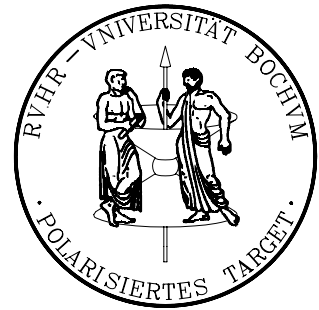


Highest polarizations in deuterated compounds



9th International Workshop on
Polarized Targets and Techniques,
Bad Honnef, 27.-29.10.2003

St. Goertz, J. Heckmann, W. Meyer, E. Radtke and
G. Reicherz

1. Increasing the polarization of weakly magnetic nuclei
 - The non-Zeeman heat capacity
 - Inhomogeneous interactions
 - Saturation measurements in ${}^6\text{LiD}$
2. Magnetic field dependence of the polarization in D-Butanol
 - Chemical doping with the usual radicals
 - Results achieved with radiation doping
 - The structure of the radiation induced defect
 - The idea
3. The trityl radical and its EPR
4. Results on trityl doped hydrocarbons
5. Polyethylene: Is it really the whole story ?
6. Summary

How to increase the polarization of a nuclear species with a weak magnetic moment ?

Obvious: Decrease its Zeeman temperature

$$P_I = \mathcal{B}_I \left(\frac{g_I \mu_K B}{2T_Z^I} \right) = \mathcal{B}_I \left(\frac{1}{2} \omega_I \alpha_I \right)$$

And how to do that ?

Theory: Minimize the electron dipolar temperature

$$\beta_{eq} = \frac{c_Z^S}{c_Z^S + (T_Z/T_D)c_D} \alpha_L$$

And what does that mean ?

Theory: Minimize the electron dipolar heat capacity

$$c_D \sim D^2 \sim B_l^2, \quad B_l \simeq g_e \mu_B N_S$$

Is it enough to minimize N_S ? – **NO !**

In practice: Inhomogeneous interactions present !

- Anisotropy of the g-factor
- Hyperfine interactions

$$D^2 \sim B_{l,hom}^2 + B_{l,inhom}^2$$

Is it possible at all to maintain an internal equilibrium such that there is a well defined non-Zeeman temperature?

Example: The F-Center in ${}^6\text{LiD}$, $N_S \simeq 2 \cdot 10^{19}/g$

Total width: $\sigma \simeq 8 G$ HFS: $a \simeq 4 G$

Dipolar broadening: $B_l \simeq g_e \mu_B N_S \simeq 0.4 G$

Hyperfine splitting causes well separated spin packets!

Answer: YES! → EPR saturation curves

Measurement of the

- amplitude ΔV and the
- field separation ΔB_{PP}

of the **modulated EPR absorption signal** vs. B_1

Provotorov: Analytic expression for the absorption signal

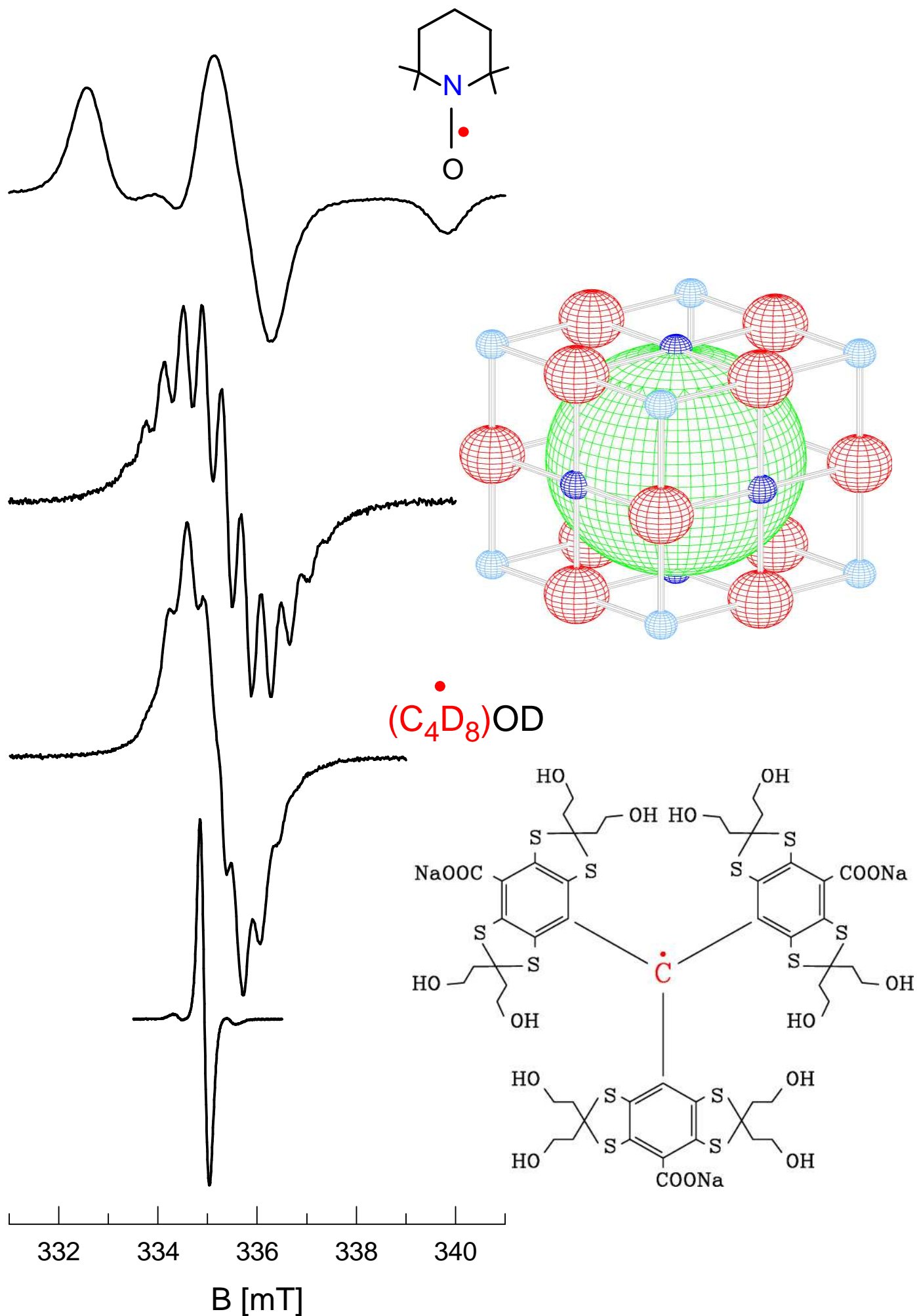
Weak (non-saturating) μ -wave field:

$$v \sim B_1 \frac{dg}{d\Delta}$$

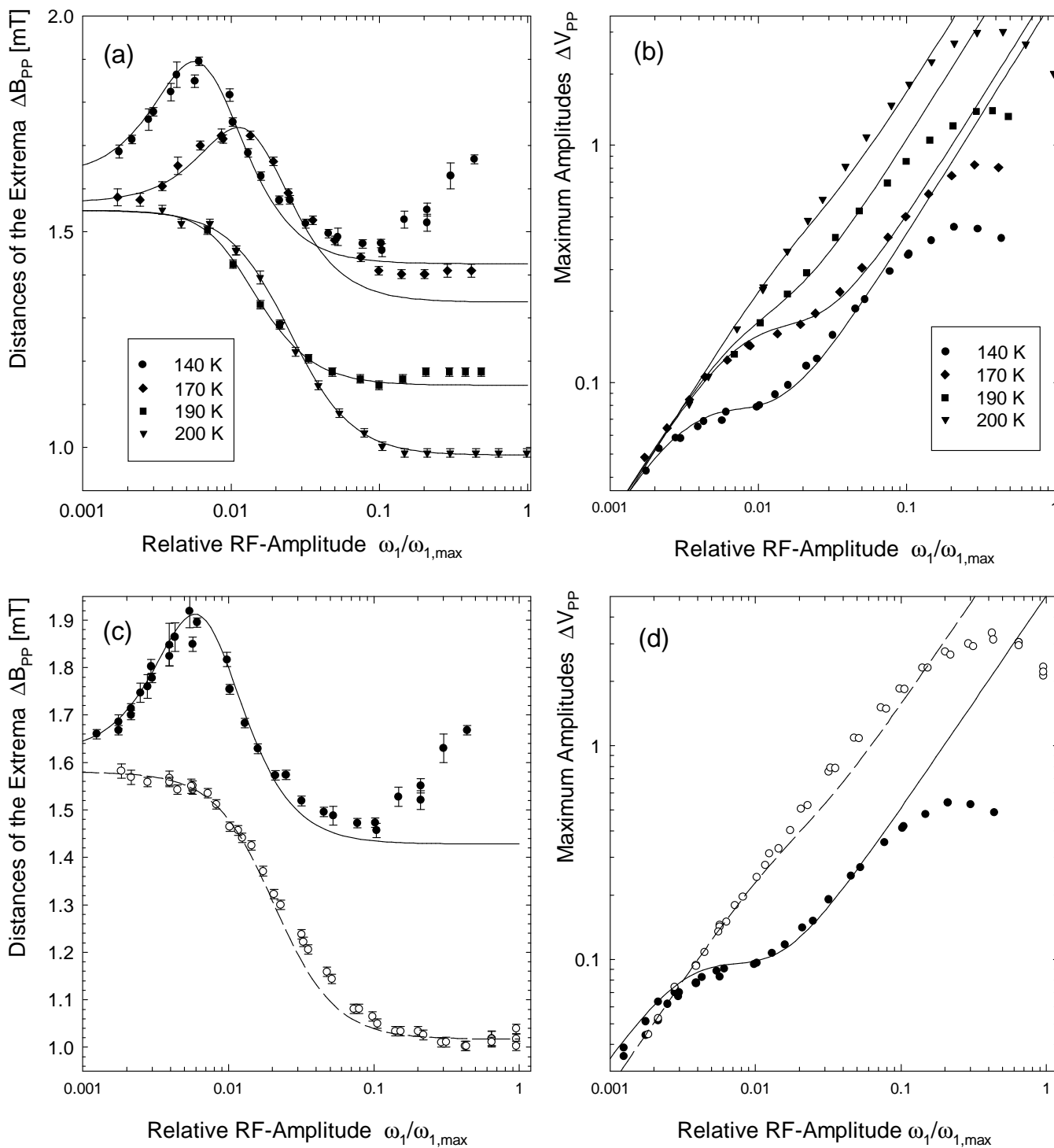
Strong (saturating) μ -wave field:

$$v \sim B_1 g(\Delta) \frac{\Delta}{\Delta^2 + (T_Z/T_D) D^2}$$

Different paramagnetic centers in a deuterated environment



EPR-Saturation curves of F-centers irradiated ^6LiD at 9.4 GHz (0.34 T) and 77K



Extracted parameters:

Irradiation temperature [K]	$(T_Z/T_D) (D^2/\sigma^2)$	T_Z [ms]
140	5.7	300
160	~ 5	300
170	4.6	56
180	1.6	15
190	1.9	10
200	1.0	8

Also inhomogeneously broadened electronic spin systems display a well defined non-Zeeman temperature

if

- the dipolar interaction is not too weak

\Leftrightarrow the spin concentration is not too low

$\Rightarrow D \sim \frac{1}{10} \sigma$ seems to be sufficient

Similar conclusions drawn by Atsarkin & Rodak (1972)

