Highest Polarizations in Deuterated Solid State Target Materials

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1. Dynamic Nuclear Polarization
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3. Magnetic field dependence of D-Butanol
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The Dynamic Nuclear Polarization (DNP)

Basic principle:
State of lowest energy is favoured

$$P = \frac{\langle I_z \rangle}{I_z^{max}} = \mathcal{B}_I\left(\frac{\mu B}{2kT}\right) \overset{2.5\,T,\,1K}{=} 0.25\,\%\ \text{(Proton)}$$

$$= 0.05\,\%\ \text{(Deuteron)}$$

⇒'Brute Force': Maximize B and Minimize T

Trick:
Transfer of polarization from particles with high μ

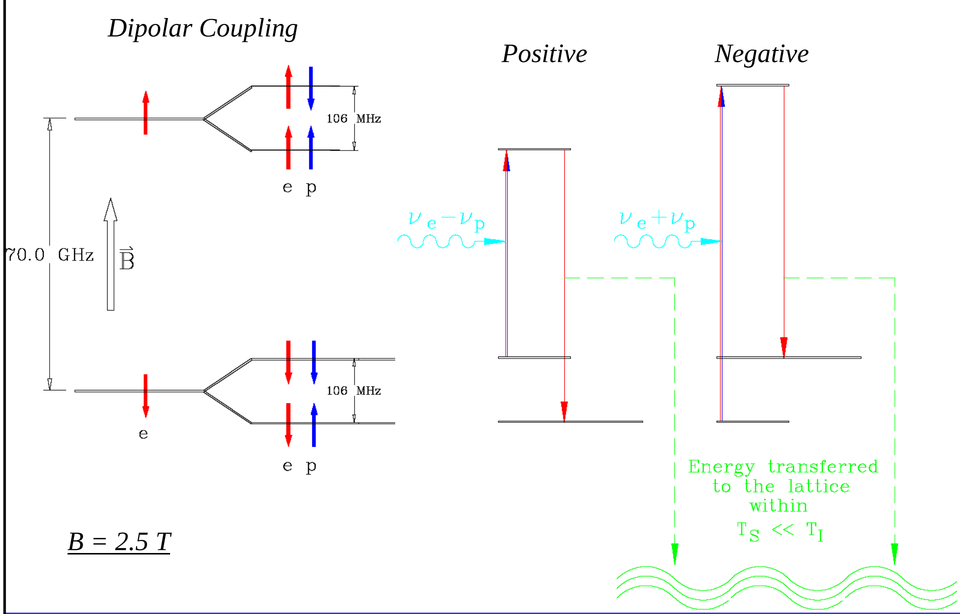
$$\text{Electrons:}\quad P \overset{2.5\,T,\,1K}{=} 93\,\%$$

Doping with paramagnetic centres:

10^3 nuclei fed by 1 unpaired electron from:

- Chemically stable radical → Liquids
- Radiation induced defects → Solids

The Solid State Effect

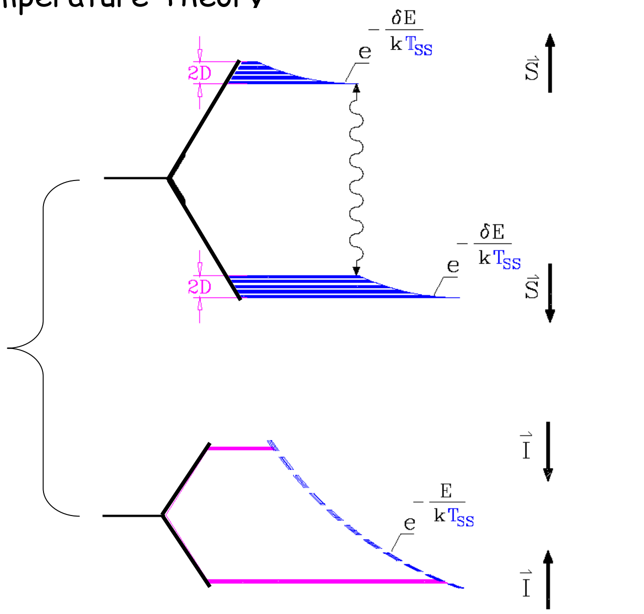


DNP in the Spin Temperature Theory

Many electrons
in an external field

$2D \geq h\,\nu_p$
magnetic
electron – nucleus
interaction

Protons
in an external field
$\mu_p = \mu_e/660$



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

Obvious: Decrease its Zeeman temperature

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

And how to do that ?

