ESR Applications in Polarized Target Material Research

D. Buschert, F. Greffrath, J. Heckmann, C. Heß, W. Meyer,
P. Pfaff, E. Radtke, G. Reicherz, M. Schiemann

- Introduction
- X-band ESR
- V-band ESR
- Combination of X- and V-band results
- Summary

Introduction: experimental situation

ESR samples: - chemically or radiation doped target materials
- beads or chips with mm-dimensions
- have to be kept under liquid nitrogen

`Conventional´ ESR: sample in electric field knot in single mode cavity, requires:

sample dimensions $\ll$ wavelength of μ-waves

$\rightarrow$ low fields / frequencies, e.g. B=340 mT, ν = 9.5 GHz (X-band, $\lambda \approx$ 3 cm)

ESR at DNP fields? (e.g. B=2.5 T, ν = 70 GHz (V-band, $\lambda \approx$ 4 mm)

sample dimensions $\approx$ wavelength of μ-waves

- no commercial solutions $\rightarrow$ own developments

Introduction: experimental wish list

- *ESR linewidth and shape*
- *radical concentration (in irradiated material)*
- *characterization of (radiation induced) radicals*
- *temperature stability (of radiation induced radicals)*
- *relaxation times*

→ ***X-band ESR (340 mT)***

- *linewidth and shape at DNP field* → ***V-band ESR (2.5 T)***

Spintemperature theory:

$$P_{I,max} = \mathcal{B}_I \left(I \frac{\hbar\omega_0}{2kT_L} \frac{\omega_I}{D} \frac{1}{\sqrt{\delta(1+f)}} \right)$$

D : *ESR linewidth*

Linewidth dominated by:

HFS	$\mathcal{H} = \vec{S} \cdot \mathbf{A} \cdot \vec{I}$
g-anisotropy	$\mathcal{H} = \mu_B \vec{B} \cdot \mathbf{g} \cdot \vec{S}$

X-band spectrometer

- *Commercial spectrometer* (Magnettech) *featuring*
  - *tunable Gunn oszillator*
  - *high-Q cylindrical single mode cavity*
  - *AFC (33 kHz)*
  - *Lock-In amplification (1, 10 and 100 kHz)*
- *Microwave setup modified* (S. Goertz)
  - → *precise low power measurements*
  - → *reproducible saturation experiments (60 dB power range)*
- *Normal operation: at 77 K (glass dewar, liquid nitrogen)*
- *Oxford ESR-cryostat: RT to 4 K continuously (routine operation* → D. Buschert)
- *Advantage: extremely precise and reproducible measurements*
- *Limitation: linewidth measurements → extrapolation of factor 7 on field scale*

X-band spectrometer

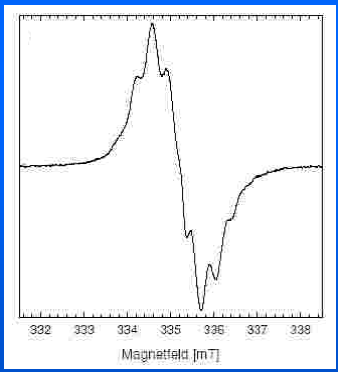
X-band spectrometer

X-band ESR: radical characterization

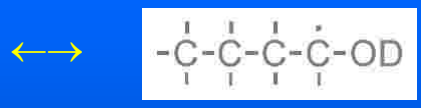
First irradiation of d-butanol: what kind of radical ??

- irradiation with ^{90}Sr source produces same radicals as LINAC in Bonn

- systematic studies with partly deuterated butanol and other alcohols



→ ***Hydroxyalkyl-radical*** (→ S. Goertz)

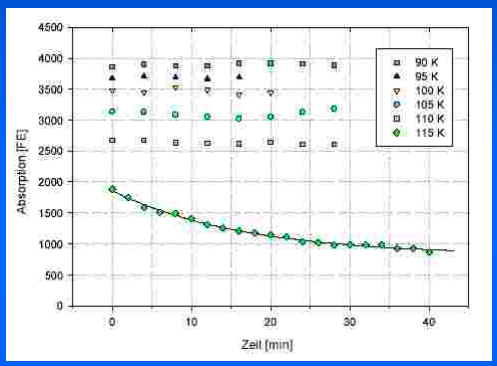


X-band ESR: temperature stability

Irradiated d-butanol: temperature stability ?

ESR measurements:

- *ESR signal constant below T=115 K*
- *significant decrease at T=115 K* (→ J. Harmsen)

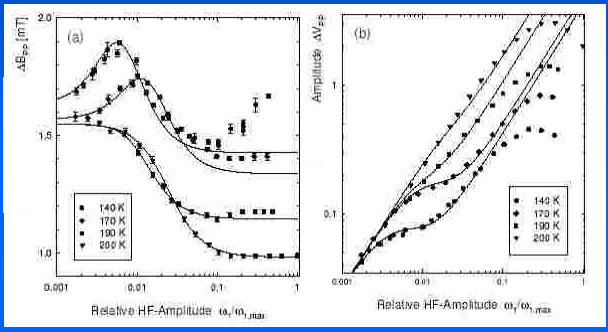


- first use of Oxford ESR cryostat, operated with liquid nitrogen, accuracy ± 2 K

- temperature stability of ammonia ?