Sovjet Physics Uspekhi **15** No.3 251-265

For COMPASS: ~ 1 liter of 6LiD irradiated at 185 K
yielding some $2 \cdot 10^{19}$ F-centers/g

2001 -2003: $\bar{P} = \frac{1}{2}(P_+ + P_-) \simeq 51 \dots 53\%$

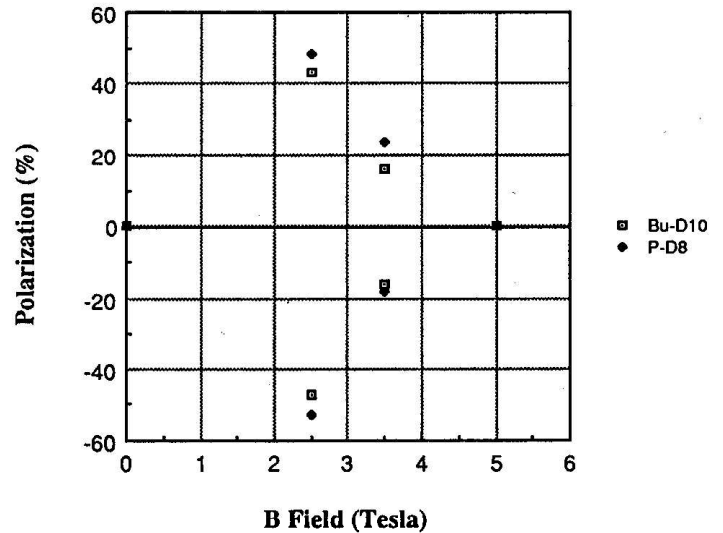
Further information on the COMPASS LiD target:

Kaori Kondo, Jaakko Koivuniemi, Ch. Rohlf

Magnetic field dependence of chemically doped D-Butanol

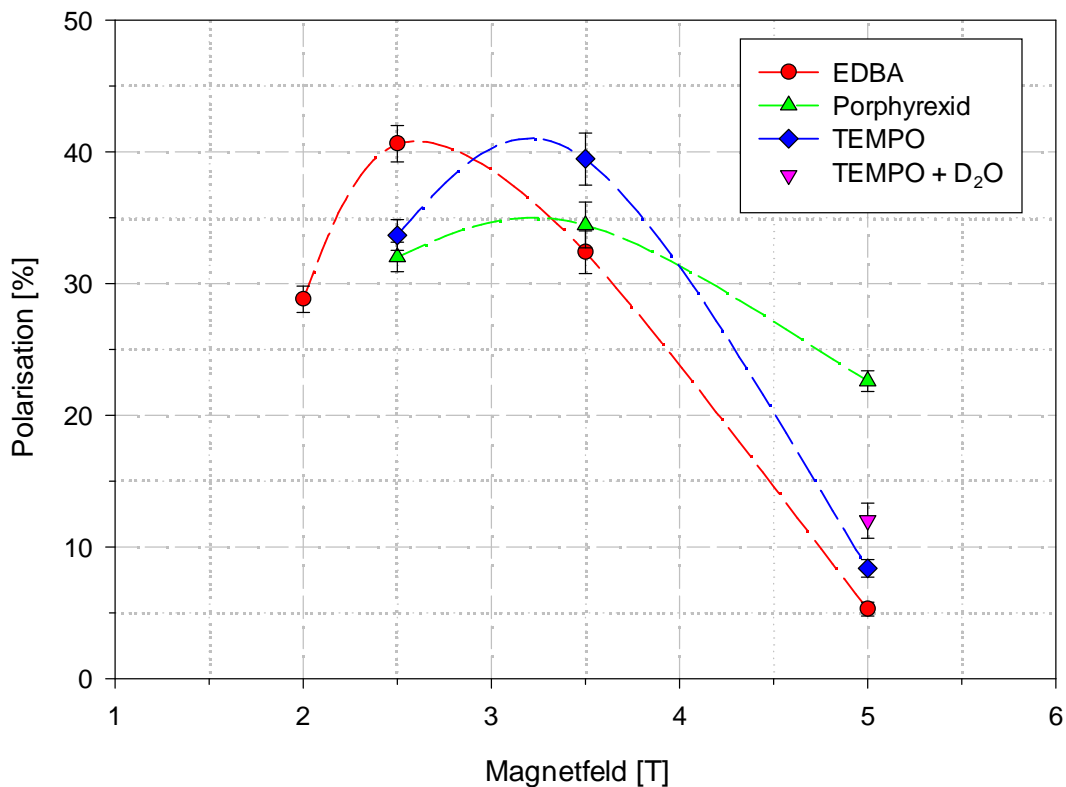
First hint reported by S. Trentalange et. al.

Proc. 9th Int. Symposium on High Energy Spin Physics, Bonn 1990



$$P_I = \mathcal{B}_I \left(\frac{g_I \mu_K B}{2T_Z^I} \right) = \mathcal{B}_I \left(\frac{1}{2} \omega_I \alpha_I \right) = \mathcal{B}_I (\sim B^2) !$$

