Electrons

“A”ction of Electromagnetic Radiation($\mathbf{B}_1$, $\mathbf{E}_1$)

Common Frequencies of Alternating Magn. Flux Density ($\mathbf{B}_1$) for Protons ($\nu_\mathrm{p}(\mathbf{B}_1)$) & Electrons ($\nu_\mathrm{e}(\mathbf{B}_1)$):



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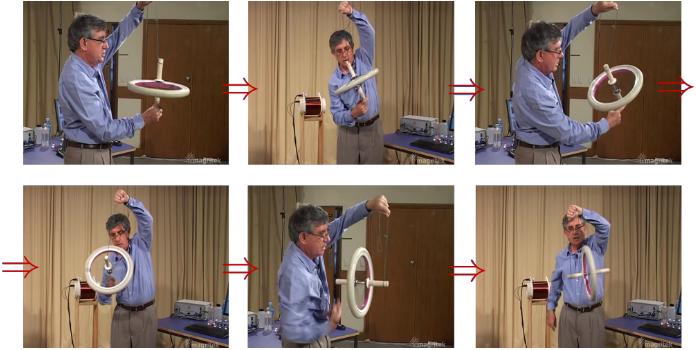
Precession & Mechanical Gyroscope Resonance

Analogy with the Ensemble of Nuclei or Electrons

applied frequency = natural frequency



[3]

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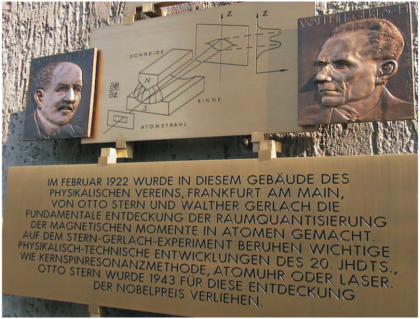
[3] https://www.drcmr.dk/MR
https://www.youtube.com/watch?v=7aRKAXD4dAg

Stern-Gerlach Experiment

- **1922** Beam of silver atoms [Kr] $4\,d^{10}\,5\,s^{1}$, is split by non-homogeneous magnetic field into "two" lines (***Otto Stern & Walther Gerlach***)



IM FEBRUAR 1922 WURDE IN DIESEM GEBÄUDE DES PHYSIKALISCHEN VEREINS, FRANKFURT AM MAIN, VON OTTO STERN UND WALTHER GERLACH DIE FUNDAMENTALE ENTDECKUNG DER RAUMQUANTISIERUNG DER MAGNETISCHEN MOMENTE IN ATOMEN GEMACHT. AUF DEM STERN-GERLACH-EXPERIMENT BERUHEN WICHTIGE PHYSIKALISCH-TECHNISCHE ENTWICKLUNGEN DES 20. JHDTS., WIE KERNSPINRESONANZMETHODE, ATOMUHR ODER LASER. OTTO STERN WURDE 1943 FÜR DIESE ENTDECKUNG DER NOBELPREIS VERLIEHEN.

[4]

- **1924-1925** Explanation of "S-G" experiment by the existence of intrinsic angular momentum (***Wolfgang Pauli & George Uhlenbeck & Samuel Goudsmit***)

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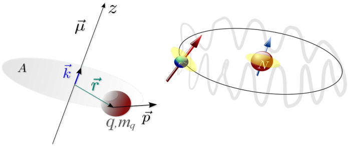
[4] A memorial plaque at the University of Frankfurt

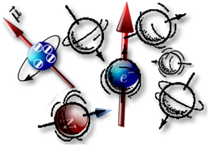
Orbital* & Intrinsic (Spin) Angular Momentum (AM)

Magnetic Moment $\vec{\mu}$ and AM Relations

Orbital AM



Intrinsic AM (Spin)



$$\boxed{\vec{\mu}_l = \frac{q}{2m_q}\vec{l} = \gamma_q \vec{l}} \quad \text{(IV)}$$

$$\boxed{\vec{\mu}_j = g_{\mathrm{e(N)}}\frac{q}{2m_q}\vec{j} = \gamma_j \vec{j}} \quad \text{(V)}$$

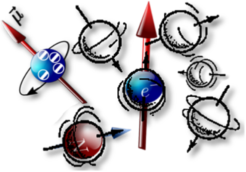
q	charge carrier
γ_q	magnetogyric ratio
γ_j	spin magnetogyric ratio

m_q	charge carrier mass
$g_{\mathrm{e(N)}}$	nuclear or electronic g-factor
$j \equiv S$ or I	nuclear or electron spin

* Defined as: $\vec{l} = \vec{r} \times \vec{p}$, measure of rotational motion dynamics

Orbital & Intrinsic (Spin) Angular Momentum (AM)

Do the Nuclei and Electrons Rotate, Indeed?



Spin[5]

. . . is pure quantum-mechanical property ,

which is not related to spinning/rotating particle ,

such an idea is only used as a limited model for educational purposes

- Neutrons are not charge carriers even though they do have a spin!
- If the particles were spinning ⇒ ⇒ the spinning speed $>> c$!
- We don't know the exact particle shape nor the rotational axes!