Theory: Minimize the dipolar width D of the electron Zeeman states

$$D \sim B_l \simeq g_e \mu_B N_S$$

Is it enough to minimize N_S ? - NO!

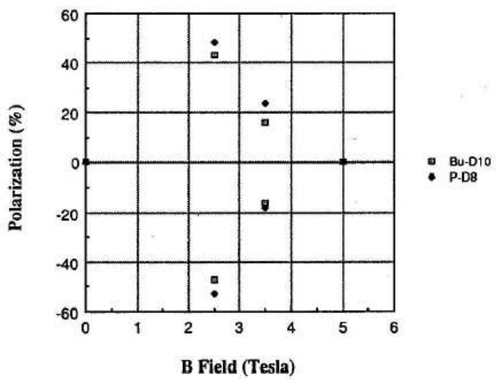
In practice: Inhomogeneous interactions present !

- Anisotropy of the g-factor
- Hyperfine interactions

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

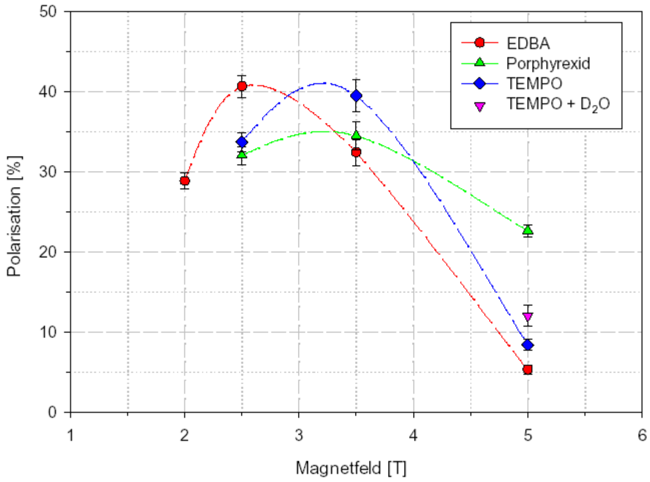
Magnetic field dependence of conventionally doped D-Butanol

First hint reported by
S.Trentalange et. al.
Proc. 9th Int. Symposium
on High Energy Spin Physics,
Bonn 1990



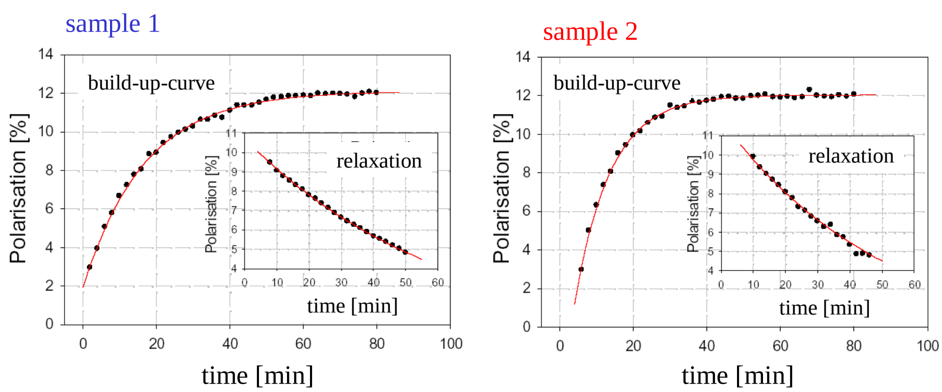
$$P_I = \mathcal{B}_I\left(\frac{g_I \mu_K B}{2T_Z^I}\right) = \mathcal{B}_I\left(\sim B^2\right) \,!$$

