NMR SPECTROSCOPY
RESEARCH–SERVICE GROUP
IOCB PRAGUE

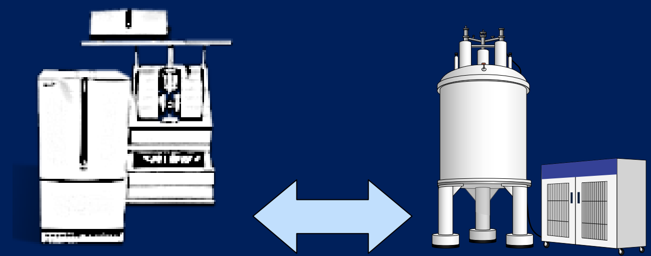
Electron Paramagnetic Resonance (EPR) at IOCB

Recent Case Studies & Future Instrumental Upgrades

Ján Tarábek

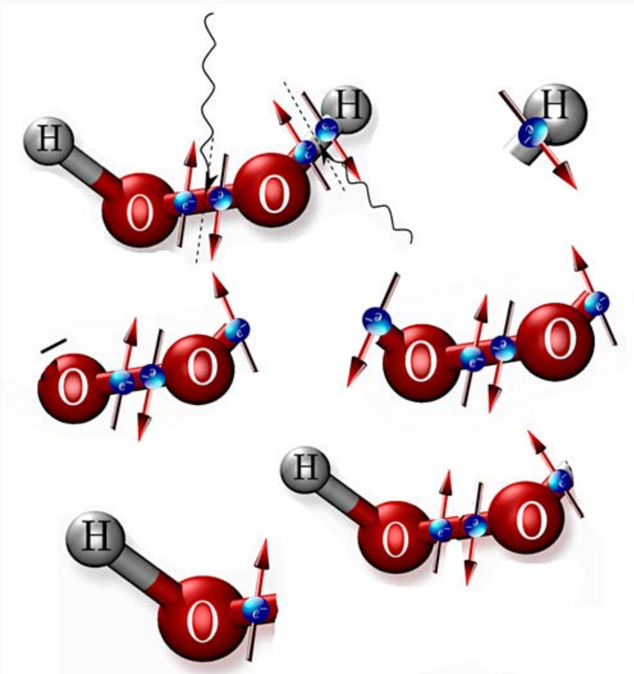
MAGNETIC RESONANCE DAY

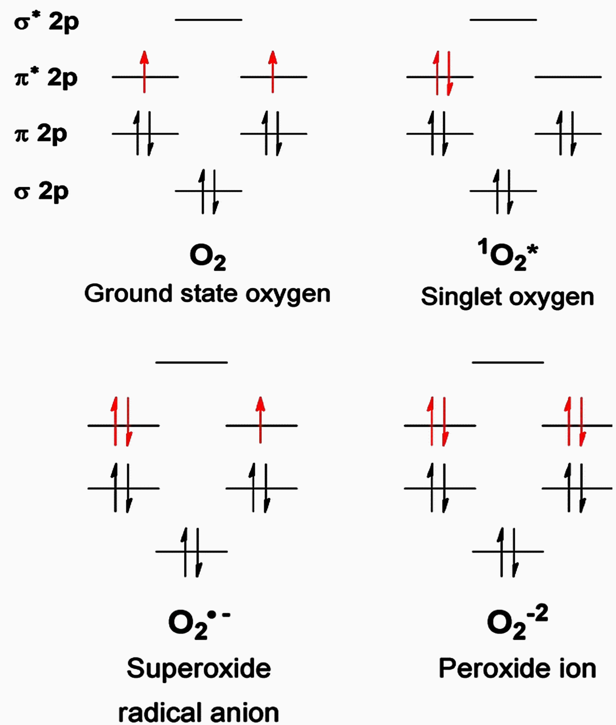
2021-09-23



EPR/NMR Essentials (Comparison)

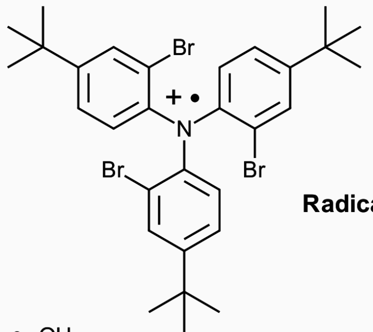
Simplified Scheme of Hydrogen Peroxide & ROS[a]



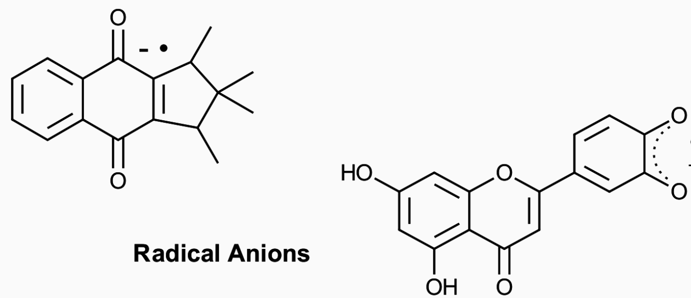


⚠ [a] **ROS** ≡ Reactive Oxygen Species

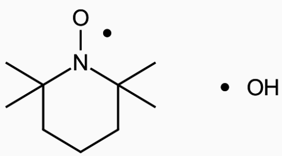
K. Krumova & G. Cosa, **Overview of ROS** in *Singlet Oxygen: Applications in Biosciences and Nanosciences* **2016**, 1, pp. 1-21



