NMR Spectroscopy of Organic Compounds

Lesson 10:
EPR

NMR SPECTROSCOPY
RESEARCH-SERVICE GROUP
IOCB PRAGUE

Ján Tarábek

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

NMR Analogy

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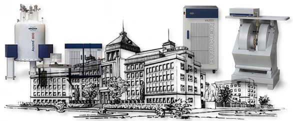

NMR Spectroscopy Department

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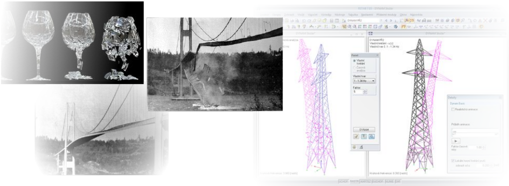
Contents

Mechanical Resonances in Physics

Resonance

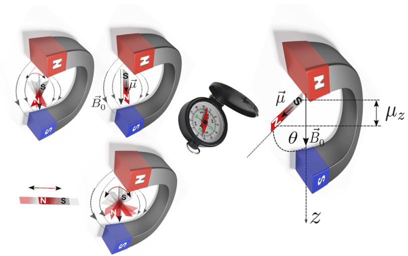
Physical phenomenon ⇒ Vibration/Oscillation amplitude of a pendulum/oscillator is getting higher in comparison to its natural ground state. It occurs if the frequency ν_{applied} of the periodically applied force equals to the natural one ν_{own}. The applied stimulus may not be necessarily strong.



[1]

[1] http://if.vsb.cz/bf/28.html#aplikace_2

Resonance of Magnetic Needle in Magnetic Field



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

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

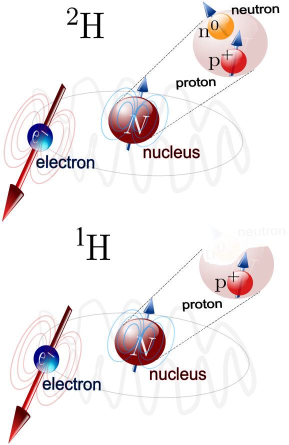
$$\varepsilon(0°) = -\mu B_0 \quad \varepsilon(180°) = \mu B_0$$

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

[2] ⚠ Magnetic Flux Density

Electrons & Nuclei like a Tiny Magnets?

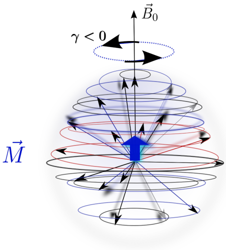
Schematic View of Deuterium & Protium



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

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

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

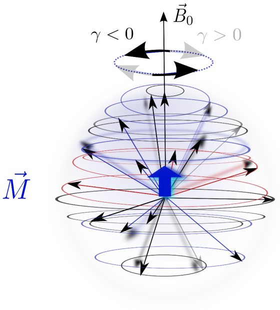


* $\gamma \equiv$ magnetogyric ratio

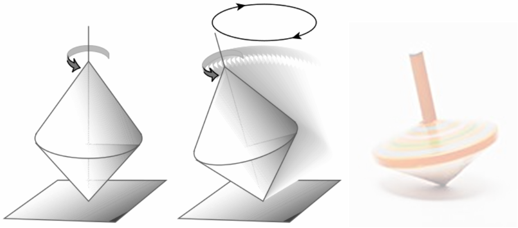
$\vec{M} = (1/V)\sum \vec{\mu} \equiv$ magnetization

Precession

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



Gyroskop in Gravitational Field:



Electrons & Nuclei like a Tiny Magnets?

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

Nucleus	$\gamma^{*}\,/10^{6}\ \mathrm{rad\,s^{-1}\,T^{-1}}$	**Nat. Abund. / %**	$\nu_{\mathrm{N(e)}}$/MHz **at** 11.74 T
^{1}H	267.522	99.985	−500.000
^{12}C	–	98.930	–
^{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	–	99.962	–
^{17}O	−36.281	0.038	67.782
^{31}P	108.394	100.000	−202.606
e^{-}	−176085.971	–	329016.005

$\Downarrow$

Free electron is $\approx$ 650-time stronger than proton

* $\gamma \equiv$ magnetogyric ratio

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Free electron is ≈ 650-time stronger than proton