Systematic investigations on chemically doped D-Butanol Bochum 2001



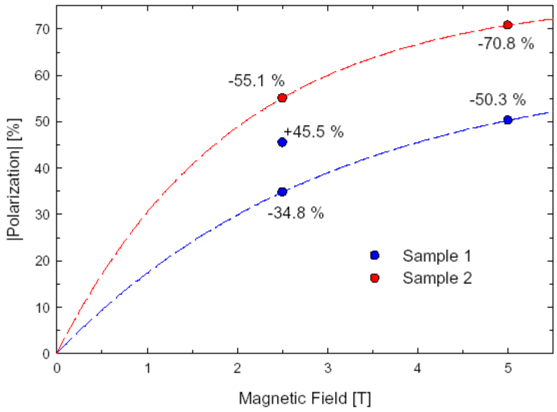
Doping method responsible or material itself ?

Test: Paramagnetic doping via irradiation at 90K (liqu. A)
Sample 1: 1 • 10^{19}e/g , Sample 2: 2•10^{19}e/g



With the same setup the results at 2.5T and 1K: ↔ 7 – 8% for chem. doped

Results at dilution temperature:



under same condition we have got: 35% for chem. doped butanol

Doping method is responsible for the reached polarization!

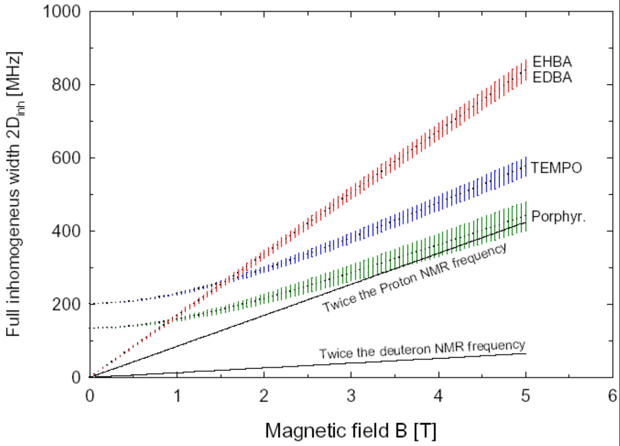
Magnetic field dependence of conventionally doped D-Butanol:

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

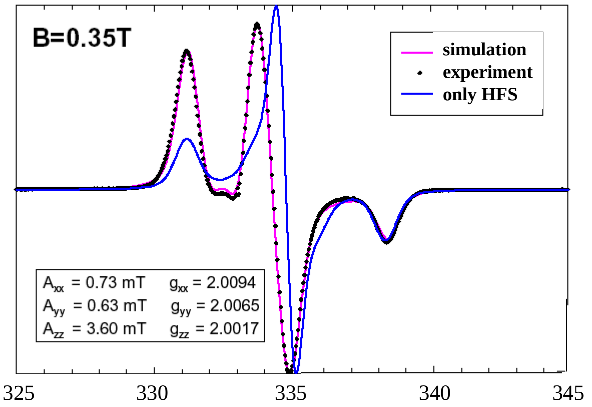
From simulations of X-Band EPR signals:

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

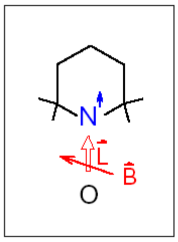
- Dipolar int. is too weak to connect the spin packets
  ⇒No or hindered spectral diffusion
  ⇒No common non-Zeeman temperature