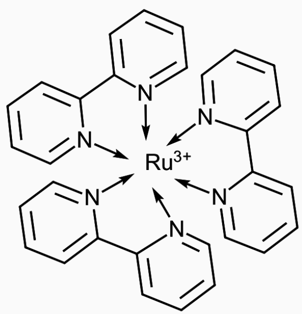
Radical Cation



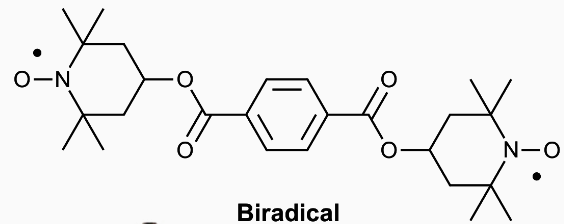
Radical Anions



Neutral Radicals

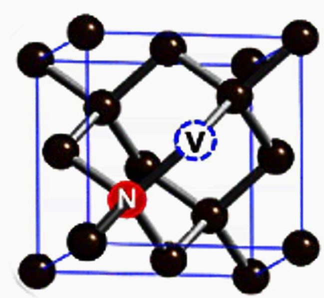


Coordination Compound



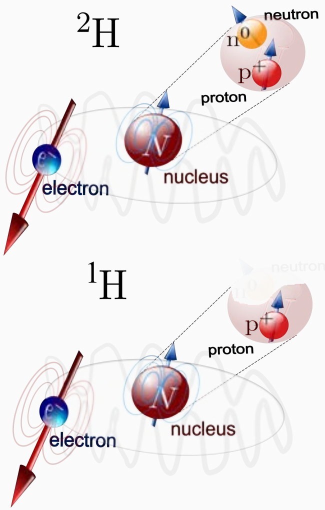
Biradical

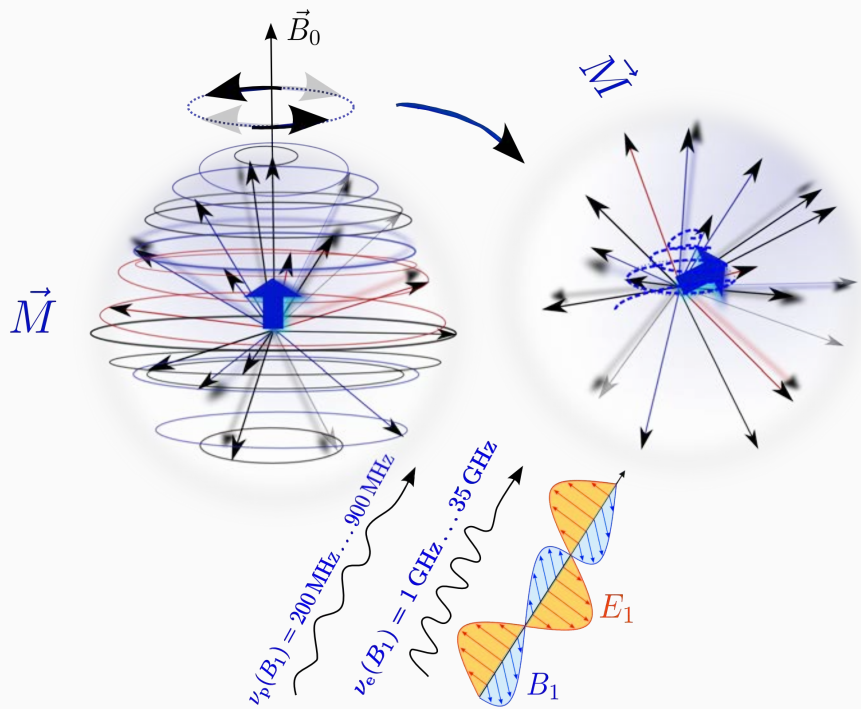
System of conducting electrons
(part of the **graphite** structure)



Part of the **nanodiamond** structure with nitrogen atom (**N**) & vacancy (**V**)

Common Features & Differences / **Magnetism & Magnetic Resonance**





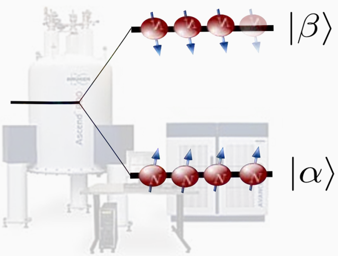
$\vec{B}_0 \Rightarrow$ external **magnetic flux density**/field

$\vec{M} \Rightarrow$ **magnetization**

$\nu_p\ (\nu_e) \Rightarrow$ matching **frequency for protons (electrons)**

Common Features & Differences / **Energies & Population Difference**

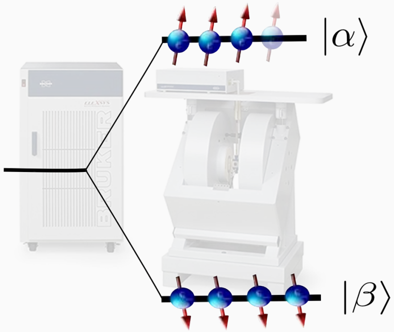
Proton (NMR)



$$\begin{aligned}\Delta\varepsilon_{\mathrm{p}} &= h\nu_{\mathrm{p}} \\ &= g_{\mathrm{p}}\hbar\gamma_{\mathrm{p}}B_0(\mathrm{NMR})\end{aligned}$$

$$\begin{aligned}\text{for } \nu_{\mathrm{p}} &= 600\,\mathrm{MHz} \\ B_0(\mathrm{NMR}) &= 14.0919\,\mathrm{T} \\ N_{|\beta\rangle}/N_{|\alpha\rangle} &= 99.990\,\%\ (T = 298\,\mathrm{K})\end{aligned}$$

Electron (EPR)



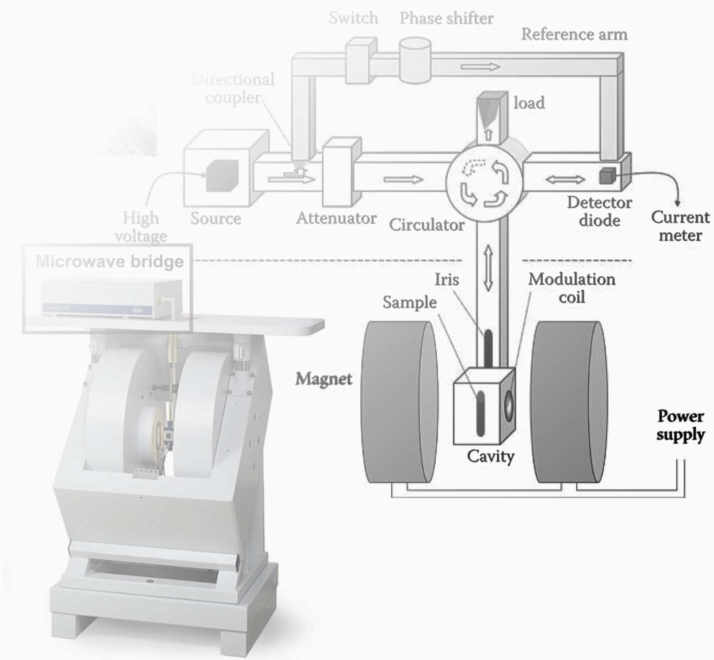
$$\begin{aligned}\Delta\varepsilon_{\mathrm{e}} &= h\nu_{\mathrm{e}} \\ &= g_{\mathrm{e}}\hbar\gamma_{\mathrm{e}}B_0(\mathrm{EPR})\end{aligned}$$

$$\begin{aligned}\text{for } \nu_{\mathrm{e}} &= 9.8\,\mathrm{GHz} \\ B_0(\mathrm{EPR}) &= 0.3497\,\mathrm{T} \\ N_{|\alpha\rangle}/N_{|\beta\rangle} &= 99.842\,\%\ (T = 298\,\mathrm{K})\end{aligned}$$