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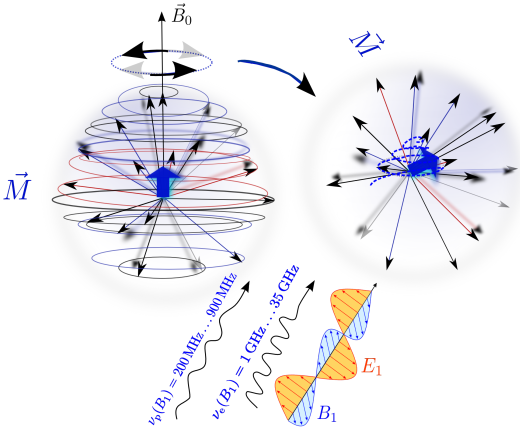
Magnetic Resonance of Protons & Electrons

"A"ction of Electromagnetic Radiation (B_1, E_1)

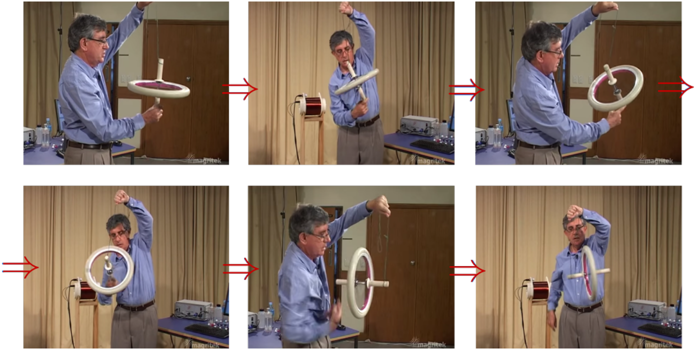
Common Frequencies of Alternating Magn. Flux Density (B_1) for Protons $(\nu_p(B_1))$ & Electrons $(\nu_e(B_1))$:



Precession & Mechanical Gyroskop Resonance

Nuclei & Electrons Analogy

applied frequency = natural frequency

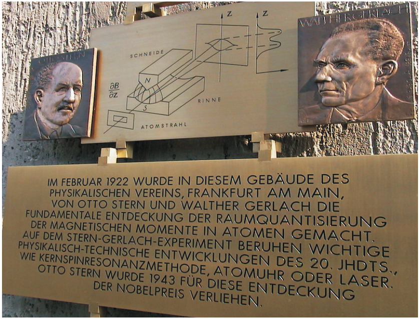


[3]

[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 inhomogeneous magnetic field into "two" lines (***Otto Stern & Walther Gerlach***)



[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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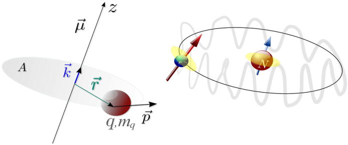
[4] Building of Experimental Physics/Frankfurt am Mein

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

Magnetic Moment $\vec{\mu}$ Relation

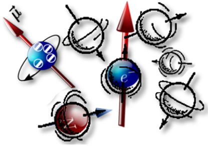
Orbital AM



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

q	charge carrier
γ_q	magnetogyric ratio
γ_j	spin magnetogyric ratio

Intrinsic AM (Spin)



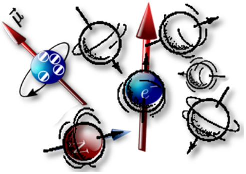
$$\vec{\mu}_j = g_{\mathrm{e(N)}}\frac{q}{2m_q}\vec{j} = \gamma_j \vec{j} \qquad \text{(V)}$$

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]

It is pure quantum-mechanical property,

which is not related to spinning/rotating particle,

although such an idea is used as a learning model

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

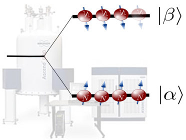
[5] http://www.mriquestions/index.html
https://www.youtube.com/watch?v=v1_-LsQLwkA
D.P. Goldenberg, *Principles of NMR Spectroscopy. An Illustrated Guide.*,
eISBN 978-1-938787-86-7

Energies (ε) in NMR and EPR

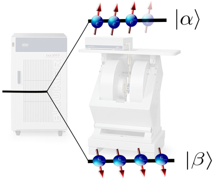
Ground (gr)-Excited (ex) State Populations at $T = 298\,\mathrm{K}$

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

Proton (NMR)



Electron (EPR)



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

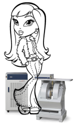
$$\frac{N_{|\alpha\rangle}}{N_{|\beta\rangle}} = 99.842\,\% \qquad \text{(VIII)}$$

Energies (ε) in NMR and EPR

Conditions for Recording of Spectra

Proton (NMR)

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



Electron (EPR)