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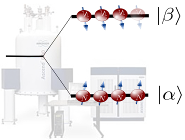
[5] `https://mriquestions.com/what-is-spin.html`
`https://www.youtube.com/watch?v=v1_-LsQLwkA`
`https://www.youtube.com/watch?v=pWlk1gLkF2Y`
D.P. Goldenberg, *Principles of NMR Spectroscopy. An Illustrated Guide.*

Energies (ε) in NMR and EPR

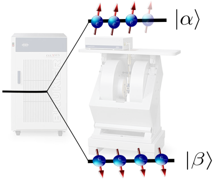
Ground (gr)-Excited (ex) State Populations at $T = 298\,\mathrm{K}$

$$\frac{N_{\mathrm{ex}}}{N_{\mathrm{gr}}} = \exp\left(-\frac{\Delta\varepsilon}{k_{\mathrm{B}}T}\right) \approx 1 - \frac{\Delta\varepsilon}{k_{\mathrm{B}}T} \qquad \text{(VI)}$$

Proton (NMR)



Electron (EPR)



$$\boxed{\frac{N_{|\beta\rangle}}{N_{|\alpha\rangle}} = 99.990\,\%} \qquad \text{(VII)}$$

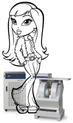
$$\boxed{\frac{N_{|\alpha\rangle}}{N_{|\beta\rangle}} = 99.842\,\%} \qquad \text{(VIII)}$$

Energies (ε) in NMR and EPR

Conditions for Recording of Spectra

Proton (NMR)

$$\begin{aligned} \Delta\varepsilon_{\mathrm{p}} &= h\nu_{\mathrm{p}} \\ &= g_{\mathrm{p}}\hbar\gamma_{\mathrm{p}}B_0(\mathrm{NMR}) \\ \text{for } \nu_{\mathrm{p}} &= 600\,\mathrm{MHz} \\ B_0(\mathrm{NMR}) &= 14.0919\,\mathrm{T} \end{aligned} \qquad \text{(IX)}$$



Electron (EPR)

$$\begin{aligned} \Delta\varepsilon_{\mathrm{e}} &= h\nu_{\mathrm{e}} \\ &= -g_{\mathrm{e}}\hbar\gamma_{\mathrm{e}}B_0(\mathrm{EPR}) \\ \text{for } \nu_{\mathrm{e}} &= 9.8\,\mathrm{GHz} \\ B_0(\mathrm{EPR}) &= 0.3497\,\mathrm{T} \end{aligned} \qquad \text{(X)}$$

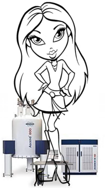
$$\begin{aligned} \mu_{\mathrm{N}} &= \hbar\gamma_{\mathrm{p}} \ \text{(Nuclear magneton)} \\ &= 5.05078324(13)\cdot 10^{-27}\ \mathrm{J\,T^{-1}} \end{aligned}$$

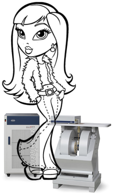
$$\begin{aligned} \mu_{\mathrm{B}} &= -\hbar\gamma_{\mathrm{e}} \ \text{(Bohr magneton)} \\ &= 9.27400915(23)\cdot 10^{-24}\ \mathrm{J\,T^{-1}} \end{aligned}$$

NMR & EPR Spectroscopy

Common Ways How to Meet the Resonance Condition

$$\text{frequency} = \nu(B_0)$$





Proton (NMR)

Electron (EPR)

$$\text{frequency}(\nu_\mathrm{p}) \neq \text{const.}$$
$$B_0(\text{NMR}) = \text{const.}$$

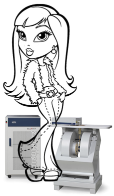
$$\text{frequency}(\nu_\mathrm{e}) = \text{const.}$$
$$B_0(\text{EPR}) \neq \text{const.}^{**}$$

** CW $\equiv$ continuous wave

NMR & EPR like “Stepsisters”

NMR

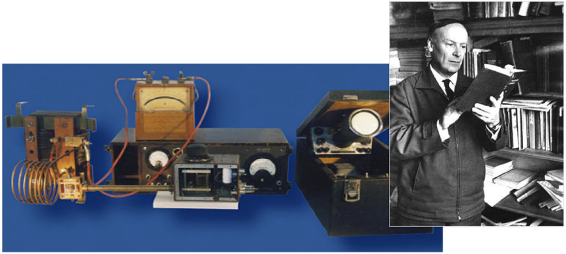
EPR



★ **“Birhdate”:**	1938-1946	1944–1946
🚺 **“Mother”:**	Quantum Mechanics (+ 📡)	
🚹 **“Fathers”:**	Isidor Rabi, Edward Purcell, Henry Torrey, Robert Pound, Felix Bloch, William Hansen a Martin Packard	Evgeny Zavoisky & Brebis Bleaney

EPR Discovery by Evgeny Zavoisky

- **1940-41** He started to follow up the NMR solid-state experiments ⇒ Results were not reproducible (problems with field homogeneity)
- **1944** 1st EPR experiments on $CuCl_2 \cdot 2\,H_2O$, $CuSO_4 \cdot 5\,H_2O$, $MnSO_4 \cdot H_2O$
- Additional EPR development by ***Brebis Bleaney***


[6]

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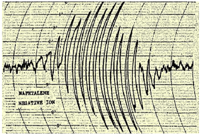
[6] `https://kpfu.ru/eng/about-the-university/kfu-structure/museums/evgeny-zavoisky-lab-museum`

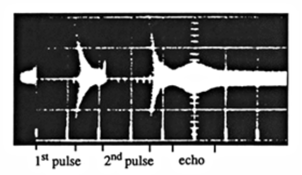
Splitting of EPR Spectra & Pulsed Technique

- **1953** Splitting of EPR spectra detected for the first time: Wuster's Blue, Naphthalene$^{\bullet-}$ (***Weissman, Townsend, Paul, Pake***)



[7]

- **1958** 1st EPR pulsed experiment (***Richard Blume***)



[8]

- **1987** FT EPR Spectrometer commercially available (***Bruker***)

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[7] 📕 *J. Chem. Phys.* 21, **1953**, 2227-2228

[8] 📕 R. J. Blume; *Phys. Rev.* **1958**, 109, 1867-1873

EPR Spectroscopy

⚠ EPR[9]

Electron **P**aramagnetic **R**esonance ⇒ form of spectroscopy, concerned with the microwave-induced transitions of unpaired electrons having a net spin & orbital angular momentum.

Most of the stable molecules possess e^--configuration with "paired" spins ⇒
⇒ **EPR is not so widely used like NMR**, however
⇒ **EPR is the only one direct method to study paramagnetic species**

⚠ What is the EPR Mission?