EPR of TEMPO in n-Butanol: Experiment & Simulation

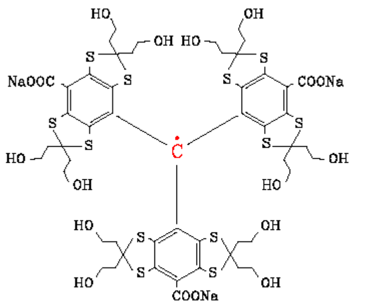


B [mT] at 9.38 GHz



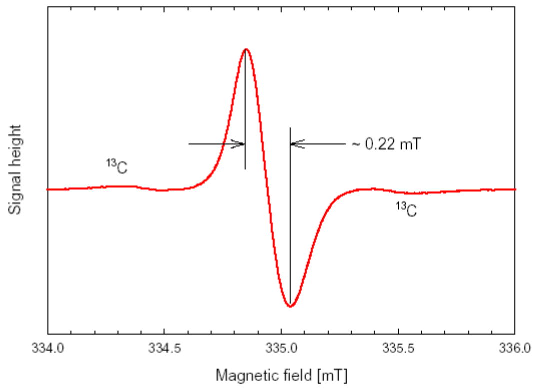
Dream: Chemically stable radical with a very narrow EPR line

The trityl radical

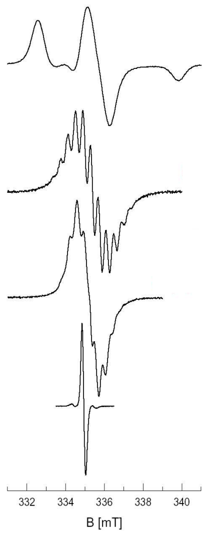


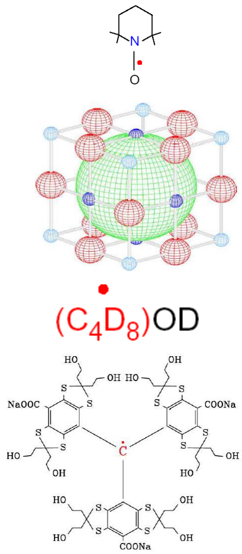
OX063: $C_{52}H_{60}Na_3O_{18}S_{12}$ MW: 1426.78

The X-band EPR absorption signal



EPR lines of dif. radicals in D-Butanol at x-band





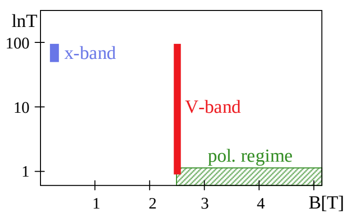
Additional to the standard equipment of

- high magnetic field
- low temperature refrigerator
- microwave field for DNP
- NMR for pol. measurement

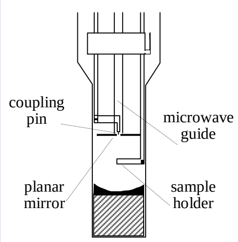
now: EPR-apparatus for paramagnetic dopant studies (Bochum: > 1997)

Standard: X-band spectrometer

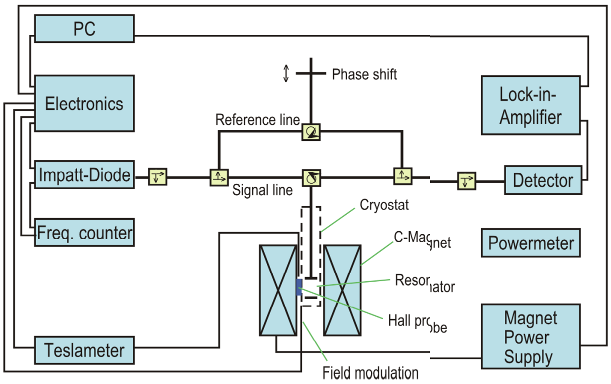
↳ 9.35 GHz at 0.35T (77K)