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

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

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

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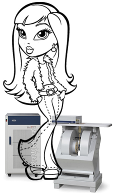
NMR & EPR Spectroscopy

Common Ways How to Meet the Resonance Condition

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

Proton (NMR)

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

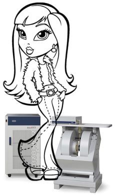


Electron (EPR)

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

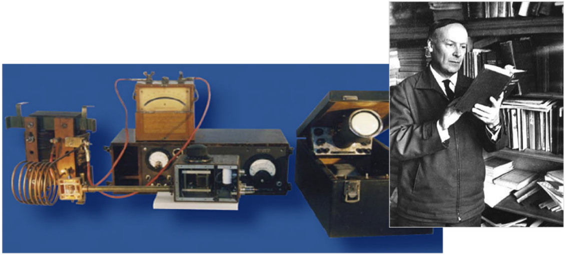
** CW ≡ continuous wave

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***

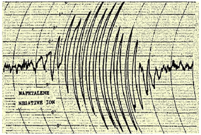


[6]

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

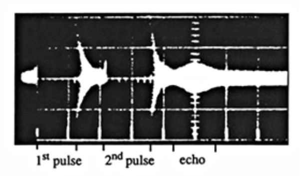
Splitting of EPR Spectra & Pulsed Technique

- **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***)

[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 applied like NMR**, however
⇒ **EPR is the only one direct method to study pramagnetic 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

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

Examples of Paramagnetic Compounds/Materials

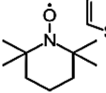
Paramagnetic

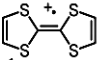
≋ O_2

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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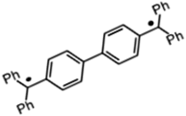

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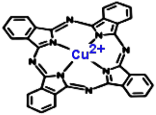

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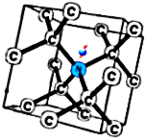

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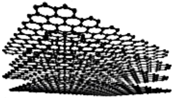

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EPR in Natural Sciences

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

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

Materials and Industrial Research

- 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

Biology

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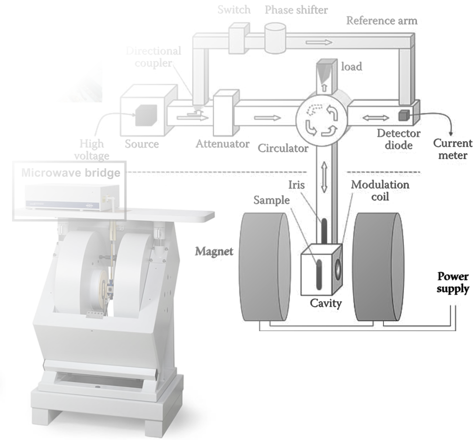
CW EPR & FT NMR Spectrometers

General View & Comparison

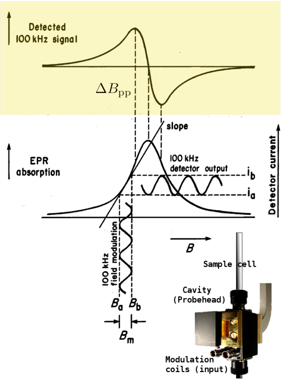
CW EPR Spectrometer

Detailed View & Recorded Spectrum

Magnet & Microwave bridge



Recording of an EPR Spectrum



Essential EPR Parameters

Common Recording Conditions for EPR Spectra

Phase#**:**

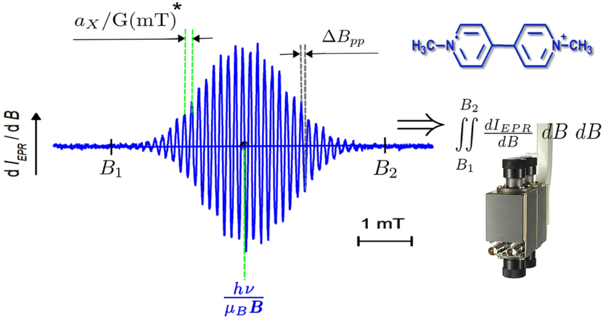
+

$^{\$}$:

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

:

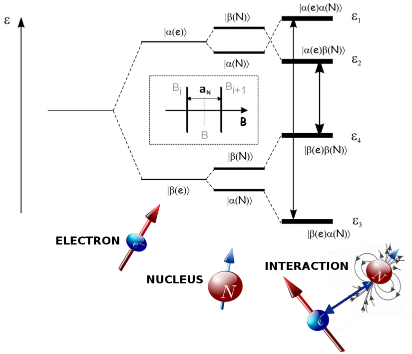
from ≈ $1{\cdot}10^{-9}$ mol dm^{-3}
to ≈ 0.1 mol dm^{-3}



\# 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 $I_{\mathrm{N}} = 1/2$ (^{1}H)

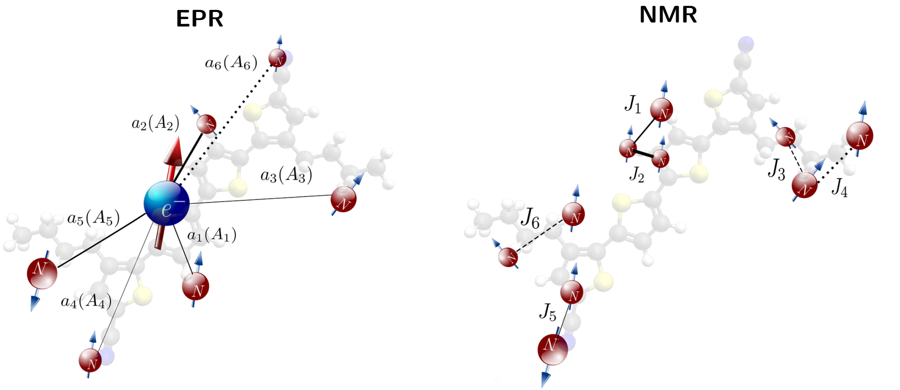


$$g\mu_{\mathrm{B}}(B_{i+1} - B_i) = g\mu_{\mathrm{B}} a_{\mathrm{N}}^{*} \text{ (Splitting const.)} = A_{\mathrm{N}}^{**} \text{ (Coupling const.)} \qquad \text{(XI)}$$

*G(mT) $\quad$ ** 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

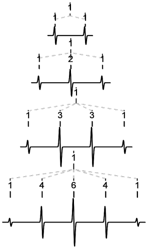
Multiplicity & Intensity

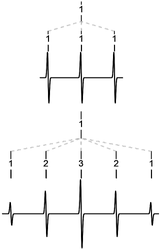
$$I_\mathsf{N} = \tfrac{1}{2}(^1\mathrm{H})$$

$N = 0$:					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





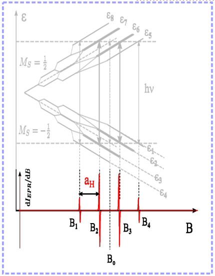
number of lines $(N_\mathsf{L}) = 2NI_\mathsf{N} + 1$; for k-groups: $N_\mathsf{L} = \prod_{i=1}^{k}(2N_i I_{\mathsf{N}i} + 1)$ (XII)

Splitting in EPR/NMR

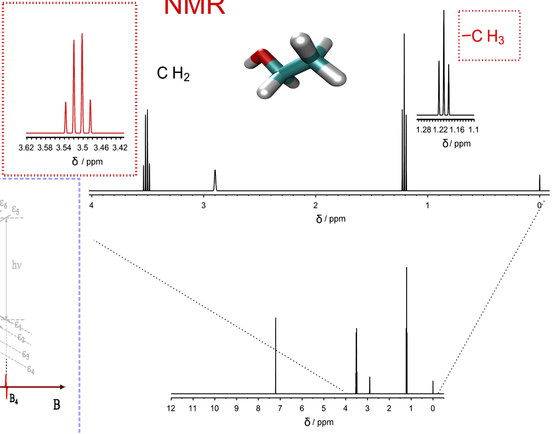
Three Equivalent Nuclei with $I = 1/2$ ($\cdot CH_3$/ $-CH_3$)