- Determination of unpaired e^--centers (incl. quantitative information like c, n, N)
- Find the chemical structure of unpaired e^--center within sample/material
- Find the information about dynamics of unpaired e^--center

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[9] https://goldbook.iupac.org/terms/view/E02005

Examples of Paramagnetic Compounds/Materials

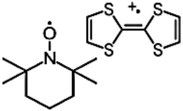
Paramagnetic

O_2

Diamagnatic

N_2

- **Radicals**–organic, inorganic, neutral (e.g. HO$^\bullet$, nitroxyl), ions
- **Structures with more than one unpaired e$^-$** (e.g. O_2, bi(di)radicals)
- **Transition-metal complexes** (e.g. Cu^{2+}, Co^{2+}, Mn^{2+}, Fe^{3+})
- **Defects** in (ordered) **solid-state structures** (e.g. in diamonds, glasses)
- **Conducting Electrons** (e.g. in graphite)



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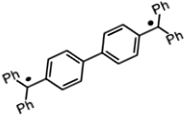

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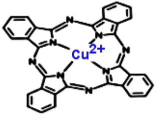

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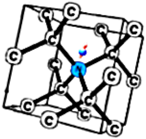

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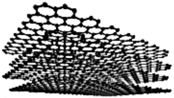


EPR in Natural Sciences

Chemistry

- Redox processes (electrochemistry)
- Kinetics of radical reactions
- Biradicals (triplet states)
- Coordination chemistry / Catalysis
- Spin trapping
- Photochemistry

Physics

- Measurements of magnetic susceptibility
- Cond. electrons in (semi-)conductor
- Crystal field in single crystals
- Defect in crystals

Materials and Industrial Research

- Polymer properties
- Defects in diamond
- Defect in optical fibers/glasses
- Shelf-life of fermented beverages
- Organic semiconductor(s) (defects)
- Degratation of polymers/paints/food

Biology

- Oximetry (LiPc/O2)
- Spin trapping of ROS/RNS
- Free radicals *in vivo*/*in vitro*
- Antioxidants/Radical Scavengers
- Spin labeling and spin probe technique
- Radiation effect/demage on biological samples

CW EPR & FT NMR Spectrometers

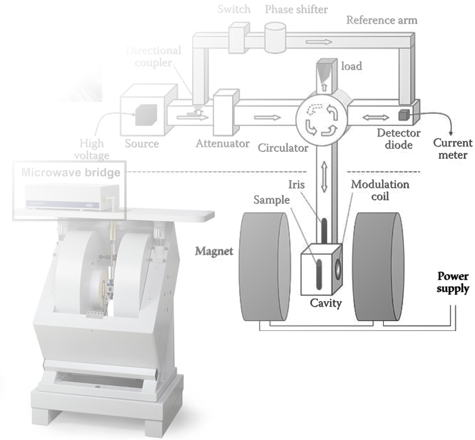
General View & Comparison

See EPR & NMR (400 MHz) Spectroscopy instruments at IOCB

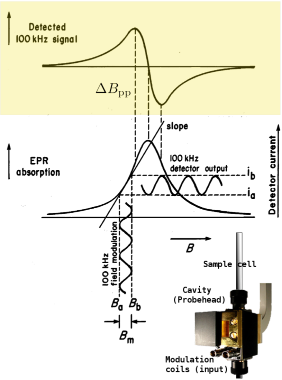
CW EPR Spectrometer

Detailed View & Recorded Spectrum

Magnet & Microwave bridge



Recording of an EPR Spectrum



Essential EPR Parameters

Common Recording Conditions for EPR Spectra

Phase[#]**:**

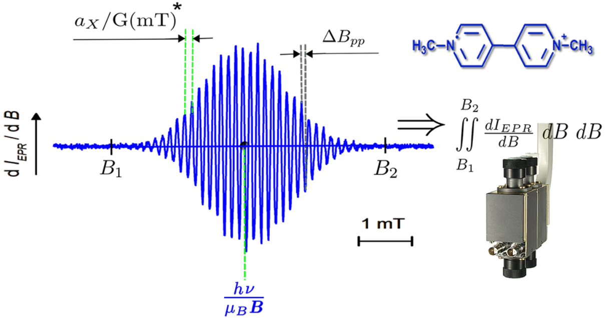
≋ + 🧊

🌡° [$]:

from ≈ 77 K (−196 °C)
to ≈ 500 K (227 °C)

🧪 :

from ≈ $1{\cdot}10^{-9}$ mol dm^{-3}
to ≈ 0.1 mol dm^{-3}



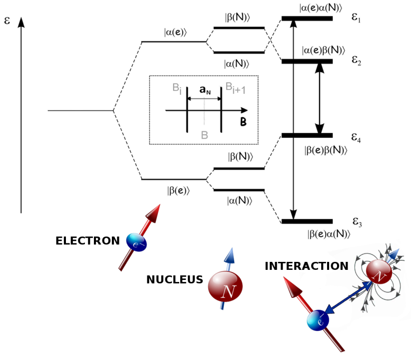
$$\Longrightarrow \int_{B_1}^{B_2}\!\!\int \frac{dI_{EPR}}{dB}\, dB\, dB$$

[#] gaseous, as well [$] 🌡° extension 3.8 K – 1273 K

[*] 1 G(Gauss) = 0.1 mT

Splitting of the EPR Spectrum

Hyperfine Coupling/Interaction with Nucleus $I_N = 1/2$ (^{1}H)



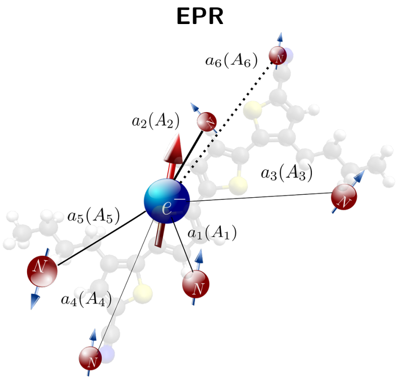
$$g\mu_B(B_{i+1} - B_i) = g\mu_B a_N^{*} \text{ (Splitting const.)} = A_N^{**} \text{ (Coupling const.)} \tag{XI}$$

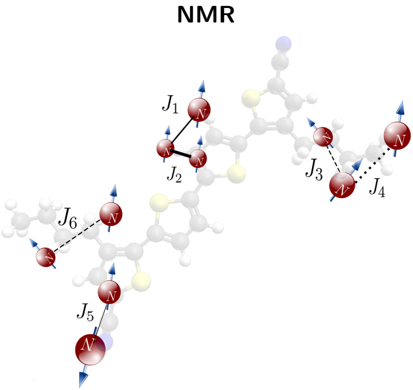
* G(mT)

** usually converted into $A/h \Rightarrow$ MHz (cm^{-1})

Splitting of the EPR Spectrum

Schematic View of e-N in EPR & N−N in NMR ⇒ Analogy.





