Development of deuterated polymer polarized targets materials

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Content

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2. The trityl radicals – progress for deuterated target materials

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   — trityl radical doped CD_2 C_8D_8

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Polarized Solid Targets

- Used in high energy particle physics experiments for studying the nucleon structure since about 50 years
- Present target materials for high energy spin physics experiments:

NH_3	COMPASS experiment at CERN (160-190GeV)
^6LiD	COMPASS experiment at CERN (160-190GeV)
CH_2 , CD_2	GDH experiment in SPRING-8
Butanol	Experiments at ELSA (Bonn < 3.0GeV) and
D-butanol	MAMI (Mainz < 1.5GeV) accelerators

- Physics observable determined by single or double asymmetry measurements A

$$A = \frac{1}{P_T} \cdot \frac{1}{f} \cdot \frac{N\uparrow - N\downarrow}{N\uparrow + N\downarrow}$$

$$f = \frac{\#\text{polarizable particles}}{\#\text{all particles}}$$

P_T : target polarization

$N\uparrow,\downarrow$: counting rates for spin $\uparrow,\downarrow$ to magnetic field

$$f = 0.1 \ldots 0.3 \ldots 0.5$$

DNP solid targets

The Principle of Dynamic Nuclear Polarization

- **Thermal Equilibrium (TE)**

$$P = \frac{\langle I_Z \rangle}{I_Z^{\max}} = B_I\left(\frac{\mu B}{2kT}\right) \quad \propto \left(\frac{B}{T}\right)$$

B/T	P_p[%]	P_d[%]	P_e[%]
2.5T/1K	0.25	0.05	93
15T/10mK	91	30	100

- **Dynamic Nuclear Polarization (DNP)**
  - Transfer of polarization from paramagnetic electrons to the nuclei
  - Parameters of DNP: temperature; magnetic field; microwave power; electron relaxation time; the relation of EPR linewidth and nuclear Larmor frequency…
- **Doping with paramagnetic electrons:**

~ 10^3 nuclei feeded by 1 unpaired electron from:

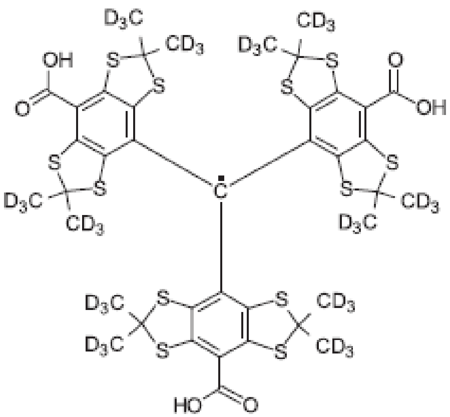
- Chemically stable radical → Solids
- Radiation induced defects → Solids

In the 1970 already 80-90% in protonated materials

Until 2003 40-50% in deuterated materials

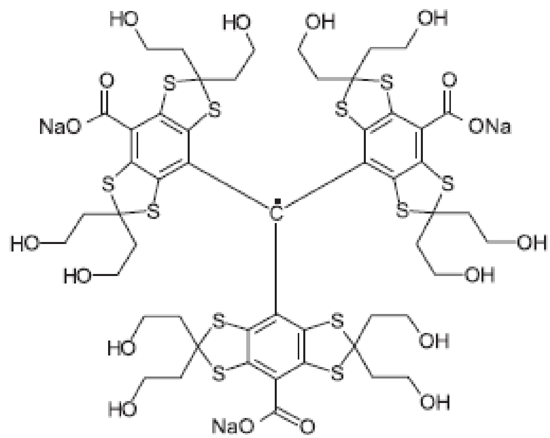
The Trityl Radicals (Malmö Group(Sweden); General Electric)

— Important Progress for Deuterated Materials



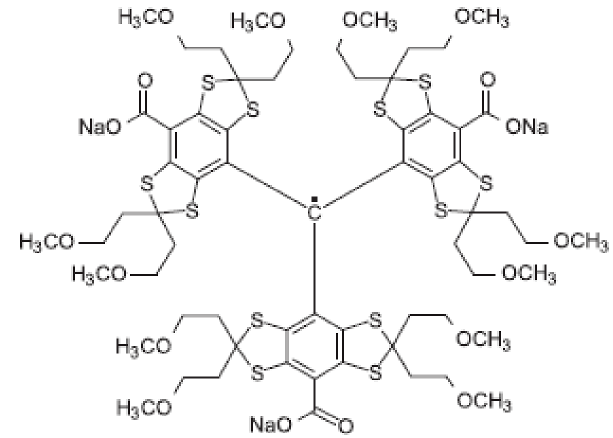
Finland D36'(AH110355 deutero acid form)used for butanol-d10