EPR

$\bullet CH_3$



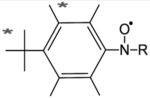
NMR



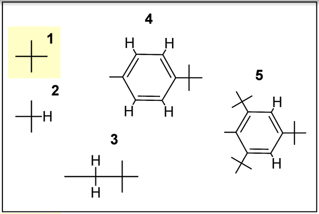
NMR SPECTROSCOPY IOCB PRAGUE

Hyperfine Splitting by N Nuclei*

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



-R =

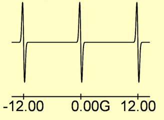


a_N (-NO-) = 12 G

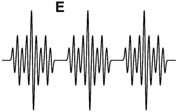
a_H (-CH-) = 5 G
a_H ($-CH_2-$) = 10 G

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

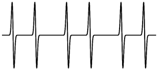
B



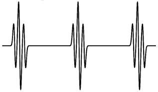
E



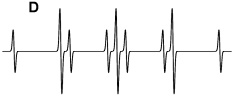
A



C



D



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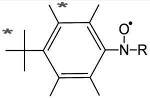
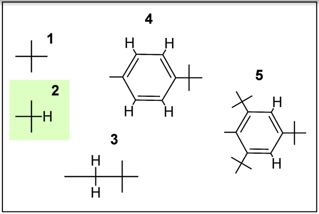
Hyperfine Splitting by N Nuclei*

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



-R =



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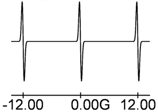
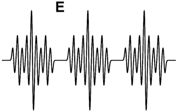
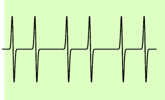
B



E



A



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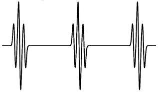
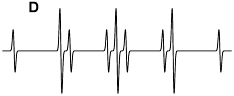


D



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Hyperfine Splitting by N Nuclei*

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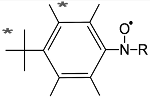

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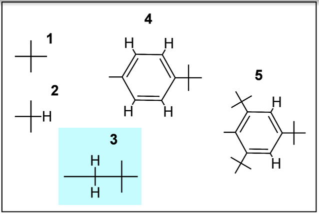

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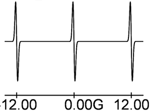

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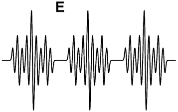
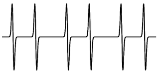


A



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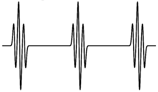
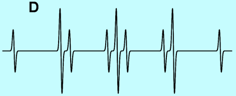


D

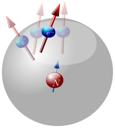


* Splitting from t-**butyl** & $-CH_3$ can be neglected

Essence 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):

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

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 $\varepsilon_{\text{iso}}^{\text{FC}} = -(2/3)\mu_o\vec{\mu}_S\vec{\mu}_I|\Psi(0)|^2 = (1/\hbar^2)A_{\text{iso}}S_zI_z$

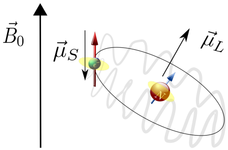
** Hyperfine Interaction Matrix ($\boldsymbol{T}_{\text{dip}}$ is orientational matrix of the e ↔ N interaction)

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

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



$\lambda \Rightarrow$ spin-orbit coupling constant

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

Basic Energy Relation:

$$\Delta\varepsilon = h\nu = g\mu_\mathrm{B}B \qquad \text{(XVII)}$$

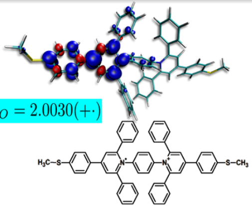
$\Delta g = g - g_\mathrm{e}$ is **very small for free (organic) radicals**, but can be **significant for paramag. transition metal ions**

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

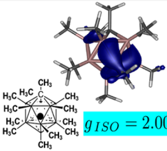
If the $\boldsymbol{B}$ changes, then $\boldsymbol{\nu}$ changes accordingly due to the resonance condition (XVII).