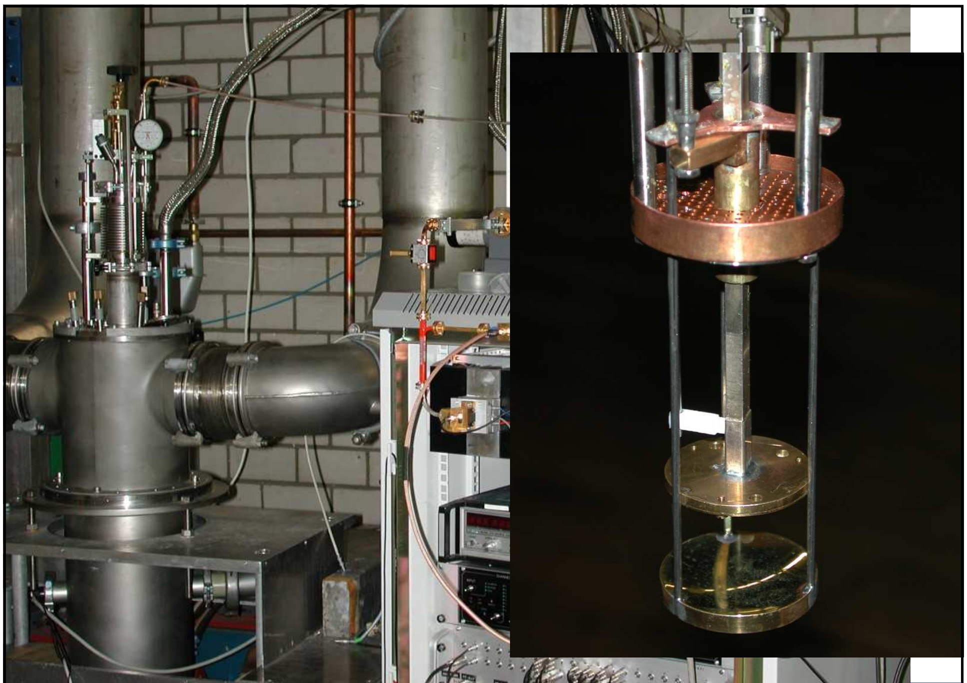


new in Bochum (2004)
V-band EPR-spectrometer
↳ 70GHz at 2.5T
(300K → 1K)