- better temperature adjustment with ^{4}He ? (→ D. Buschert)

X-band ESR: relaxation times



$T_{irr.}[K]$	$T_Z[ms]$
140	300
160	300
170	56
180	15
190	10
200	8

Saturation studies on ^{6}LiD: (→ S. Goertz)

- *Linewidth and signal amplitude dependent on irradiation temperature*
- *both follow spintemperature theory*

→ *extraction of Zeeman relaxation times*

→ *optimum irradiation temperature (180 – 190 K) due to electron spin dynamics (radical production temperature independent, same concentrations)*

V-band spectrometer

- *Self developed spectrometer setup (mw layout in principle like in X-band), featuring:*
  - *tunable IMPATT oscillator*
  - *AFC (33 kHz)* (→ Magnettech)
  - *Lock-In amplification (10 and 100 kHz)*
  - *multimodal tunable Fabry-Pèrot resonator*
- *Implemented in 1 K polarization apparatus (^{4}He cryostat, 2.5 T C-magnet)*
- *Operation modes:*
  - *at room temperature*
  - *in precooled and evacuated cryostat ($\geq$ 77 K)*
  - *at 1 K in ^{4}He mode*
- *Advantage: ESR (linewidth measurements) at DNP field*
- *Limitation: no time-consuming systematic studies (conditions can hardly be kept constant)*

V-band spectrometer

V-band spectrometer

Head of ESR insert with mirror and coupling pin adjustment

Fabry-Pèrot resonator

V-band ESR: linewidth

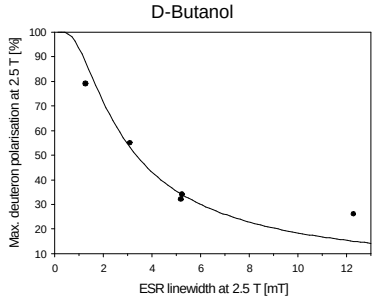
Material	Radical	FWHM $[mT]$
D-Butanol	EDBA	12.30 ± 0.20
D-Butanol	TEMPO	5.25 ± 0.15
D-Butanol	Porphyrexid	5.20 ± 0.23
$^{14}ND_3$	$^{14}ND_2$	4.80 ± 0.20
$^{15}ND_3$	$^{15}ND_2$	3.95 ± 0.15
D-Butanol	Hydroxyalkyl	3.10 ± 0.20
^{6}LiD	F-center	1.80 ± 0.01
D-Butanol	Finland D36	1.28 ± 0.03
D-Propandiol	Finland H36	0.97 ± 0.04
D-Propandiol	OX063	0.86 ± 0.03

Spintemperature theory:

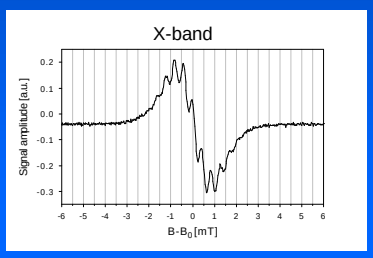
$$P_{I,max} = \mathcal{B}_I \left(I \frac{\hbar\omega_0}{2NI_z} \frac{\omega_l}{D} \frac{1}{\sqrt{\delta(1+\delta)}} \right)$$

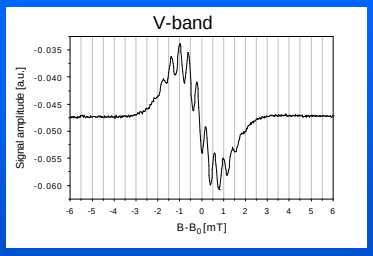
D: ESR linewidth

→ ***minimize ESR linewidth to maximize deuteron polarization***



X- and V-band ESR: lineshape and broadening





^{6}LiD:

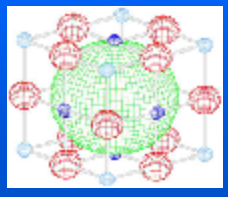
- *identical X- and V-band spectra*

→ *no field dependent contribution*
→ *ESR line solely HFS broadened*
→ *F-center is pure s-wave electron*

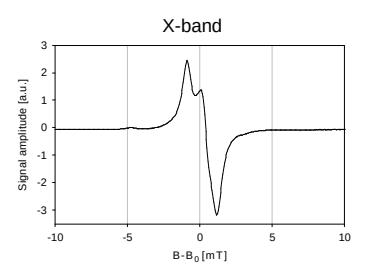
- *from HFS splitting (13 lines):*

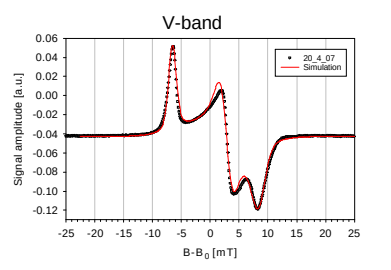
interaction of the electron with six ^{6}Li neighbours