EPR Spectrum Position

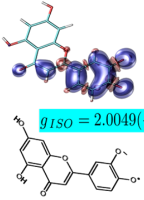
g-Value Examples



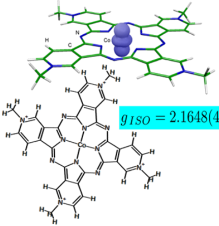
$g_{ISO} = 2.0030(+\cdot)$



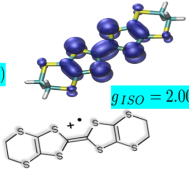
$g_{ISO} = 2.0053(0\cdot)$



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



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



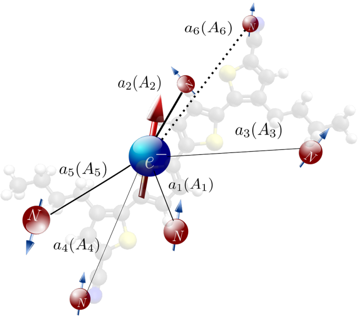
$g_{ISO} = 2.0079(+\cdot)$

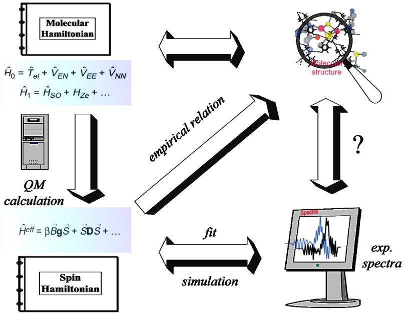
---

* $g_{\mathrm{ISO}} = (1/3)\sum_{i=1}^{3} g_i$, 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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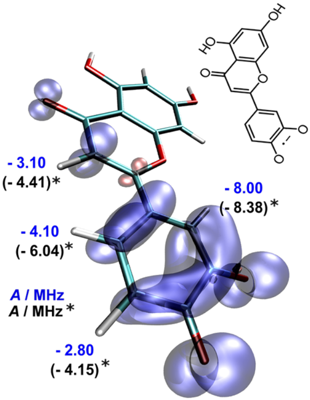
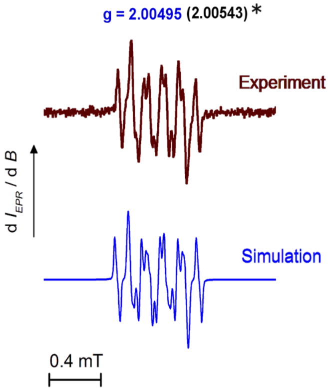
[10] F. Neese; *Curr. Opin. Chem. Biol.* **2003**, 7, 125-135

Complex Analysis of EPR Spectra

Luteolin Radical Anion

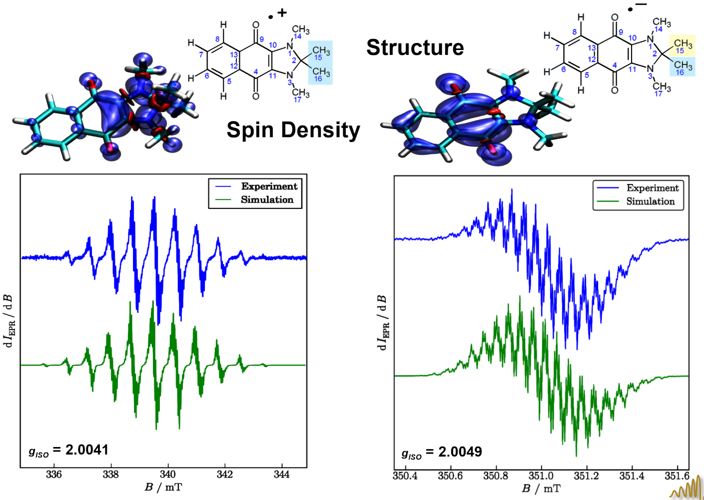




* by quantum-chemical computations

Complex Analysis of EPR Spectra

Radical Ions of Naphthoquinone Derivative



Analogy Between EPR & NMR

1. The very basic principal of EPR & NMR is the same

	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:	ΔB_{pp}/mT (CW)	⇔	$\Delta\nu_{1/2}$/Hz (pulsed)

NMR SPECTROSCOPY IOCB PRAGUE

Analogy Between EPR & NMR

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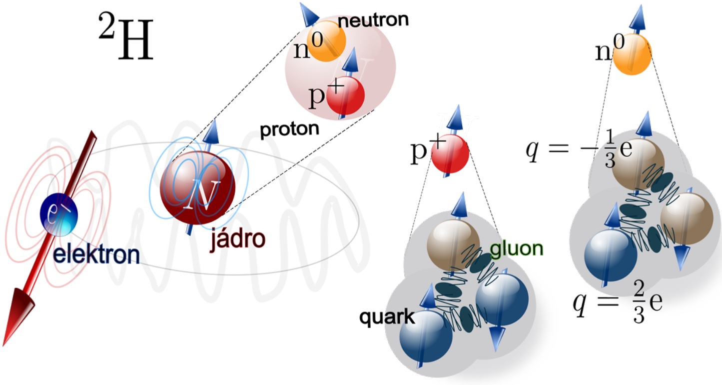
NMR SPECTROSCOPY IOCB PRAGUE