Hyperfine Splitting by N Nuclei

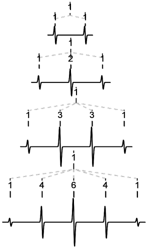
Multiplicity & Intensity

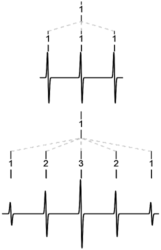
$I_{\mathsf{N}} = \frac{1}{2}(^{1}\mathrm{H})$

N = 0: 1
1: 1 1
2: 1 2 1
3: 1 3 3 1
4: 1 4 6 4 1

$I_{\mathsf{N}} = 1(^{14}\mathrm{N})$

N = 0: 1
1: 1 1 1
2: 1 2 3 2 1





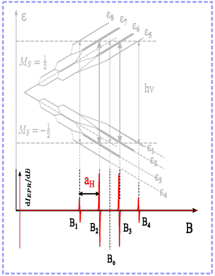
number of lines $(N_{\mathsf{L}}) = 2NI_{\mathsf{N}} + 1$; for k-groups: $N_{\mathsf{L}} = \prod_{i=1}^{k}(2N_i I_{\mathsf{N}i} + 1)$ (XII)

Splitting in EPR/NMR

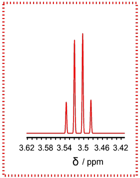
Three Equivalent Nuclei with $I = 1/2$ ($\cdot CH_3$/ $-CH_3$)

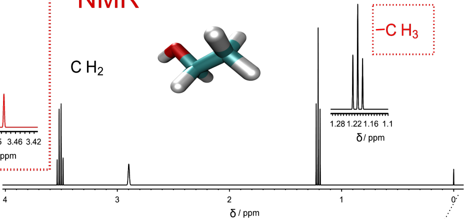
EPR

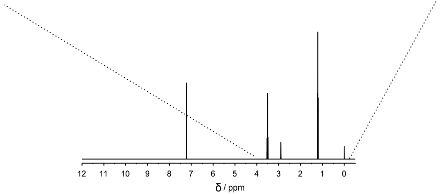
$\bullet CH_3$



NMR



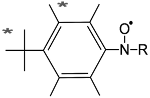




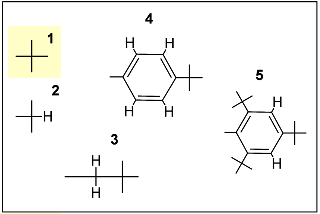
NMR SPECTROSCOPY IOCB PRAGUE

Hyperfine Splitting by N Nuclei*

Exercising Examples with ^{14}N & ^{1}H Splitting



-R =

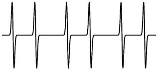


a_N (-NO-) = 12 G

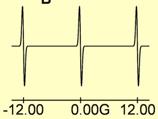
a_H (-CH-) = 5 G
a_H (-CH$_2$-) = 10 G

a_H^o (=CH-) = 3 G
a_H^m (=CH-) = 1 G

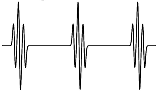
A



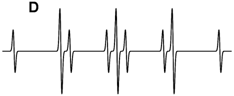
B



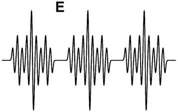
C



D



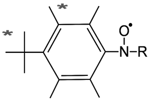
E



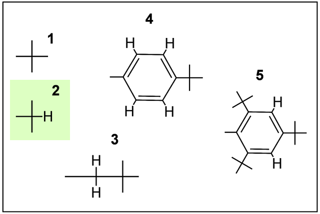
* Splitting from t-**butyl** & $-$CH$_3$ can be neglected

Hyperfine Splitting by N Nuclei*

Exercising Examples with ^{14}N & ^{1}H Splitting



-R =



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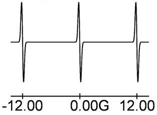
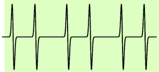
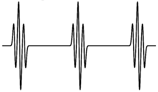


E

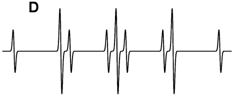
A



C



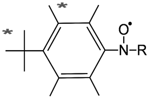
D



* Splitting from *t*-**butyl** & $-\mathrm{CH_3}$ can be neglected

Hyperfine Splitting by N Nuclei*

Exercising Examples with ^{14}N & ^{1}H Splitting



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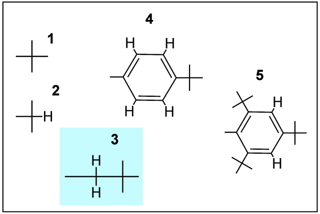
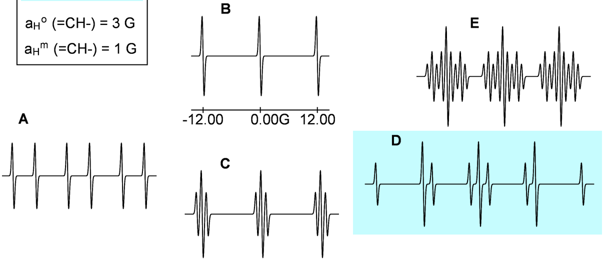