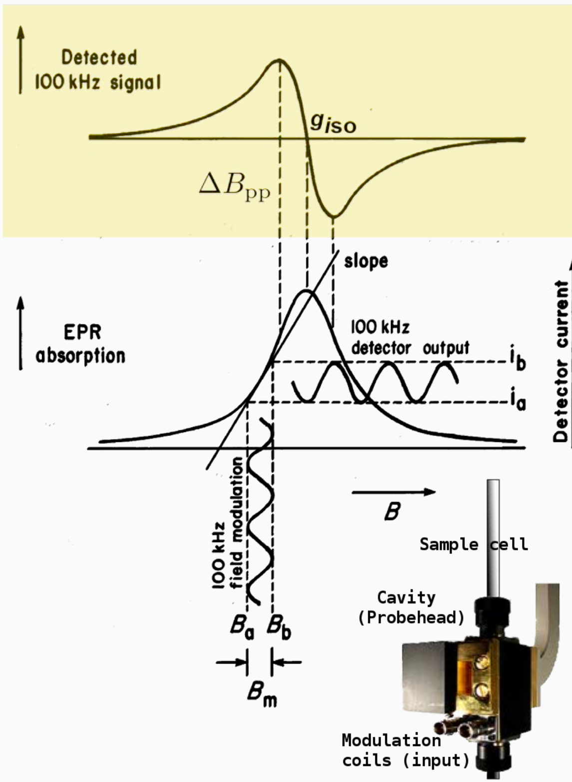
Magnetic Resonance EPR

CW[b] Spectrometer Detailed View & **EPR Spectrum**

Microwave Bridge and Magnet



Origin of Signal/Spectrum

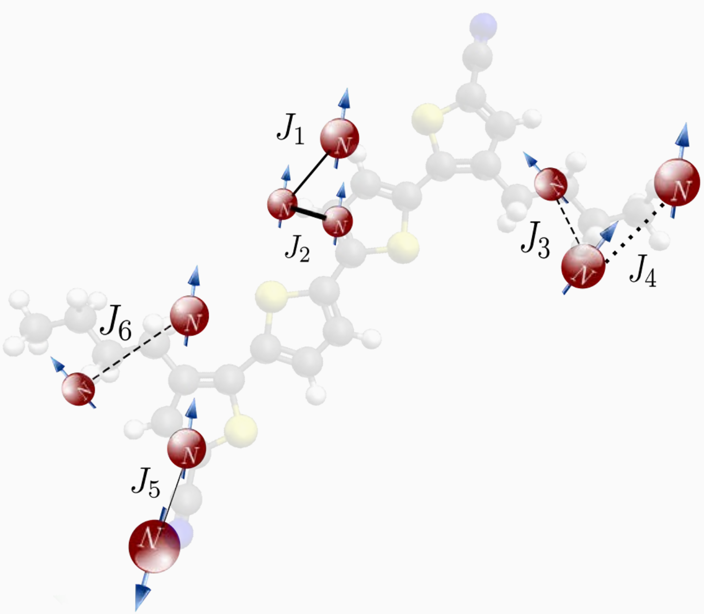


⚠ [b] **CW** $\equiv$ Continuous Wave => $\nu_e = \text{const.} \quad B_0 \neq \text{const.}$

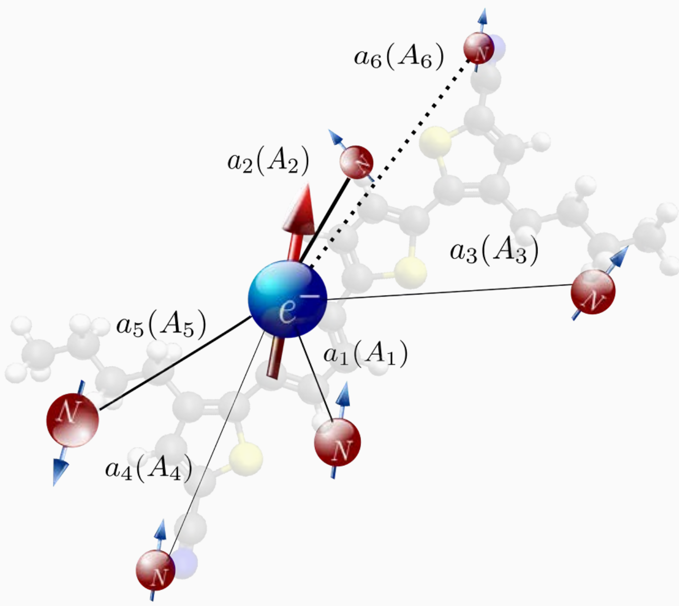
Structural Information from EPR

Splitting of the NMR/EPR Spectra (**Nu-Nu/e-Nu** Interactions)

NMR

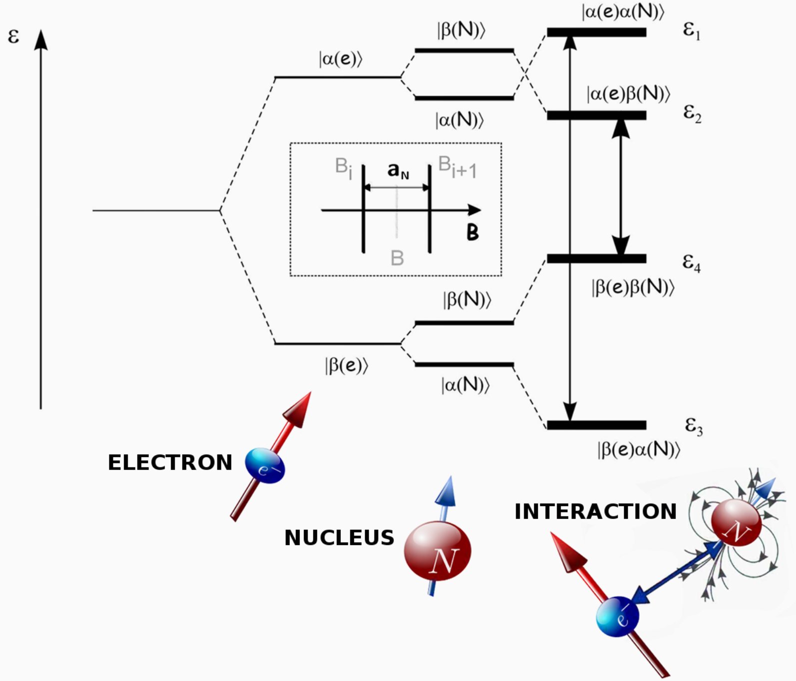


EPR



Structural Information from EPR

Example of **e-¹H** Interaction (Energies **ε**)