Systematic investigations on chemically doped D-butanol
Bochum 2001

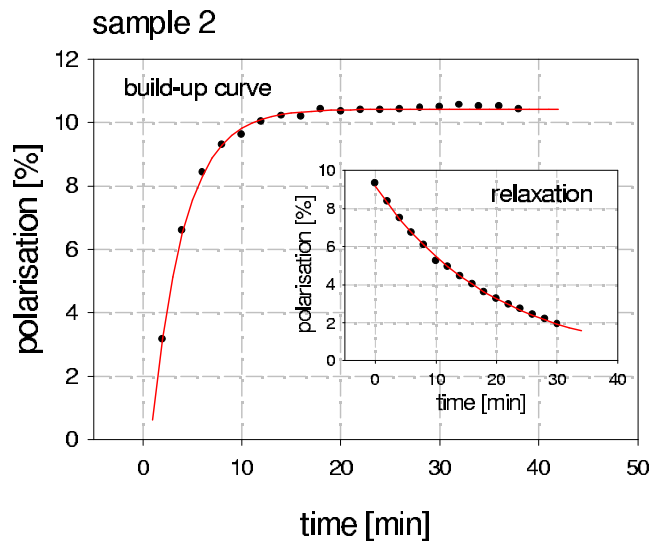
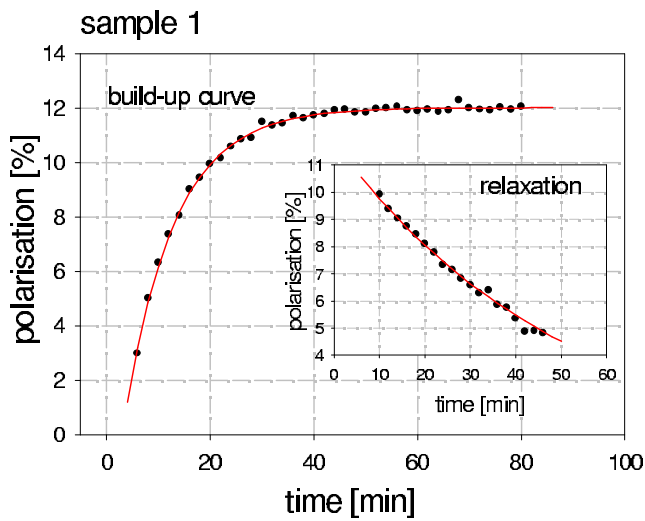


Doping method responsible or material itself?

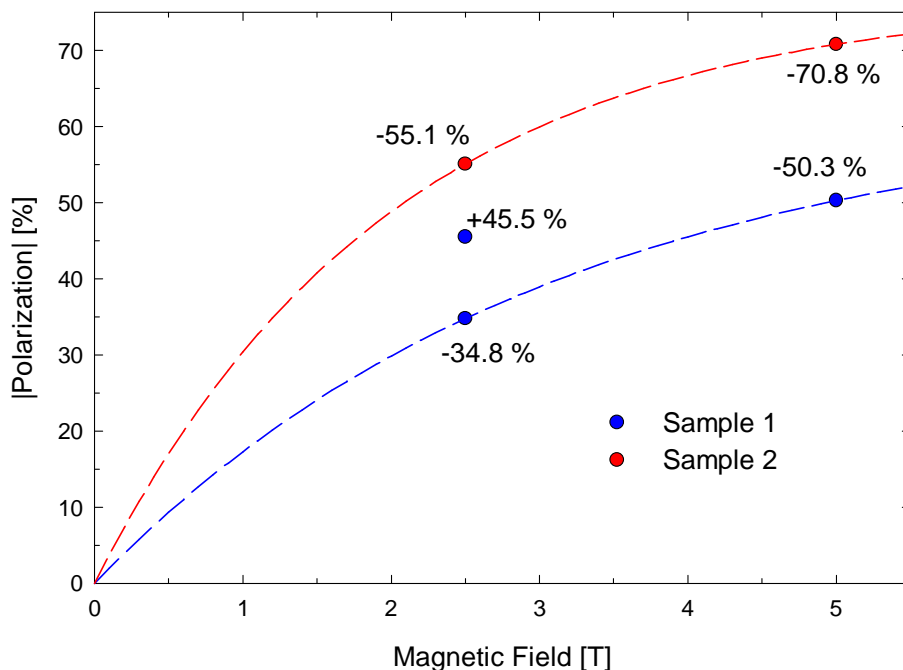
Test: Paramagnetic doping via irradiation at 90 K (LA)

Sample 1: $1 \cdot 10^{19} e/g$, Sample 2: $2 \cdot 10^{19} e/g$

Results at 2.5 T and 1 K: \leftrightarrow 7 – 8 % for chem. dop.



Results at dilution temp.: \leftrightarrow 35 % for chem. dop.



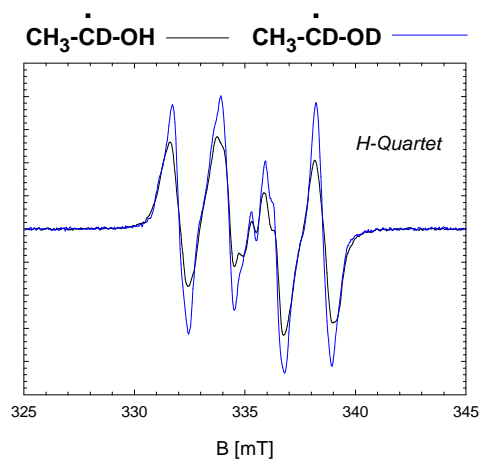
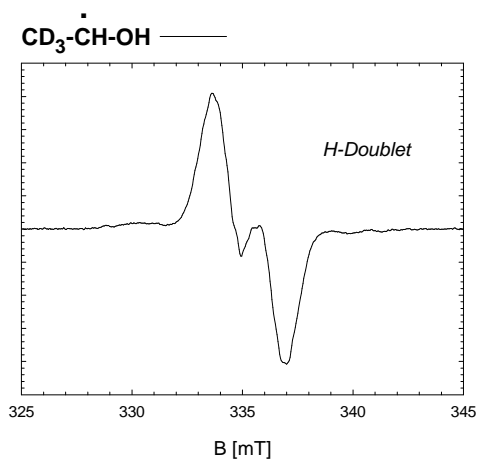
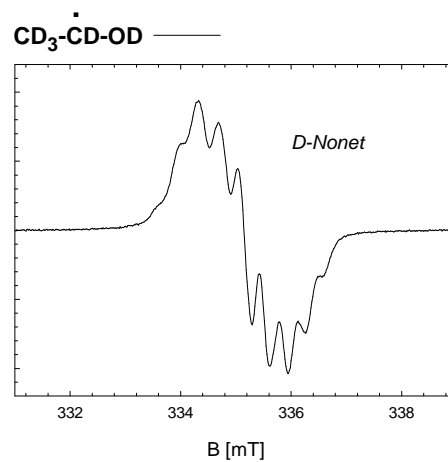
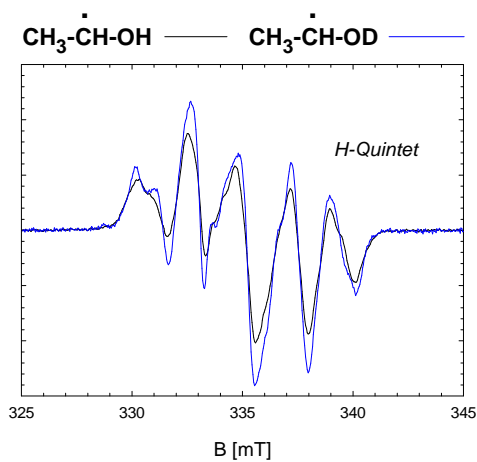
EPR structure analysis of irradiated alcohols