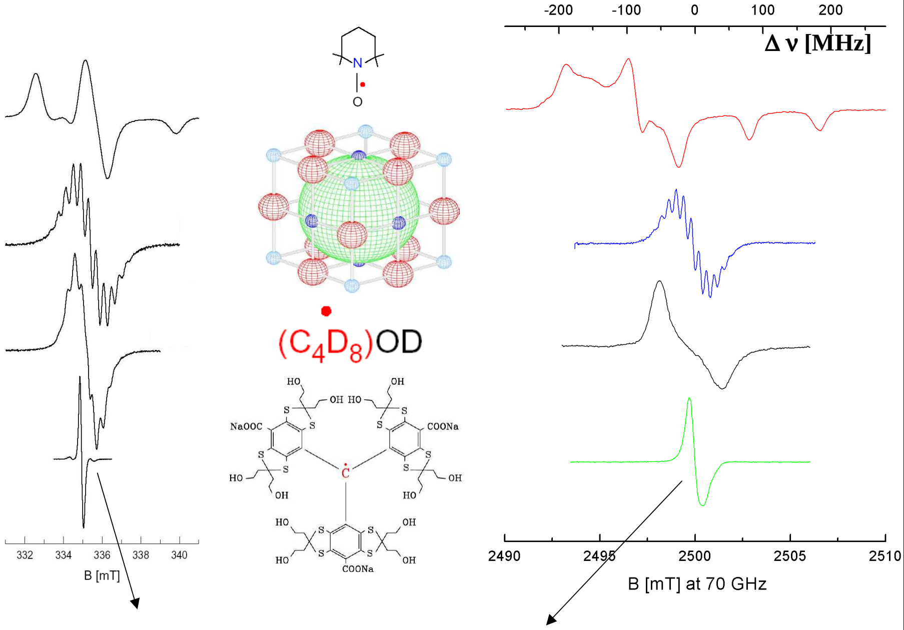


Cryostat cavity with resonator





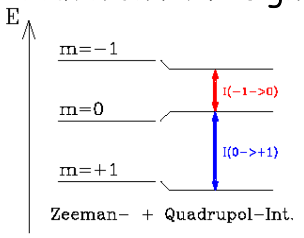
EPR lines of dif. radicals in D-Butanol

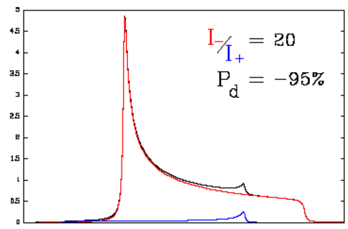


Width ≈ 0.22 mT

Width ≈ 0.7 mT ≙ 19 MHz ⇒ $\Delta g/g \approx 1.8 \cdot 10^{-4}$

The deuteron NMR signal with quadrupol interaction

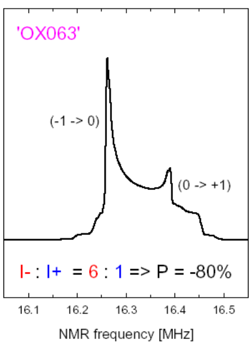




The maximum polarizations at **B = 2.5T !!!**

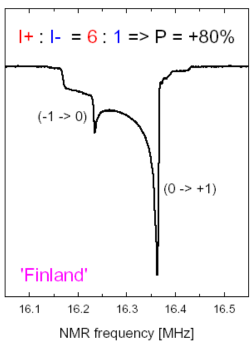
D-Propanediol :

```
      D
   D  O  D
D- C - C - C - OD
   D  D  D
```

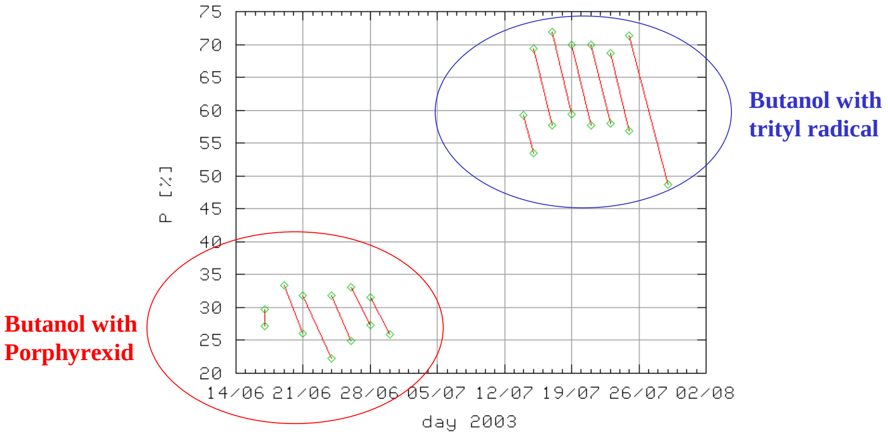


D-Butanol :

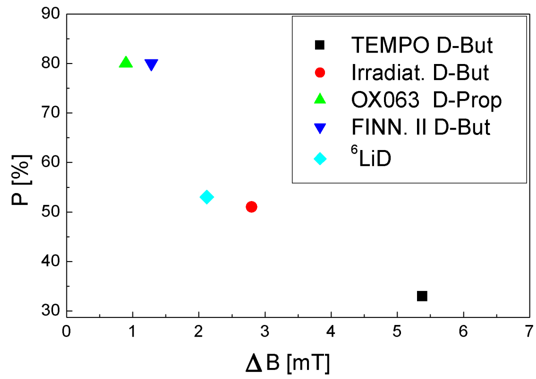
```
   D   D   D   D
D- C - C - C - C - OD
   D   D   D   D
```



Polarization path Mainz 2003



Polarization versus FWHM of the integrated EPR line



The irradiated probe ^{6}LiD is shown for comparison.

Summary

- Proton target materials can be polarized almost completely

  - under almost every condition:

    2.5 T / 100mK , 5 T / 100mK , 5 T / 1K

  - independently of the actual material

    H-Butanol, H-Propanediol, NH_3, LiH, ...

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

  2.5 T / 100mK : D-Butanol: 35 - 45%

  ND_3: ~ 30%

  - 'Low' magnetic moment of the deuteron
  - Usual radicals sufficient to cool protons

- Situation somewhat better for radiation doped 6LiD

  P ~ 50 – 55%

  $\boxed{\Rightarrow \text{Radicals optimized for cooling of deuterons}}$

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	$79\,\%$ $81\,\%$	$2.5\,T$ $2.5\,T$