→ *located at deuterium lattice site*



X- and V-band ESR: lineshape and broadening





D-Butanol (EDBA):

- *linewidth scales almost linearly with the applied field*

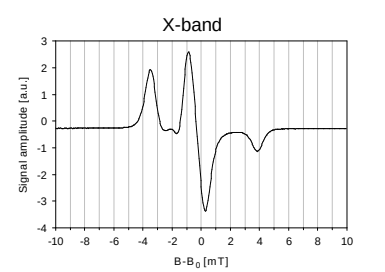
→ *line broadening almost solely due to g-anisotropy*

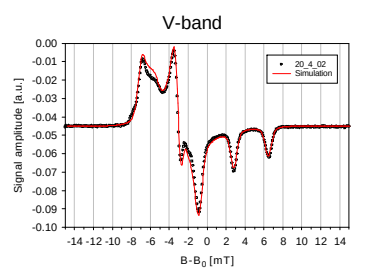
- *simulation excluding HFS fits to the data*

→ *extraction of the relative g-anisotropy*

$$\frac{\Delta g}{\bar{g}} = 6 \cdot 10^{-3}$$

X- and V-band ESR: lineshape and broadening





D-Butanol (TEMPO):

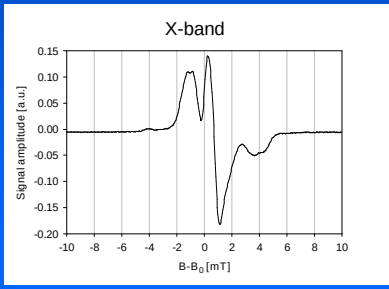
- *significant contribution of both HFS and g-anisotropy*

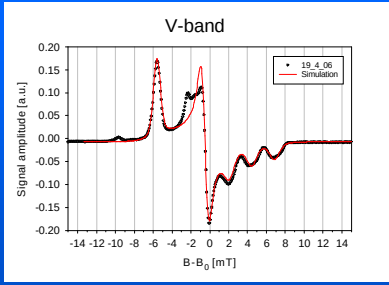
→ *simulation difficult, but: HFS constants known for TEMPO (Steinhoff et al.)*

→ *fit g-anisotropy to the data*

$$\frac{\Delta g}{\bar{g}} = 3.6 \cdot 10^{-3}$$

X- and V-band ESR: lineshape and broadening





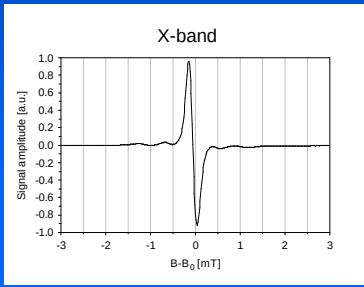
D-Butanol (Porphyrexide):

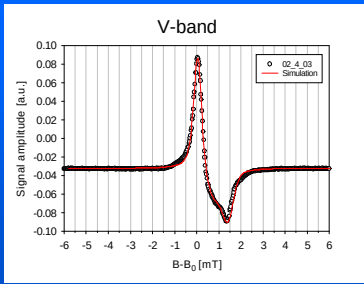
- *similar contributions as in TEMPO, but: HFS more complicated*
- *both HFS and g-anisotropy fitted to the data (start with TEMPO HFS constants, second order HFS neglected)*

→ *extraction of*

$$\frac{\Delta g}{g} = 4 \cdot 10^{-3}$$

X- and V-band ESR: lineshape and broadening





D-Butanol (Finland D36):

- *in X-band extremely narrow, weak HFS, no g-anisotropy visible*
- *in V-band asymmetric lineshape (characteristic for g-anisotropy)*

→ *simulation only with g-anisotropy fits to the data*

$$\frac{\Delta g}{g} = 5 \cdot 10^{-4}$$

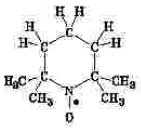
- one order of magnitude less than for `standard radicals´

Summary

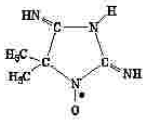
- ***Variety of `conventional´ ESR applications together with the possibility of high field ESR measurements – very useful in PT business***

- ***Combination of X- and V-band results for linewidth and shape:***
  - *identify (and quantify) line broadening mechanisms*
  - *extrapolate linewidth to even higher fields*

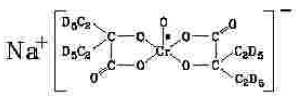
Radicals



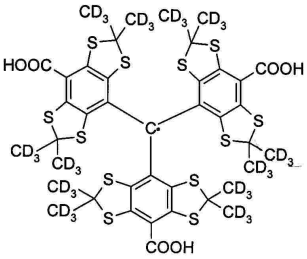
TEMPO



Porphyrexid



EDBA



Trityl radical Finland D36