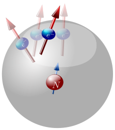


* Splitting from t-**butyl** & $-CH_3$ can be neglected

Origin of Hyperfine Splitting/Coupling Const. (a/A)

Fermi–Contact (FC)# + Dipolar Interaction** & Spin Density

$s - orbital$



Spin Density / Å^{-3}:

$$\rho_S^{\alpha-\beta}(0) = \rho^{|\alpha\rangle,\uparrow}(0) - \rho^{|\beta\rangle,\downarrow}(0)$$
$$\rho^{|\alpha\rangle,\uparrow} = N_{|\alpha\rangle}/V$$
$$\rho^{|\beta\rangle,\downarrow} = N_{|\beta\rangle}/V \qquad \text{(XIII)}$$

$$A_{\text{iso}}(a_{\text{iso}}) \propto \rho_S^{\alpha-\beta}(0) \qquad \text{(XIV)}$$

Generally (also for solid-state):

$$\mathbf{A}_{\text{total}} = \mathbf{A}_{\text{iso}}\mathbf{1} + \mathbf{T}_{\text{dip}}^{**}$$

Spin Population (Integrated $\rho_S(0)$):

$$\rho_{\text{X}}^{\Psi}(\text{pop}) = \rho_{\text{X}}^{\Psi|\alpha\rangle} - \rho_{\text{X}}^{\Psi|\beta\rangle}$$
$$\text{X} \equiv \text{Nucleus}$$
$$\Psi \equiv \text{Orbital} \qquad \text{(XV)}$$

Fermi, E., *Z. Phys.* **1930**, 60, 320-333 $\varepsilon_{\text{iso}}^{\text{FC}} = -(2/3)\mu_o \vec{\mu}_S \vec{\mu}_I |\Psi(0)|^2 = (1/\hbar^2) A_{\text{iso}} S_z I_z$

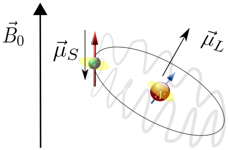
** Hyperfine Interaction Matrix ($\mathbf{T}_{\text{dip}}$ is orientational matrix of the e ↔ N interaction)

EPR Spectrum Position

Introduction & g-Value

Electrons are not isolated
on the molecule & they always possess
spin (S) & **orbital** (L)
component of their angular momentum

$$\varepsilon_{LS} = -\left(\vec{\mu}_L + \vec{\mu}_S\right)\vec{B}_0 + \lambda\vec{L}\vec{S} \tag{XVI}$$



$\lambda \Rightarrow$ spin-orbit coupling constant

$g \neq g_{\mathrm{e}} = 2.0023193043662(15)$

Basic Energy Relation:

$$\Delta\varepsilon = h\nu = g\mu_{\mathrm{B}}B \tag{XVII}$$

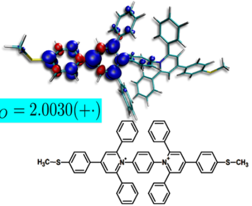
$\Delta g = g - g_{\mathrm{e}}$ is **very small for free (organic) radicals**, but can be **significant for paramag. transition metal ions**

$$g = \frac{h\nu}{\mu_{\mathrm{B}}\mathbf{B}}$$

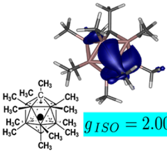
If the $\mathbf{B}$ changes, then
ν changes accordingly due to
the resonance condition (XVII).

EPR Spectrum Position

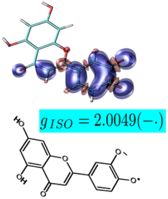
g-Value Examples



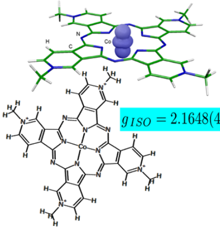
$g_{ISO} = 2.0030(+\cdot)$



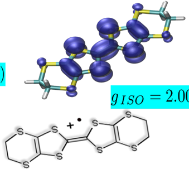
$g_{ISO} = 2.0053(0\cdot)$



$g_{ISO} = 2.0049(-\cdot)$



$g_{ISO} = 2.1648(4+\cdot)$

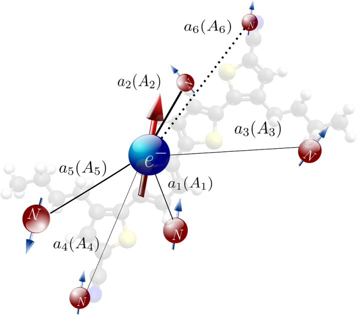


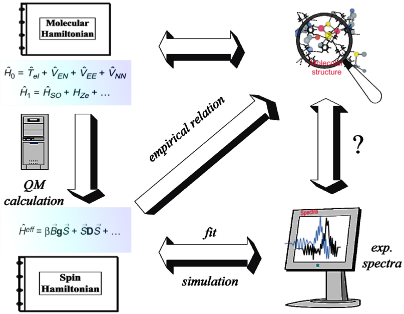
$g_{ISO} = 2.0079(+\cdot)$

* $g_{\text{ISO}} = (1/3)\sum_{i=1}^{3} g_i$, where $g_i \equiv$ diag. principal axis components of the g-matrix

Complex Analysis of EPR Spectra

Quantum Chemical Computations & Simulations of EPR Spectra





[10]

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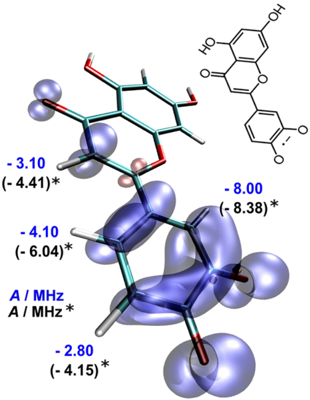
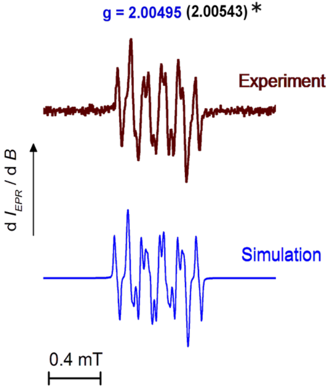
[10] F. Neese; *Curr. Opin. Chem. Biol.* **2003**, 7, 125-135