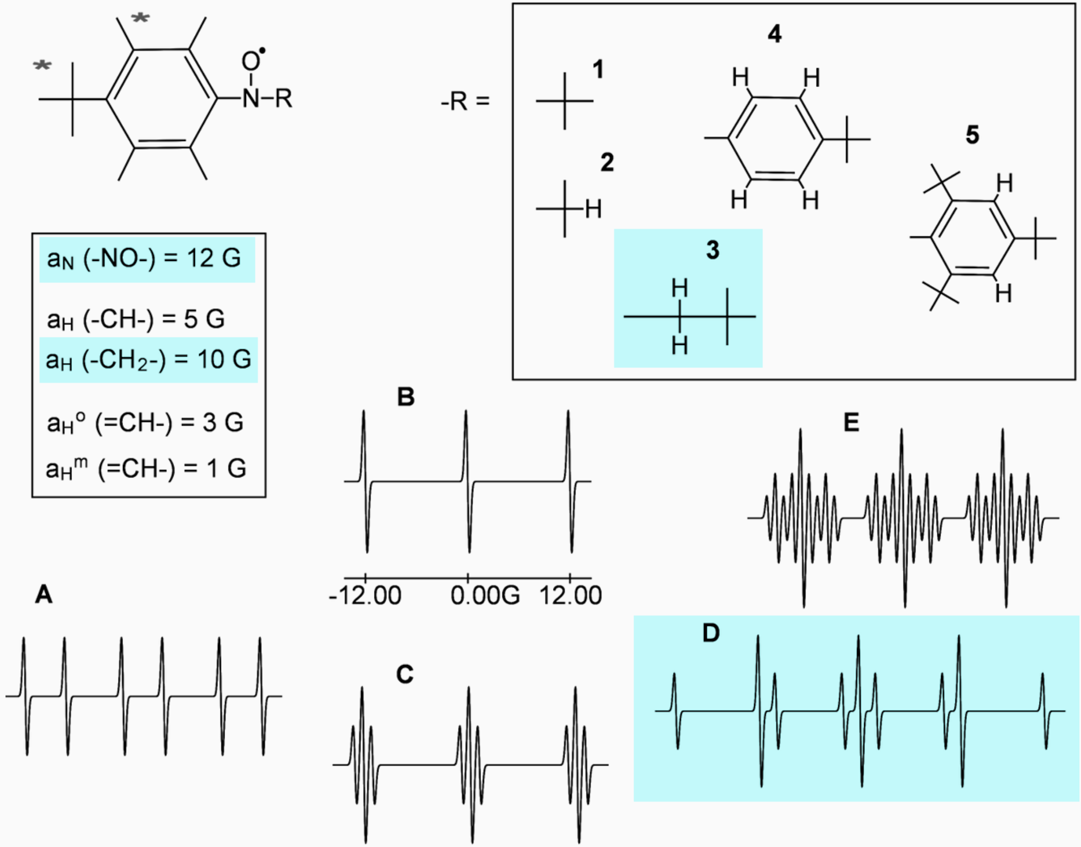
$$g\,\mu_{\mathrm{B}}\,(B_{i+1} - B_i) = g\,\mu_{\mathrm{B}}\,a_{\mathrm{H}}\ (\textbf{Splitting}\ \text{const.}) = A^{\varepsilon}_{\mathrm{H}}\ (\textbf{Coupling}\ \text{const.})$$

$[a] = \mathrm{mT\ (G)}$

$A^{\varepsilon} \Rightarrow A^{\varepsilon}/h \Rightarrow [A] = \mathrm{MHz}$

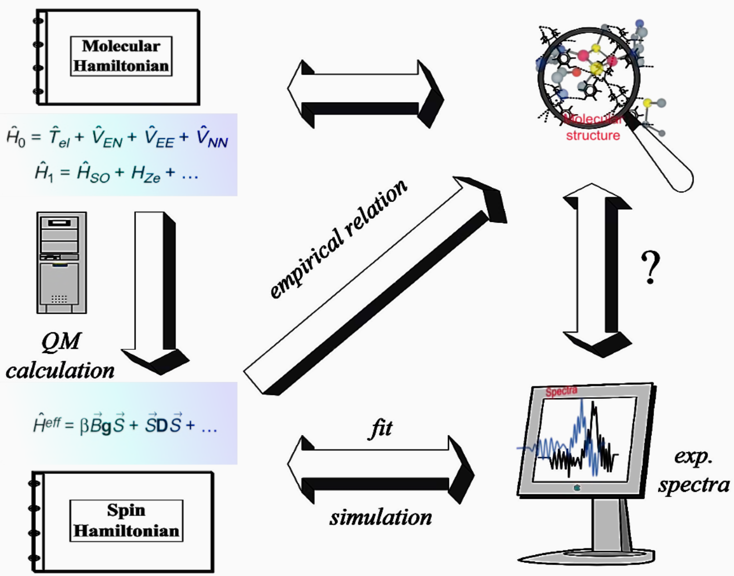
Structural Infromation from EPR

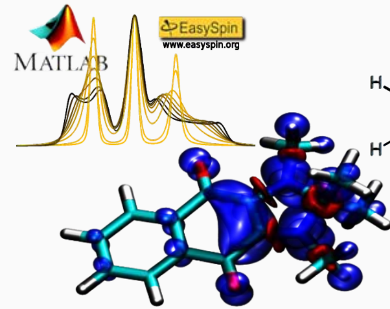
Example of Complex **e-^{1}H-^{14}N** Interaction/**Splitting**