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

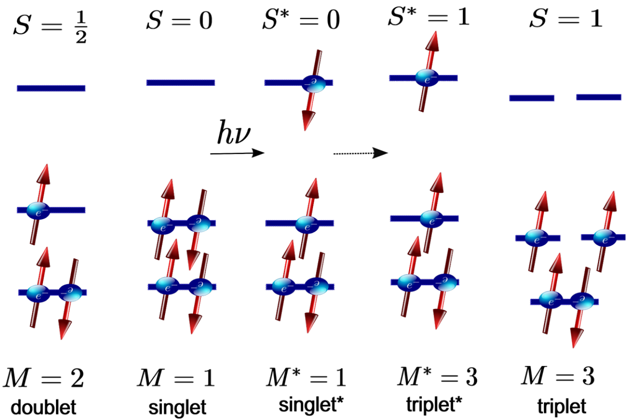
Deuterium & its Corresponding (Sub)Nuclear Particles



Multiplicity of the Electronic Configurations

Schematic View of Ground & Excited* States

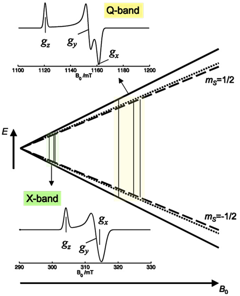
Multiplicity: $M = 2S + 1 \quad S = \sum_i s_i$



Multifrequency EPR

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

$\boxed{h\nu_{\text{EPR}} \propto B}$ [11]



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

NMR SPECTROSCOPY IOCB PRAGUE

[11] Van Doorslaer, S.; Carreti, I. et al. *Coord. Chem. Rev.* **2009**, 253, 2116-2130

Quantitative CW EPR

$DI \equiv$ Double Integral

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

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

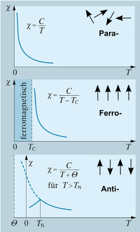
Quantitative CW EPR

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.	$\chi_{\text{int}}(\geq 1{\cdot}10^{4}; \leq 1{\cdot}10^{-2}) > 0$	$\chi_{\text{int}} = \chi_{\text{int}}(T)$

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



[12]

[12] D. Meschede; *Gerthsen Physik* **2006**, 23. Auflage, S. 398

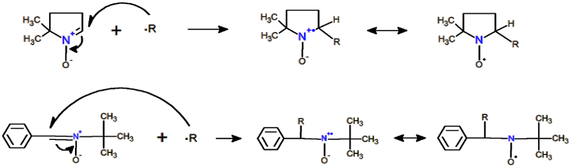
Transient Radical Studies

Spin Trapping

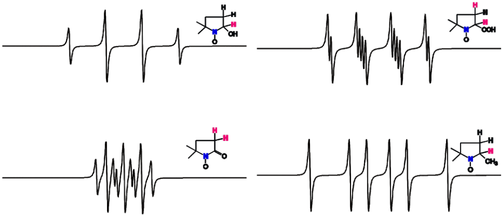
5,5-**Di**methyl-1- **p**yrroline N-**o**xide (**DMPO**)

& N-*tert*-**B**utyl-α-**p**henyl**n**itrone (**PBN**)

Mechanism

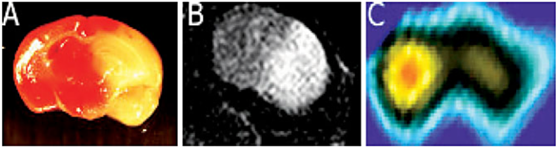


EPR Detection of adducts



EPR Imaging

Bloodstream Recovery after Ischemia [14]



A: Histology

B: MRI

C: EPR Imaging

13

[13] *Bruker* Corporation

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

Basic Differences Between CW & Pulsed EPR

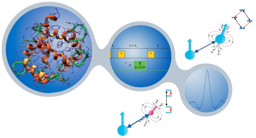
common for X-band

	Acquisition	T/K	$t_p(\frac{\pi}{2})$/ns	Excit. šířka/MHz(mT)	P/mW	$\nu(B_m)$/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 ν = 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 [15]

[15] Bruker (Biospin) Corporation *Elexys E580 EPR Spectrometer brochure* **2008**

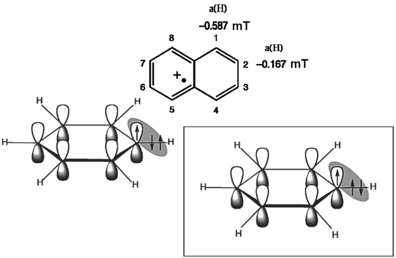
Hyperfine Splitting/Coupling Constants (a/A)

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

Spin Polarization:

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

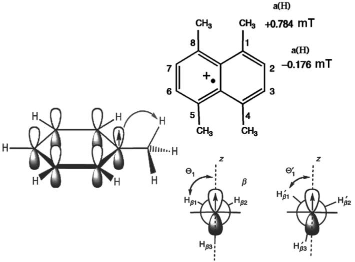
$$\boxed{A_{\text{H,iso}}(\alpha\ \text{pos.}) = Q_{\text{H}}^{\text{C–H}}\rho_{\text{C}}^{2p_z}(\text{pop})}$$



Hyperconjugation:

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

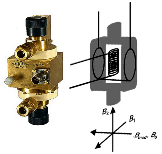
$$\boxed{A_{\text{H,iso}}(\beta\ \text{pos.}) = (K_1 + K_2\cos^2(\theta_1))\rho_{\text{C}}^{2p_z}(\text{pop})}$$

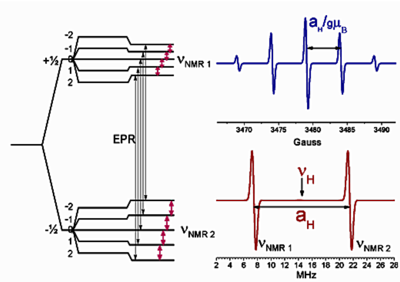


Hyperfine Splitting/Coupling Constants (a/A)

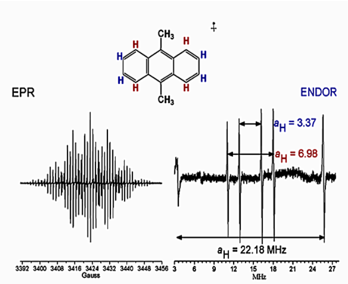
Basic Principal of the „**E**lectron **N**uclear **D**ouble **R**esonance“ (ENDOR) Spectroscopy

ENDOR Probehead/Cavity





16



16

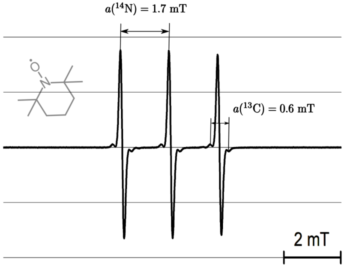
[16] D. M. Murphy & R. D. Farley; *Chem. Soc. Rev.* **20036**, 35, 249-268

Isotope Effects in EPR (Satellites)

$>$N$-$O$^{\bullet}$ *

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

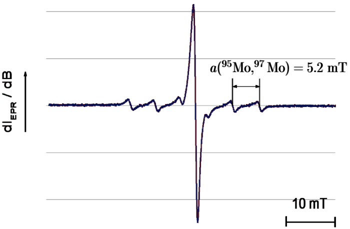
Nat. Abundance (^{13}C) $= 1.07\,\%$



Mo^{V}

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

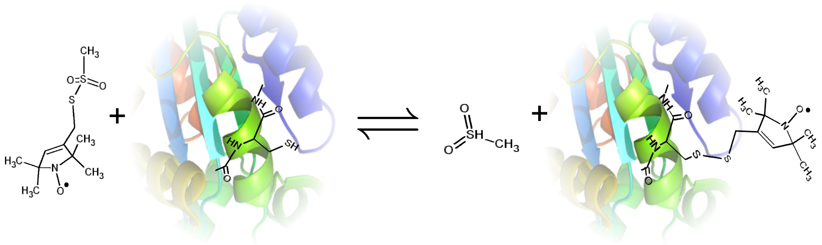
(^{97}Mo) $= 9.95\,\%$



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

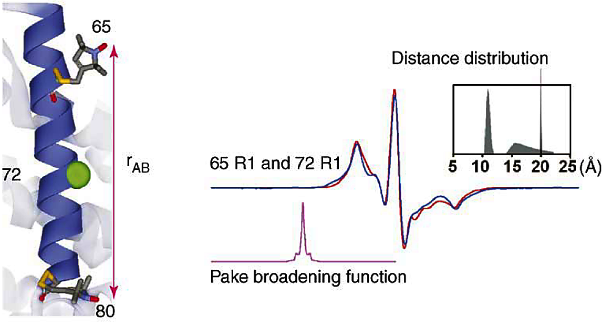
Side Direct Spin Labeling (SDSL) of Proteins/Peptides

Basic Scheme



Side Direct Spin Labeling (SDSL) of Proteins/Peptides

CW EPR Distance Estimation up to ≈ 2.5 nm



17

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