Complex Analysis of EPR Spectra

Luteolin Radical Anion[11]





* by quantum-chemical computations

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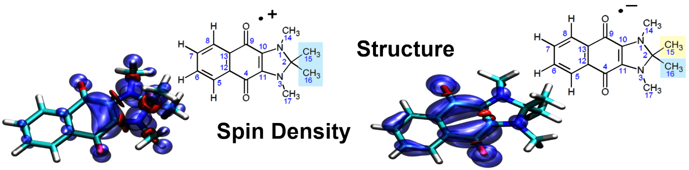
[11] Š. Ramešová et al.; *Elchim. Acta* **2013**, 110, 646-654

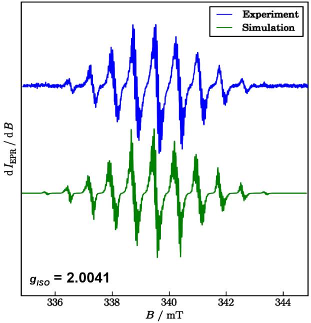
Complex Analysis of EPR Spectra

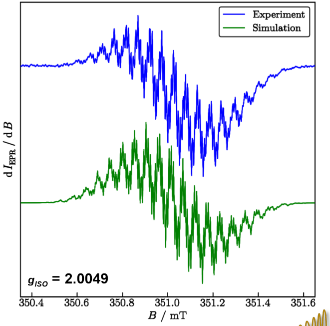
Radical Ions of Naphthoquinone Derivative[12]



Structure

Spin Density





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[12] J. Tarábek et al.; *J. Org. Chem.* **2018**, 83, 5474-5479

Analogy Between EPR & NMR

1. The very basic principle of EPR & NMR is identical

	EPR	⇔	**NMR**
Main Objective:	unpaired electron(s)	⇔	nucleus (nuclei)
Experiment:	microwave frequencies	⇔	radio frequencies
	$\nu_{\text{EPR}} = \text{const.}(\text{CW})$	⇔	$B_{\text{NMR}} = \text{const.}(\text{pulsed})$

2. EPR & NMR Spectral Parameters

	EPR	⇔	**NMR**
Coupling (Interaction):	A_{X}/MHz (e-N)	⇔	J_{XY}/Hz (N–N)
Position:	g-factor (g)	⇔	chemical shift (δ)
Intensity:	double integral (CW)	⇔	integral (pulsed)
Linewidth:	$\Delta B_{\text{pp}}/\text{mT}$ (CW)	⇔	$\Delta\nu_{1/2}/\text{Hz}$ (pulsed)

Analogy Between EPR & NMR

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2. EPR & NMR Spectral Parameters

	EPR	$\Leftrightarrow$	**NMR**
Coupling (Interaction):	A_{X}/MHz (e-N)	$\Leftrightarrow$	J_{XY}/Hz (N–N)
Position:	g-factor (g)	$\Leftrightarrow$	chemical shift (δ)
Intensity:	double integral (CW)	$\Leftrightarrow$	integral (pulsed)
Linewidth:	ΔB_{pp}/mT (CW)	$\Leftrightarrow$	$\Delta\nu_{1/2}$/Hz (pulsed)

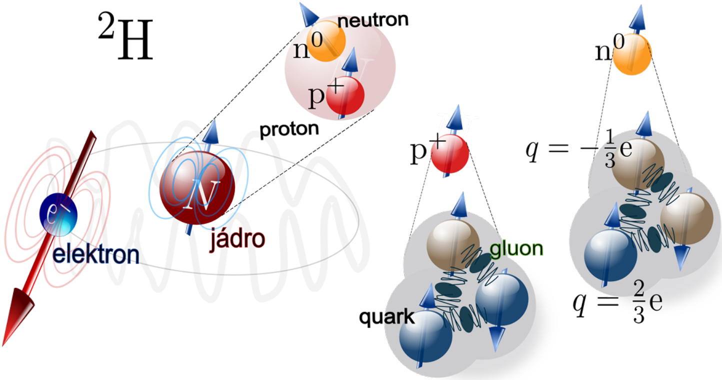
Table of Contents

Magnetic Resonance Techniques

- Nuclear Magnetic Resonance (NMR)
- Electron Paramagnetic Resonance (EPR)
- Magnetic Resonance Imaging
  (MRI, NMR & EPR)
- Nuclear Quadrupole Resonance (NQR)
- Optically Detected Magnetic Resonance (ODMR)
- Fero-/Antifero-/Feri-magnetic Resonance

NMR SPECTROSCOPY
IOCB PRAGUE

Deuterium & its Corresponding (Sub)Nuclear Particles

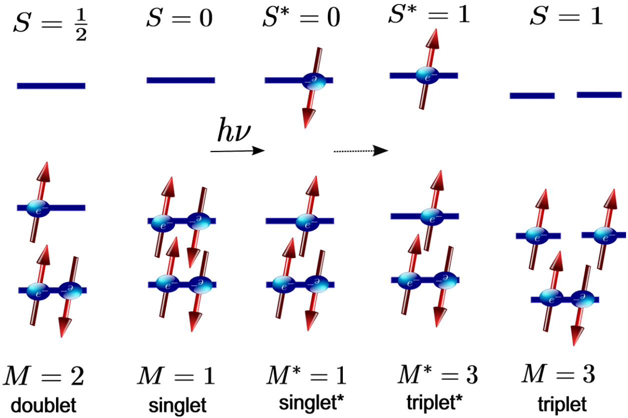


NMR SPECTROSCOPY IOCB PRAGUE

Multiplicity of the Electronic Configurations

Schematic View of Ground & Excited* States

Multiplicity: $M = 2S + 1 \quad S = \sum_i s_i$



$S = \frac{1}{2}$ | $S = 0$ | $S^* = 0$ | $S^* = 1$ | $S = 1$

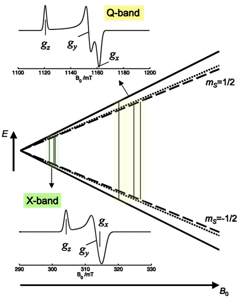
$h\nu$

$M = 2$ doublet | $M = 1$ singlet | $M^* = 1$ singlet* | $M^* = 3$ triplet* | $M = 3$ triplet