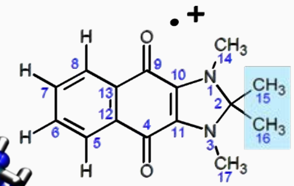


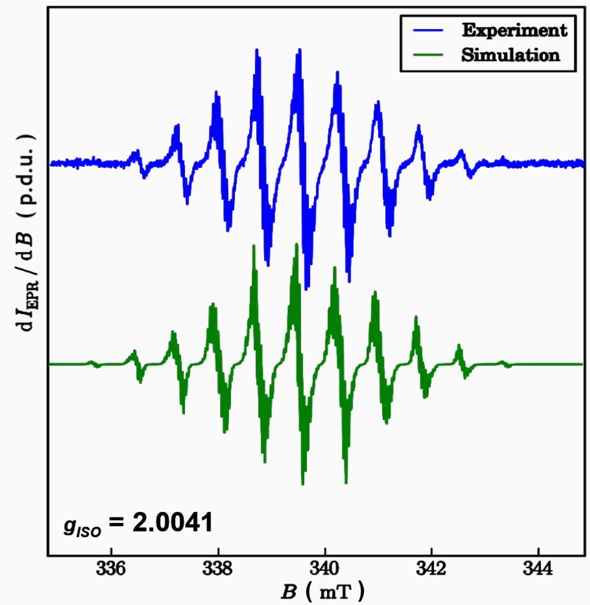
* Interaction/**Splitting** from $t - \mathbf{butyl}$ & $-\mathrm{CH}_3$ can be **neglected**

Analysis of EPR Spectra[c,d,e]

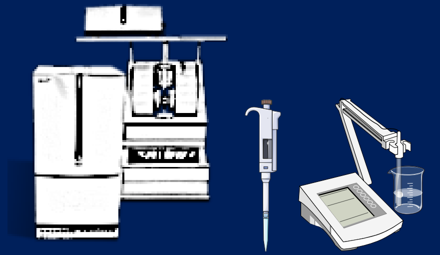






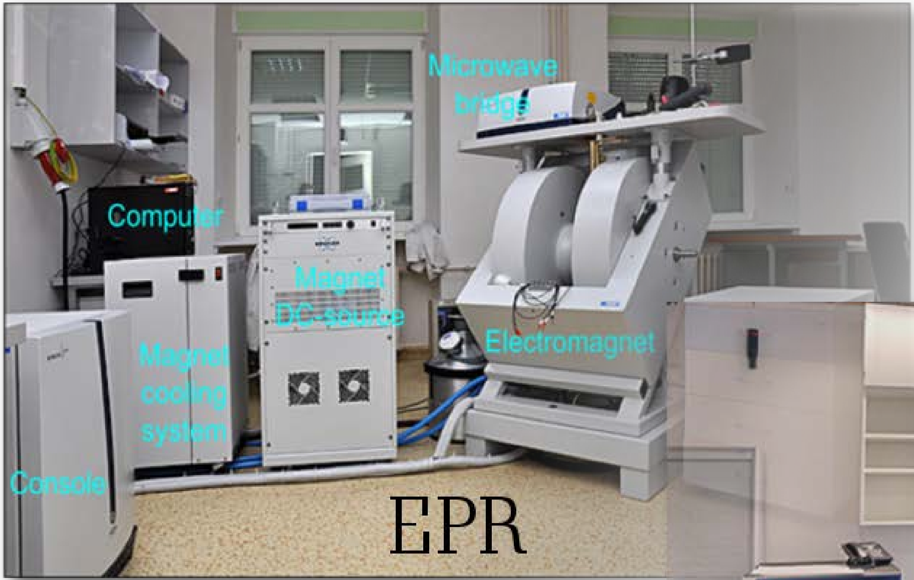


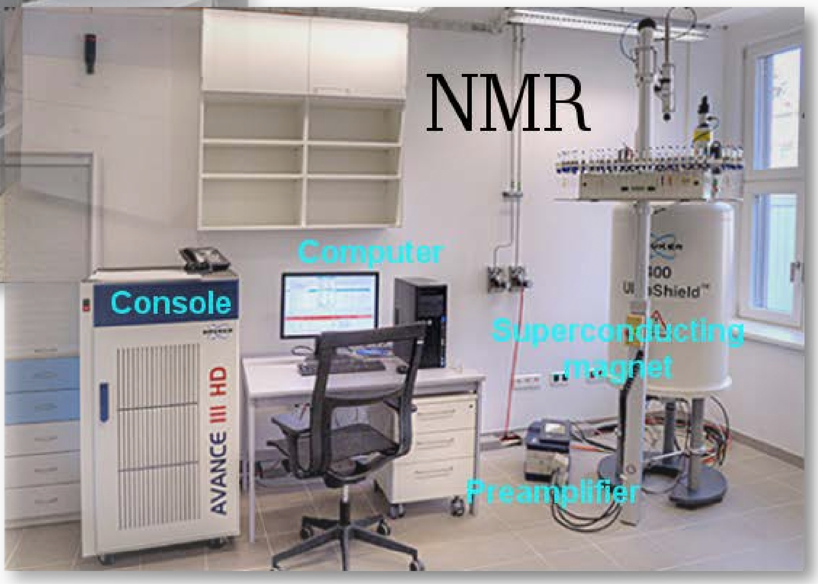
c F. Neese, *Curr. Opin. Chem. Biol.* **2003**, 7, pp. 125-135
d J. Tarábek , *J. Org. Chem.* **2018**, 83, pp. 5474-5479
e see also: easyspin.org



Practical Aspects of EPR

EPR/NMR Spectrometers / *Comparison*





Tubes/Cells for Liquid/Solid Samples[f,g] vs Temperature[h]

[f] c region from $0.01\,\mu\mathrm{M}$ to $50\,\mathrm{mM}$ (V from $50\,\mu\mathrm{l}$ to $1\,\mathrm{ml}$)