Shape of HFS dominated EPR lines:

- # of neighbouring nuclei with spin \vec{I}
- Probability $|\Psi_e(r=0)|^2$



- Interaction only with direct neighbours
- n equivalent P: $n + 1$ lines with $\Delta \sim 20 - 40 G$
- n equivalent D: $2n + 1$ lines with $\Delta \sim 3 - 6 G$





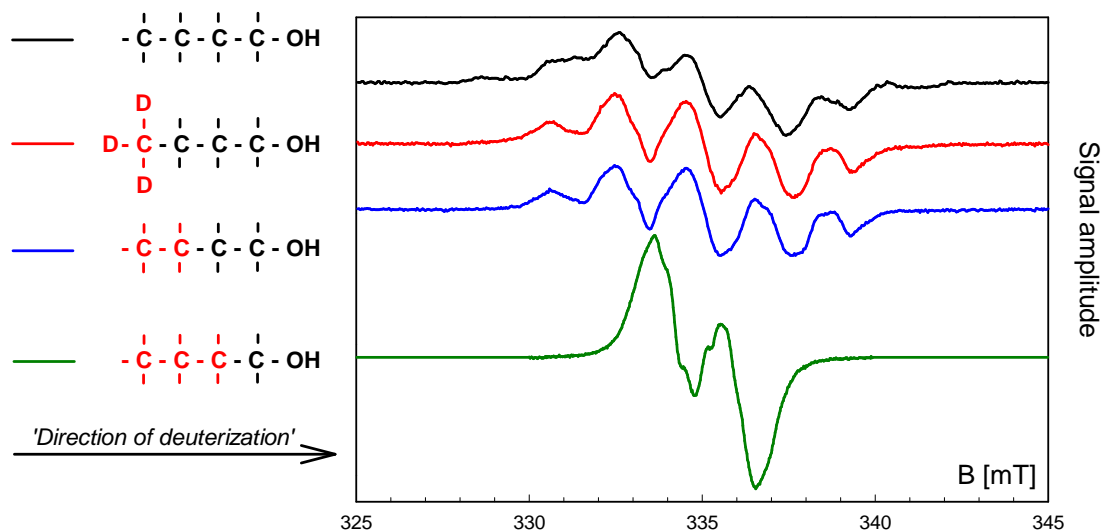
- **Hindered rotation** of the β -CH₂ group at low temp.

⇒ β -protons/deuterons not equivalent

⇒ More lines than just $n + 1$ or $2n + 1$

- Isotop effects:

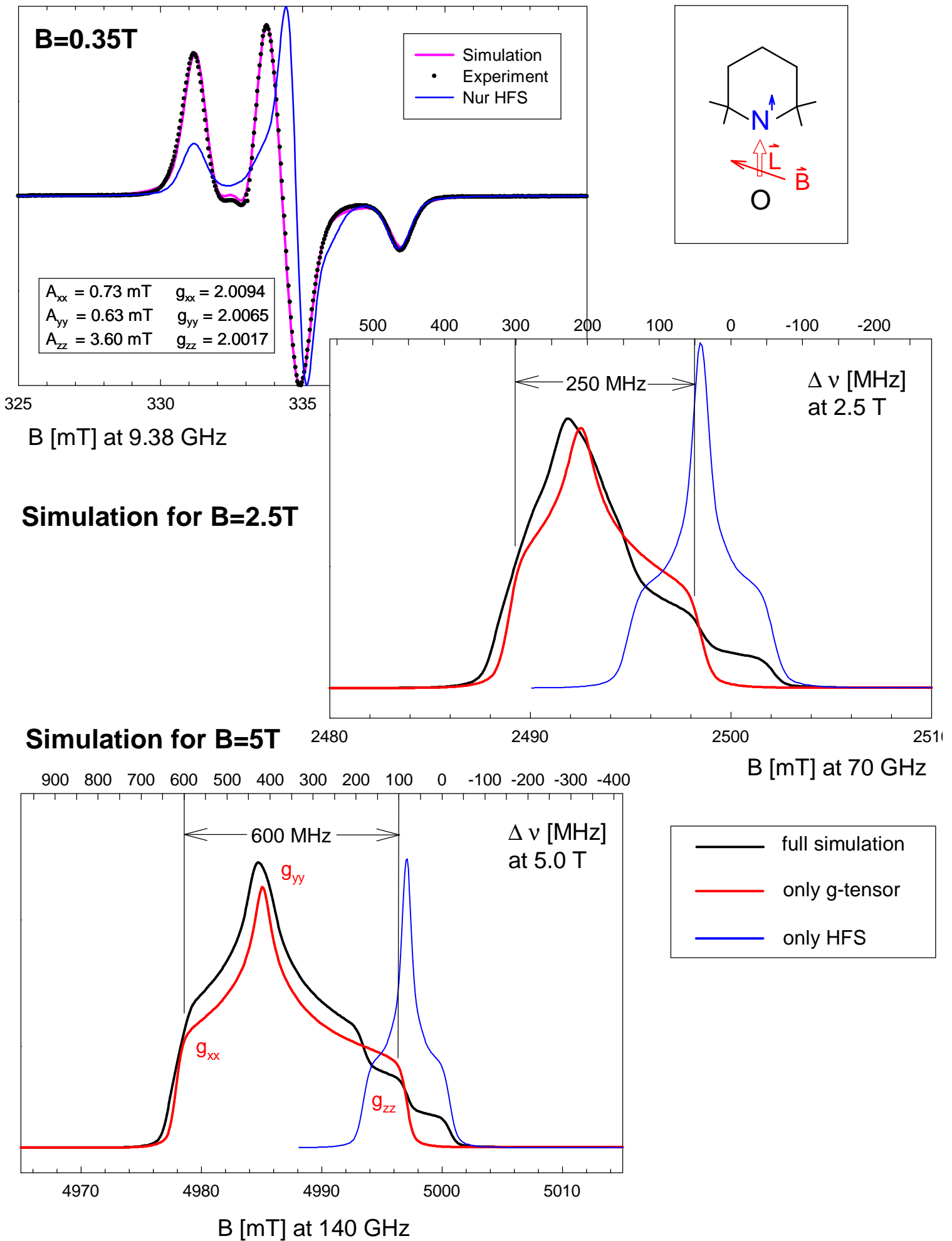
Probability for **abstraction of P or D not equal**