Multifrequency EPR

MW components can be used only for
narrow range of $\nu_{\text{EPR}} \Rightarrow$ $h\nu_{\text{EPR}} = \text{const.}$ **&** B_{EPR} **is changing**

$\boxed{h\nu_{\text{EPR}} \propto B}$ [13]



Frequency "Ranges" & Conditions:

Conditions / Range	L	S	X	Q	W	J
ν / GHz	1	3	10	35	90	270
λ / mm	300	100	30	8.60	3.30	1.11
B / T $(g = 2)$	0.04	0.11	0.36	1.25	3.22	9.64

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[13] Sabine Van Doorslaer et al. *Coord. Chem. Rev.* **2009**, 253, 2116-2130

Quantitative CW EPR

$DI \equiv$ Double Integral

$$DI_{\text{EPR}} = \text{const}_{\text{ref}} \left(G t_C N_{\text{scan}}\right) \left[\frac{P^{1/2} B_m Q n_B S(S+1)\, N_{\text{spin}}}{f(B_1, B_m)}\right]$$

const$_{ref}$	point sample calibration factor (spectrometer dependent)
G	gain
t_C/s	conversion time
N_{scan}	number of scans/averages
P/W	microwave power
B_m/G(mT)	modulation amplitude
Q	probehead/cavity quality factor
n_B	Boltzmann factor (temperature dependent)
S	the overall spin quantum number
N_{spin}	number of unpaired e$^-$
$f(B_1, B_m)$	spatial distribution of B_1 a B_m at sample-position

Double Rectangular Probehead/Cavity

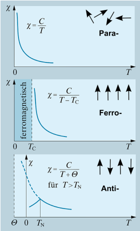
NMR SPECTROSCOPY
IOCB PRAGUE

Quantitative CW EPR

Magnetic Materials

Magnetic Susceptibility $\chi = \frac{\vec{M}}{\vec{H}}$ kde $\vec{B} = \mu_o(\vec{H} + \vec{M})$ a $\vec{M} = \frac{1}{V}\sum_{i=1}^{N} \mu_i$

Diamagnetism	$\chi_{\text{dia}}(1{\cdot}10^{-6}) < 0$	$\chi_{\text{dia}} \neq \chi_{\text{dia}}(T)$
Paramagnetism	$\chi_{\text{para}}(1{\cdot}10^{-6}) > 0$	$\chi_{\text{para}} = \chi_{\text{para}}(T)$
Cooperative Magn. Prop.	$\chi_{\text{int}}(\geq 1{\cdot}10^{4}; \leq 1{\cdot}10^{-2}) > 0$	$\chi_{\text{int}} = \chi_{\text{int}}(T)$



14

$$\chi_{\text{para}} = N_V \frac{\mu_o g^2 \mu_B^2 J(J+1)}{3k_B} \frac{1}{T}$$

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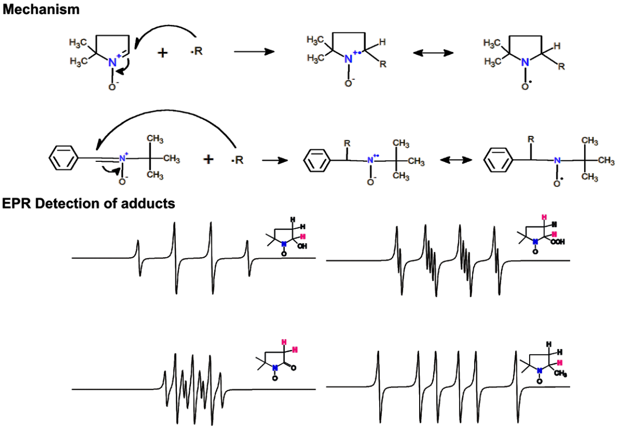
[14] D. Meschede; *Gerthsen Physik* **2006**, 23rd Edition, p. 398

Transient Radical Studies

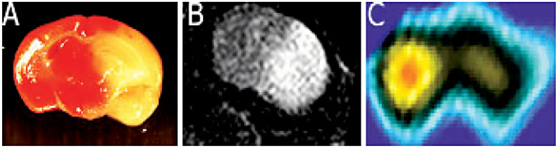
Spin Trapping

5,5-**Di**methyl-1- **p**yrroline N-**o**xide (**DMPO**)
& N-*tert*-**B**utyl-α-**p**henyl**n**itrone (**PBN**)



EPR Imaging

Bloodstream Recovery after Ischemia [16]



A: Histology

B: MRI

C: EPR Imaging

[15]

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[15] *Bruker* Corporation, Product Overview ELEXSYS-II E540 System

[16] Liu, S., Timmins, G. S., et al. *NMR Biomed* 17, **2004**, 327-334

Basic Differences Between CW & Pulsed EPR

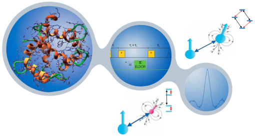
common for X-band

	Acquisition	T/K	$t_p(\frac{\pi}{2})/\mathrm{ns}$	Excit. range/MHz(mT)	P/mW	$\nu(B_m)/\mathrm{kHz}$
Pulsed	$B =$ konst $\nu \neq$ konst	$\ll 293$	$10 - 16$	$1{\cdot}10^2(3)$	$\geq 1{\cdot}10^6$	–
CW	$B \neq$ konst $\nu =$ konst	293	–	$1.67{\cdot}10^4(500)$	$2 - 20$	100