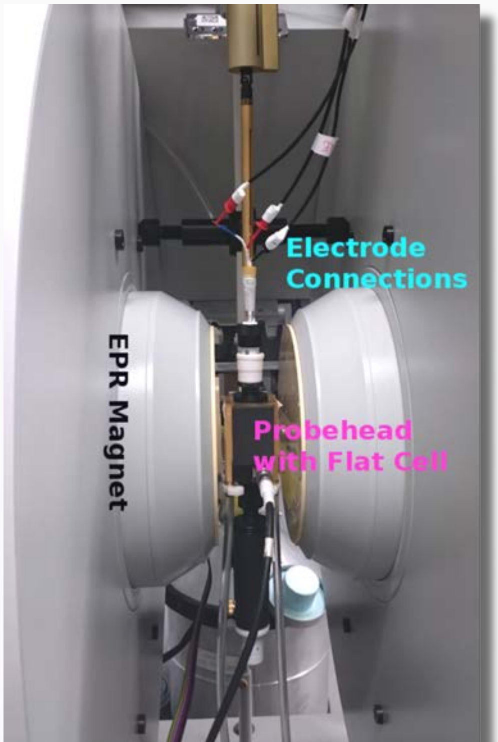
[g] Powder m from $1\,\mathrm{mg}$ to $50\,\mathrm{mg}$

[h] T from $80\,\mathrm{K}$ to $500\,\mathrm{K}$

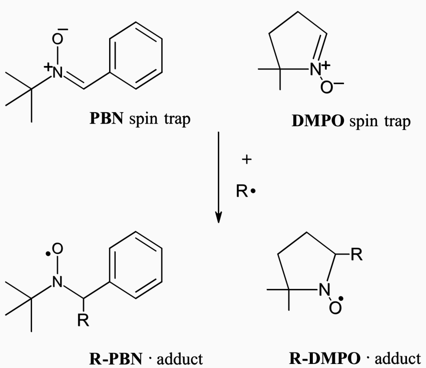
EPR Facilities

Coupled Methods/Generation of Paramagnetic Species

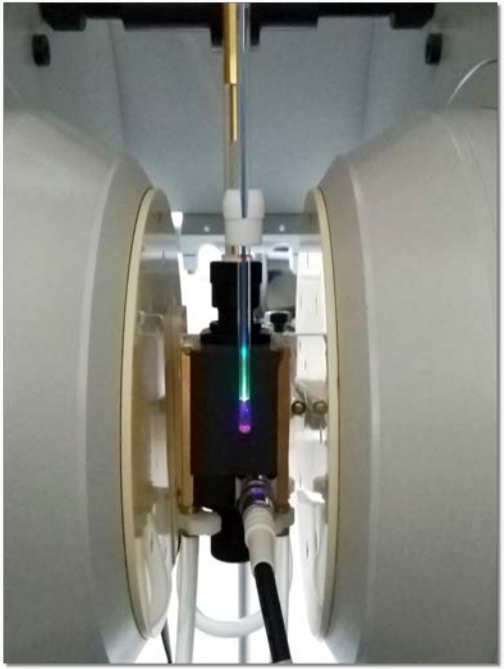
Electrochemistry

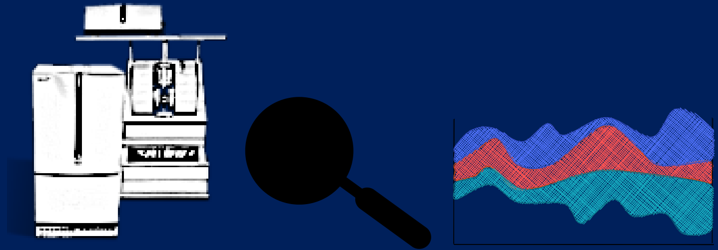


Spin Trapping

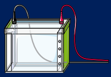


Photochemistry



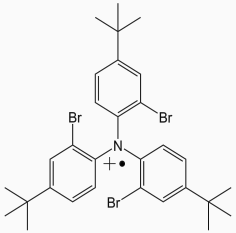


Case Studies

 *In situ* EPR *Electrochemistry*

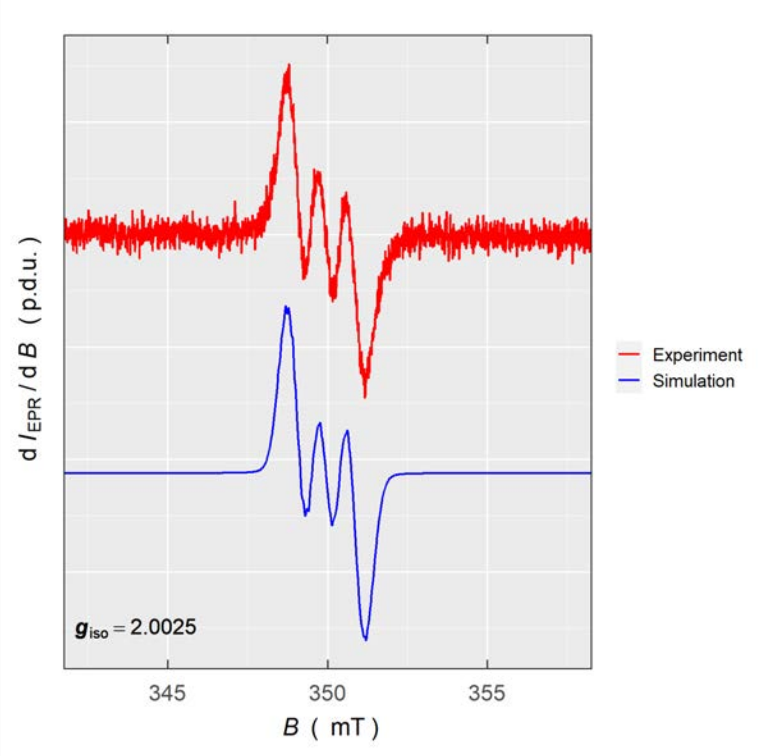
 *In situ* EPR *Photochemistry* with Spin Trapping

Stability of the Electrochemically Generated **BC Radical Cation**



Hyperfine couplings (HFCCs, A) from simulation (Sim) + computed by DFT[j].