Conclusion: The radiation induced defect in n-butanol

- consists of a unpaired electron from an **abstraction of a proton or a deuteron**
- is **located at the hydroxyl group** if it is protonated
⇒ **'Hydroxyalkyl radical'**
- **But:** **Other positions can not be completely excluded** if the hydroxyl group is deuterated.

EPR of TEMPO in n-butanol: Experiment & Simulation



Magnetic field dependence of chemically doped D-butanol

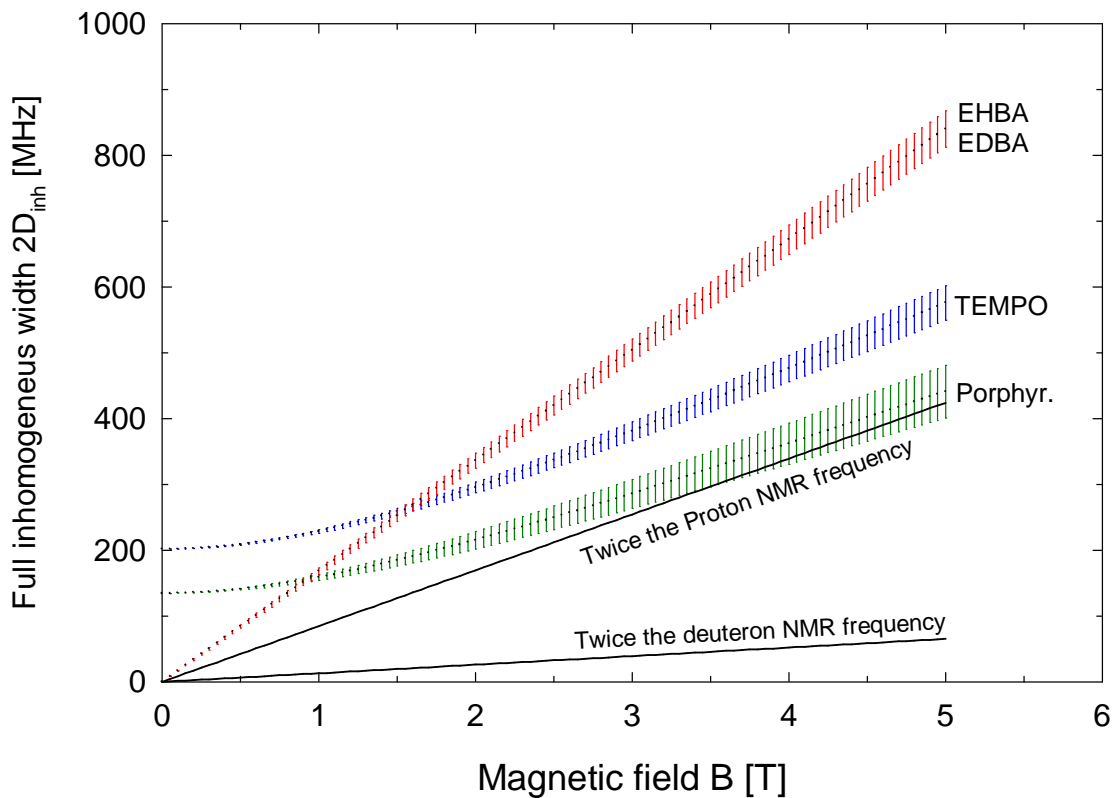
Idea:

$$\Delta E_{inhom} = \Delta g \mu_B B + A \overset{large B}{\sim} B$$

- Dipolar int. too weak to connect the spin packets
- ⇒ No or hindered spectral diffusion
- ⇒ No common non-Zeeman temperature

From simulations of X-Band EPR signals:

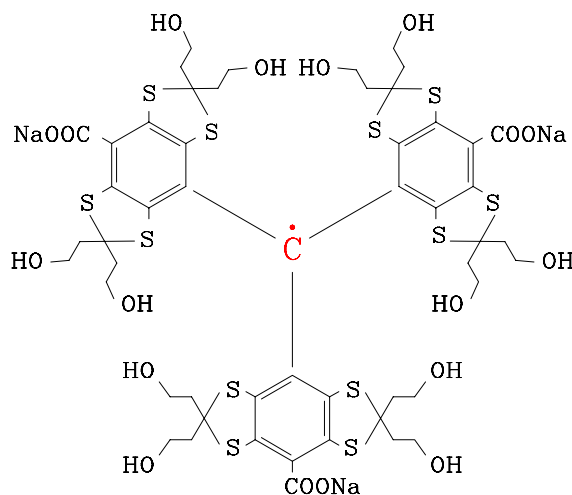
	$\Delta g/\bar{g} [10^{-3}]$
TEMPO	3.85 ± 0.2
Porphyrexid	3.0 ± 0.3
EHBA/EDBA	6.0 ± 0.2



Dream:

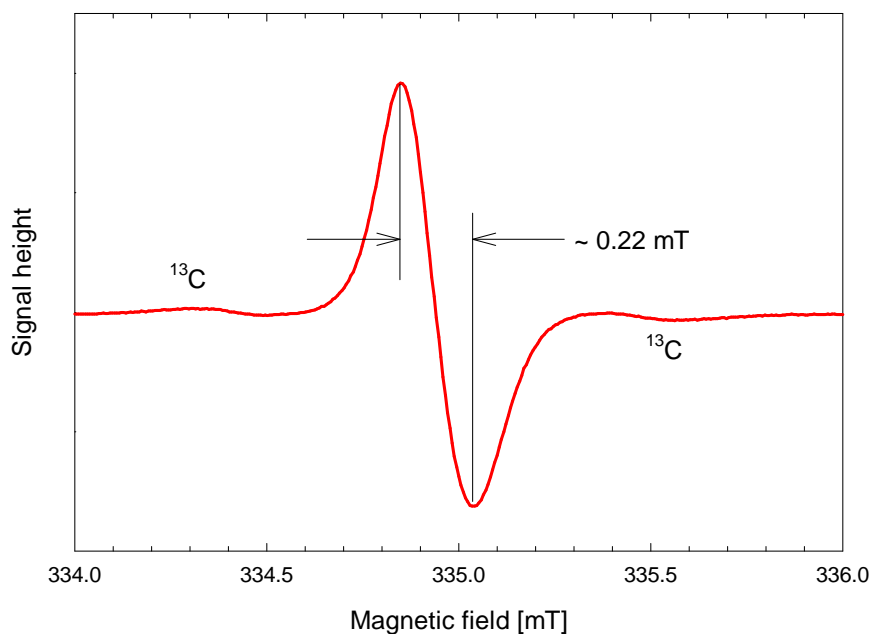
Chemically stable radical with a very narrow EPR line

The trityl radical



OX063: $C_{52}H_{60}Na_3O_{18}S_{12}$ MW: 1426.78

The X-Band EPR absorption signal

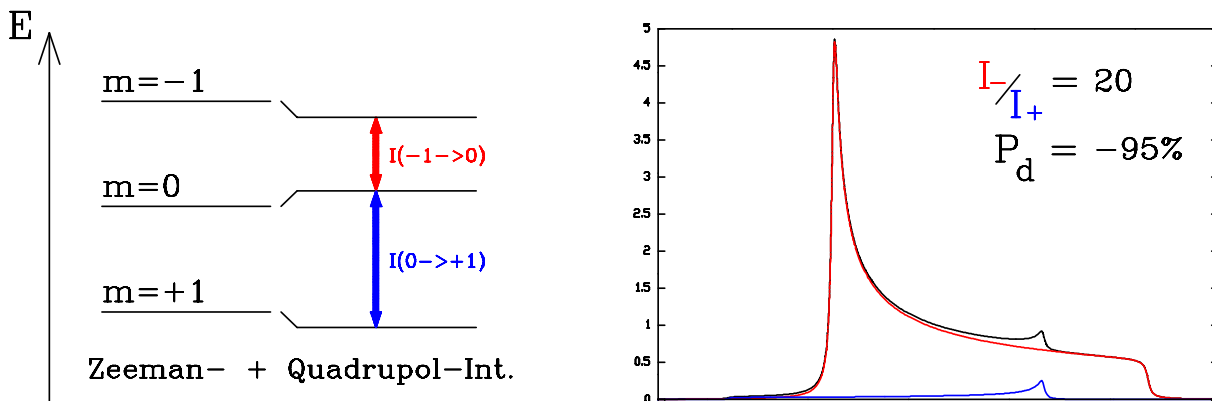


From bolometric EPR at 2.5 T:

Width $\simeq 1.5 \text{ mT} \hat{=} 40 \text{ MHz} \Rightarrow \Delta g/\bar{g} \simeq 3 \cdot 10^{-4}$

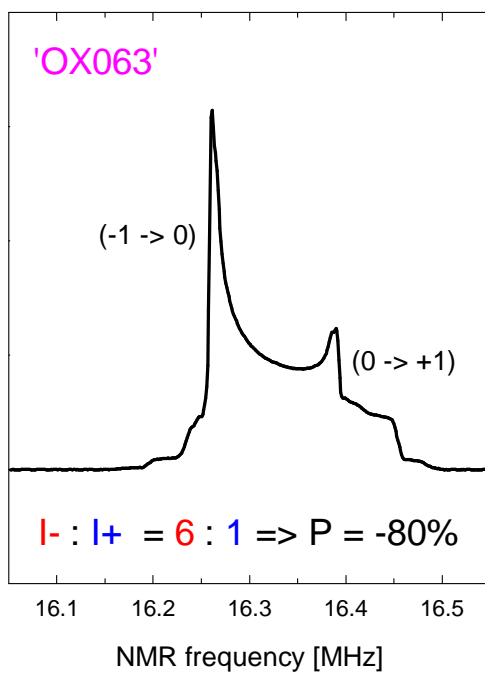
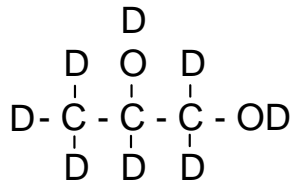
Results on trityl doped hydrocarbons