Pulsed EPR cannot completely replace the CW one

$\Downarrow$

CW & pulsed EPR $\Rightarrow$ Complementary Methods



ESEEM, 2D spectroscopy, Pulse-ENDOR, Pulse-ELDOR (DEER), Transient EPR and Multi-frequency EPR in Life science, Material science [17]

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[17] *Bruker* Corporation, Product Overview ELEXSYS E580 System

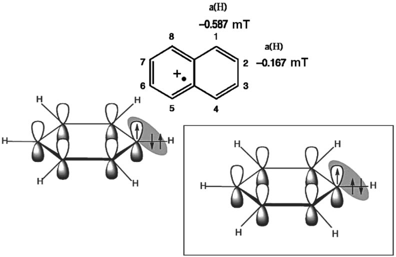
Hyperfine Splitting/Coupling Constants (a/A)

Polarization & Hyperconjugation: e$^-$ & ^{1}H Interactions

Spin Polarization:

$$A_{\text{N,iso}}(a_{\text{N,iso}}) < 0 \qquad \text{(XVIII)}$$

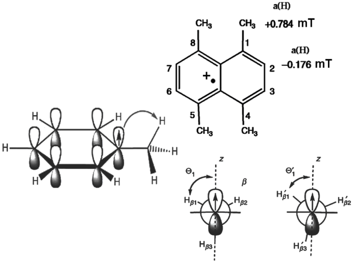
$$\boxed{A_{\text{H,iso}}(\alpha\ \text{pos.}) = Q_{\text{H}}^{\text{C–H}}\rho_{\text{C}}^{2p_z}(\text{pop})}$$



Hyperconjugation:

$$A_{\text{N,iso}}(a_{\text{N,iso}}) > 0 \qquad \text{(XIX)}$$

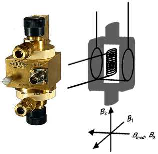
$$\boxed{A_{\text{H,iso}}(\beta\ \text{pos.}) = (K_1 + K_2\cos^2(\theta_1))\rho_{\text{C}}^{2p_z}(\text{pop})}$$

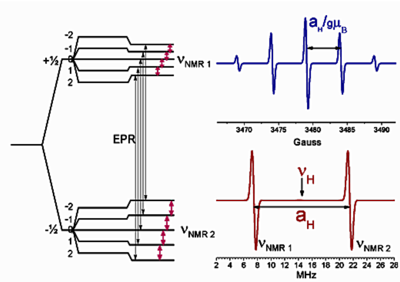


Hyperfine Splitting/Coupling Constants (a/A)

Basic Principle of the "**E**lectron **N**uclear **D**ouble **R**esonance" (ENDOR) Spectroscopy

ENDOR Probehead/Cavity





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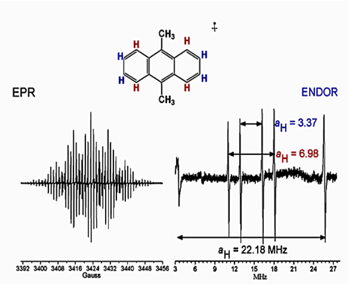

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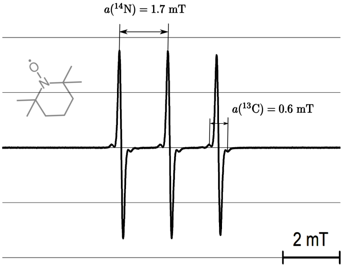
[18] D. M. Murphy & R. D. Farley; *Chem. Soc. Rev.* **2006**, 35, 249-268

Isotope Effects in EPR (Satellites)

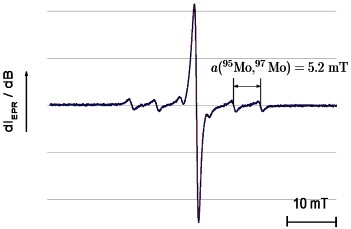
$>$N–O$^{\bullet}$*

Nat. Abundance (^{14}N) $= 99.60\,\%$
Nat. Abundance (^{13}C) $= 1.07\,\%$



Mo$^{\mathrm{V}}$

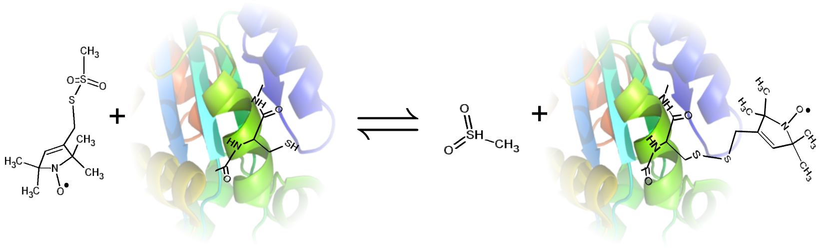
(^{95}Mo) $= 15.92\,\%$
(^{97}Mo) $= 9.95\,\%$



* 2,2,6,6-Tetramethyl-1-Piperidinoxyl (TEMPO)

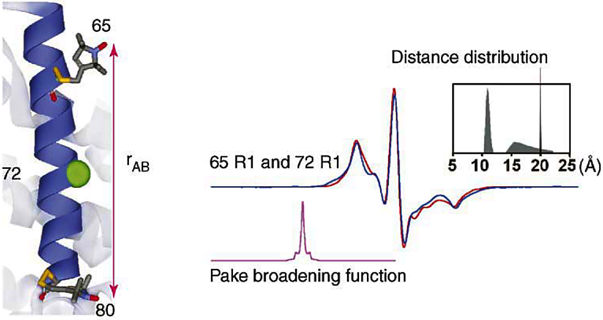
Side Direct Spin Labeling (SDSL) of Proteins/Peptides

Basic Scheme



Side Direct Spin Labeling (SDSL) of Proteins/Peptides

CW EPR Distance Estimation up to $\approx 2.5\,\mathrm{nm}$



[19]

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[19] G. E. Fannuci, D. S. Cafiso; *Curr. Opin. Struc. Biol.* **2006**, 16, 644-653