Nuclei	A^{Sim} (MHz)	A^{DFT} (MHz)
$1 \times {}^{14}\mathrm{N}$	24.172	21.267
$3 \times {}^{1}\mathrm{H}$	6.768	6.950
$3 \times {}^{1}\mathrm{H}$	5.825	4.719
$3 \times {}^{1}\mathrm{H}$	2.673	3.817
$3 \times {}^{79,81}\mathrm{Br}$	1.820	2.036

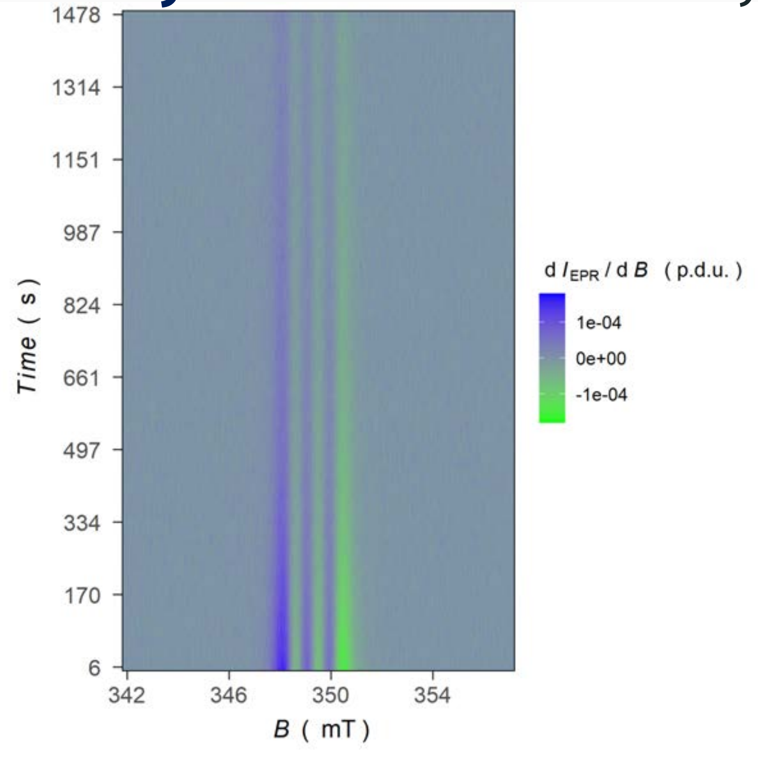


Comparison of experimental and simulated EPR spectra of **"Blues Cousin"**(**BC**), radical cation.

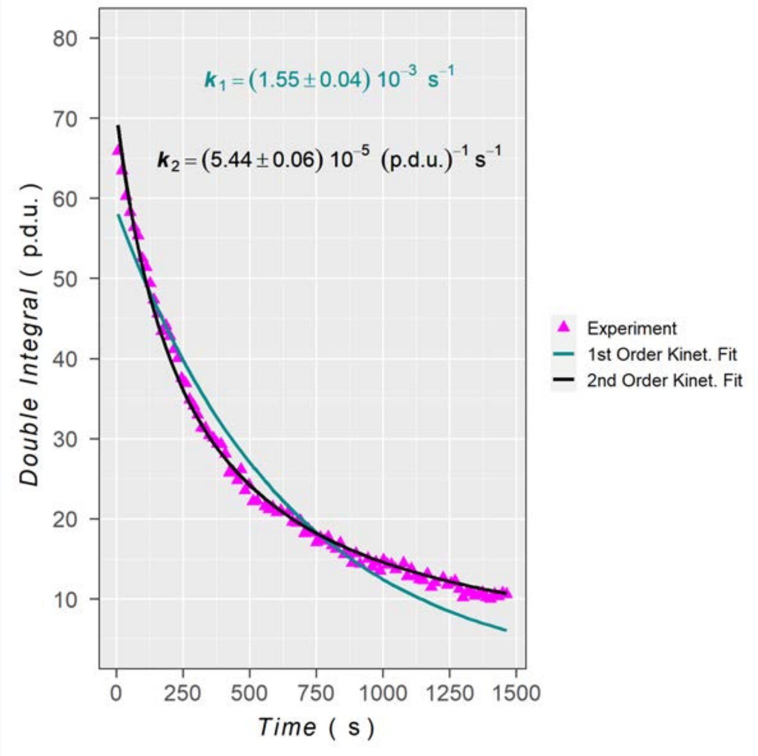
[i] **Cooperation** with the **Group** of *T. Slanina* (*D. Hidasová*, RP)

[j] **PBE0/EPR-II(C,H,N)/def2-TZVPD(Br)//B3LYP/6-31G(d,p)//C-PCM**$(\mathrm{CH_2Cl_2})$

Stability of the Electrochemically Generated **BC Radical Cation**



"Top-view" of EPR spectra recorded during kinetic stability experiment of the $\mathrm{BC}^{\bullet+}$.

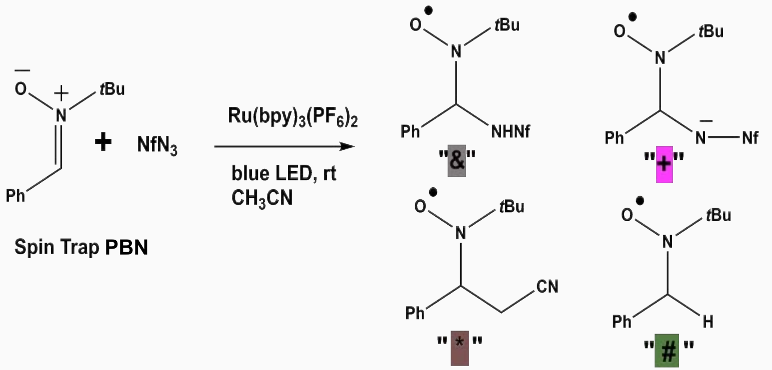


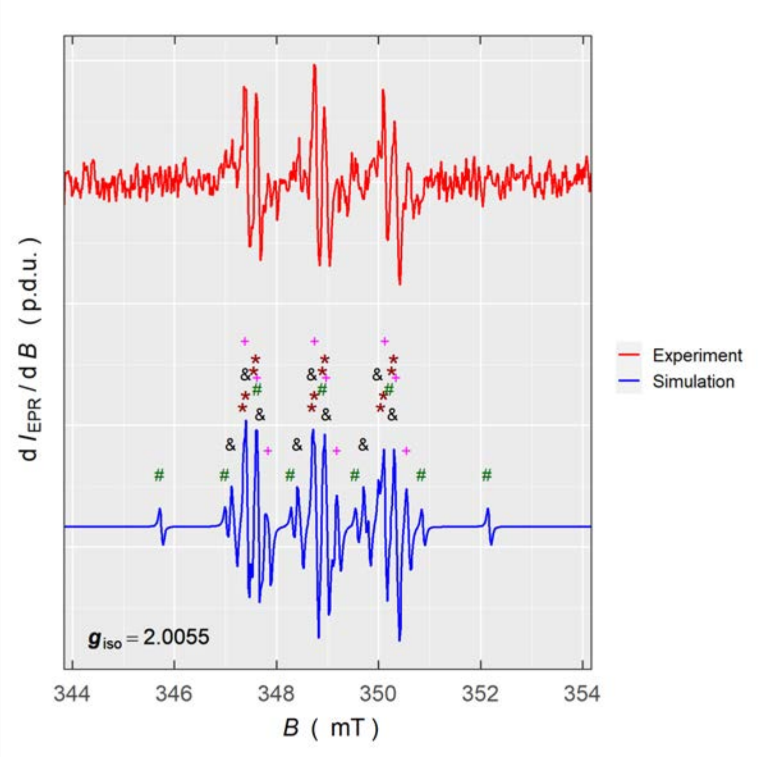
$\mathrm{BC}^{\bullet+}$ decay[k] just after the *in situ* electrochemical generation.