The deuteron NMR signal with quadrupol interaction

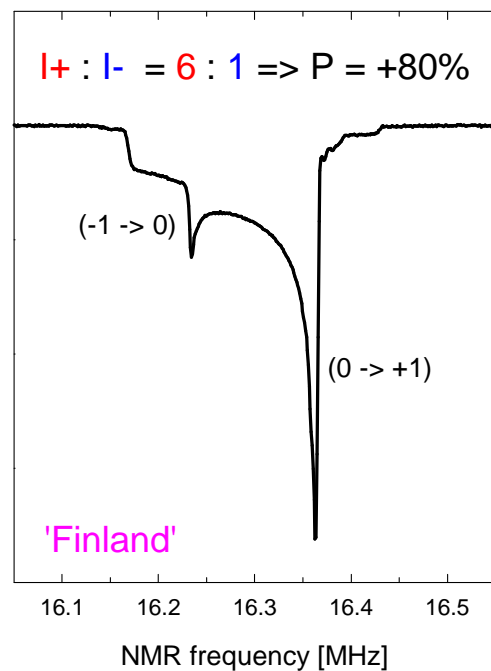
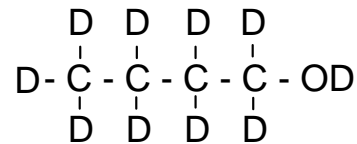


The maximum polarizations at $B = 2.5 T !!!$

D-Propandiol :

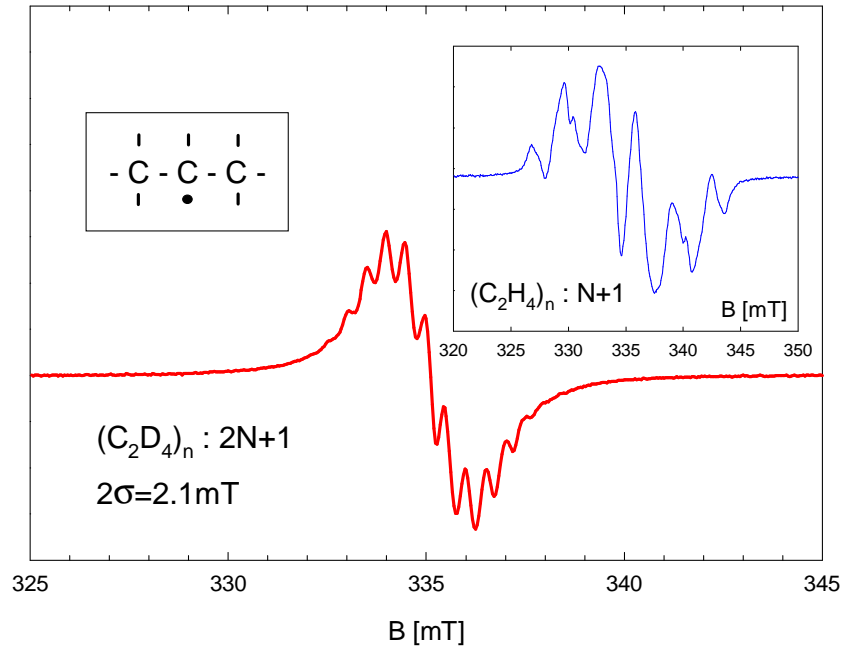


D-Butanol :



Results on radiation doped polyethylene

From X-band EPR: Defekt is the alkyl radical



No.	Irrad. in	$N_S [10^{19}/g]$	$P_{max}^+ [%]$	$P_{max}^- [%]$	τ [min] (1K)
1	LA	5.9 ± 0.4	τ too short		-
2	LA	4.3 ± 0.3	16.2	-32.7	2.5
3	LA	2.3 ± 0.2	18.8	-32.0	16.5
4	LN	2.9 ± 0.3	20.4	-31.1	14
5	LA	1.6 ± 0.2	No higher P exp.		-
CH ₂	LA	4.4 ± 0.3	45.0	-46.0	-

Why is the maximum polarization that low ?

- EPR line HFS dominated, width \sim D-butanol
- What does the strong \pm asymmetry tell us?
- Structure of plastics, chain length \sim 10.000

Summary

- Proton target materials can be polarized almost completely

– under almost every condition:

$$2.5 T / 100 mK \quad , \quad 5 T / 100 mK \quad , \quad 5 T / 1 K$$

– independently of the actual material

H-butanol, H-propanediol, NH₃, LiH, ...

- So far this was not the case for most of the deuterated materials

$$2.5 T / 100 mK : \quad \text{D-Butanol: } 35 - 45 \% \\ \text{ND}_3: \quad \quad \quad \sim 30 \%$$

– 'Low' magnetic moment of the deuteron

– Use of radicals sufficient to cool protons

- Situation somewhat better for radiation doped ⁶LiD

$$P \sim 50 - 55 \%$$

⇒ **Radicals optimized for cooling of deuterons**

How do those radicals look like ?

- **Theory:**

Minimize the non-Zeeman heat capacity

- **Recipe:**

- Minimize the inhomogeneous interactions until

$$D_{inhom} \simeq \nu_D$$

- Optimize the hom. (dipolar) interaction

$$D_{hom} \simeq \frac{(g_e \mu_B)^2}{\hbar} N_S$$

to allow for spectral diffusion

- **In practice:**

- Irradiation if HFS interaction weak: $\mu, |\Psi_e|$
- Use 'narrow EPR radicals': **Trityl radical**

Present status:

Material	Doping method	Polarization	Field
⁶ LiD	Irradiation	> 50 %	2.5 T
D-butanol	Irradiation	55 % 71 %	2.5 T 5.0 T
D-butanol D-propanediol	chem. dop. with trityl	79 % 81 %	2.5 T 2.5 T