[i] **Cooperation** with the **Group** of *T. Slanina* (*D. Hidasová*, RP)

[k] units => "p.d.u." ≡ procedure defined unit (see IUPAC)

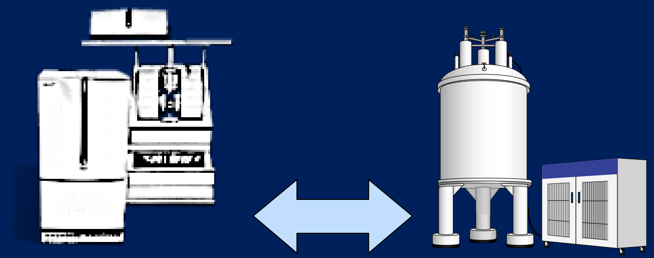
Detection of Transient Radicals by **Spin Trapping** upon **Continuous** Sample **Irradiation** (by 448 nm LED)[m]



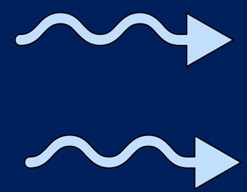


[l] **Cooperation** with the **Group** of *U. Jahn* (*Ch. Pramthaisong*, RP)

[m] Additional **DFT** computations & **MS** & **Isotopic labeling/replacement** were required

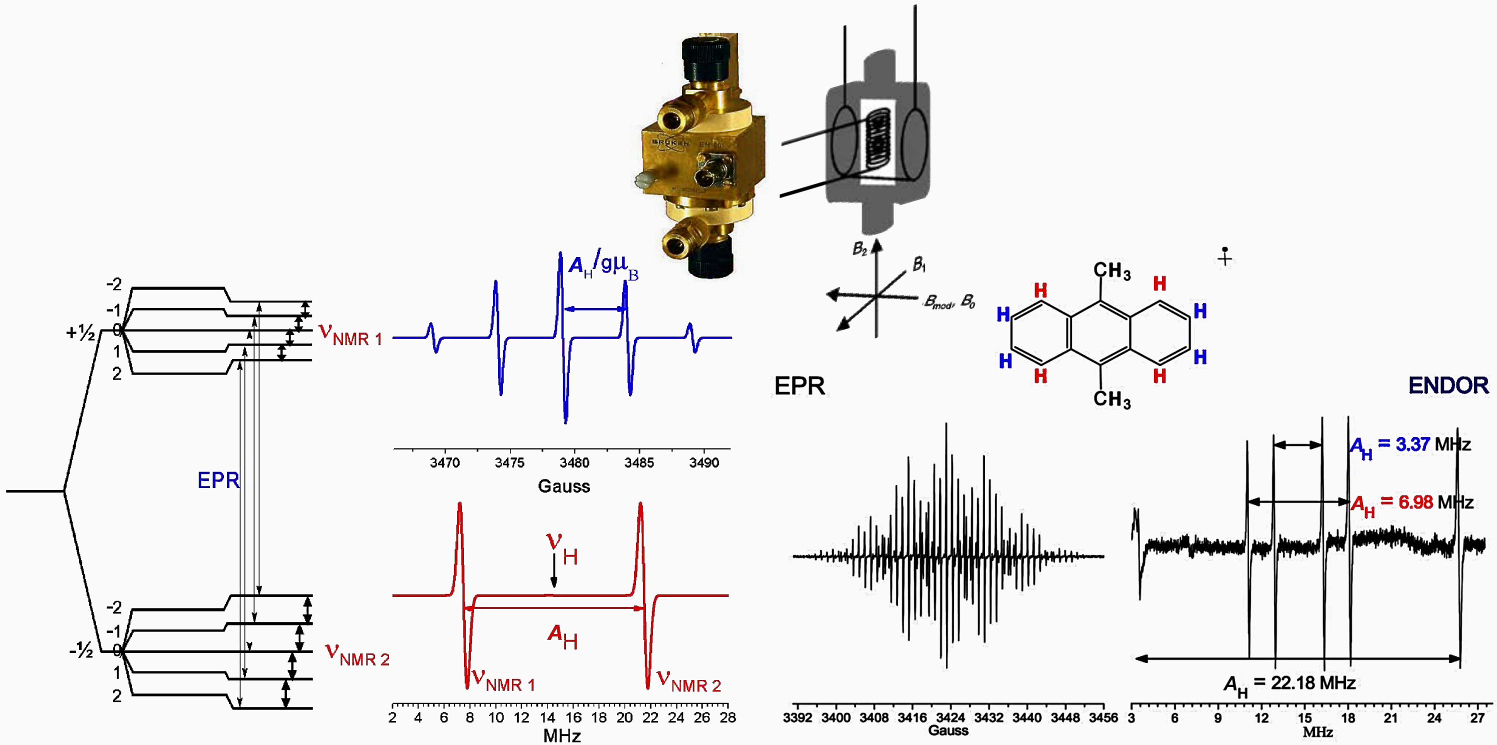


EPR Spectrometer Upgrade



Double Resonance

ENDOR Probehead & Spectra[o]



[n] **E**lectron **N**uclear **Do**uble **R**esonance

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

Cooperation & Acknowledgements

- **NMR Team**
- *P. Cígler*
- *J. Kaleta*
- *I. Starý*
- *T. Slanina*
- *U. Jahn*
- *J. Michl*
- *M. Hocek*
- *P. Bouř*

TO BE CONTINUED ...