Deuteron : up to 79% at 150mK/2.5T



Ox063(AH100136 sodium salt)used for propandiol-d8

Deuteron: up to 81% at 150mK/2.5T



Ox063Me (AH 111 501 sodium salt) used for pyruvic acid

^{13}C: up to 74% at 900mK/5.0T

St.Goertz et al.NIMA 526 (2004)43

W.Meyer, et al., NIM A 631 (2011) 1

Important parameter: EPR linewidth

- Zeeman Energy of a free electron

$$E_Z = -g_e \mu_B \vec{S} \cdot \vec{B}$$

- Contributions to the Electron Zeeman linewidth

$$\Delta E_{tot} = \underbrace{\mu_B (\vec{S} \cdot \hat{g} \cdot \vec{B}) + (\vec{S} \cdot A \cdot \vec{I})}_{in\,\mathrm{hom}} + \underbrace{E_D}_{\mathrm{hom}}$$

Hom. ⟶ Dipol-Dipol interaction ⟶ between electrons

Inhom. ⟶ Hyperfine interaction ⟶ magnetic nuclei ⟶ indep. of B_0

Inhom. ⟶ g-factor anisotropy ⟶ crystal field ⟶ dep. of B_0

- Try to minimize the energy spread ΔE_{tot}
  - Find a suitable doping method ⟶ $\Delta E_{HFS} \sim \Delta E_D$
  - Try radiation doping if only low $\boldsymbol{\mu}$ nuclei

Bochum measurements

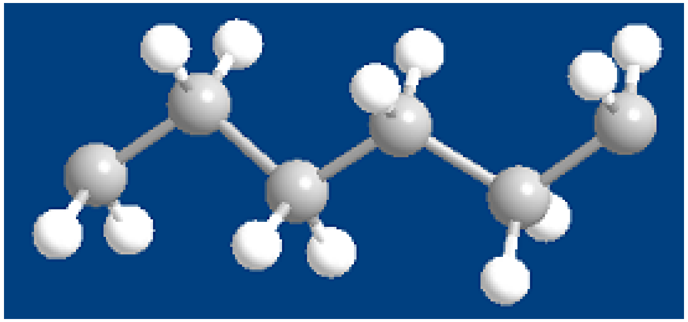
Material	Radical	$\Delta g/\bar{g}$ [10^{-3}]	FWHM [mT]	at 2.5T $P_{D,max}$ [%]
D-Butanol	EDBA	5.98 ± 0.03	12.30 ± 0.20	26
D-Butanol	TEMPO	3.61 ± 0.13	5.25 ± 0.15	34
D-Butanol	Porphyrexide	4.01 ± 0.15	5.20 ± 0.23	32
$^{14}ND_3$	$^{14}\dot{N}D_2$	$\approx 2 \dots 3$	4.80 ± 0.20	44
$^{15}ND_3$	$^{15}\dot{N}D_2$	$\approx 2 \dots 3$	3.95 ± 0.15	-
D-Butanol	Hydroxyalkyl	1.25 ± 0.04	3.10 ± 0.20	55
^{6}LiD	F-center	0.0	1.80 ± 0.01	57
D-Butanol	Finland D36	0.50 ± 0.01	1.28 ± 0.03	79
D-Propandiol	Finland H36	0.47 ± 0.01	0.97 ± 0.04	-
D-Propandiol	OX063	0.28 ± 0.01	0.86 ± 0.03	81

J. Heckmann, et al., Phys. Rev. B 74 (2006) 134418.

Result: The smaller the EPR linewidth, the higher the deuteron polarization value.

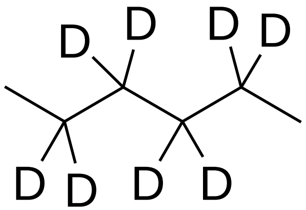
Introduction to D-polymer materials

Poly(Ethylene-D4) CD_2

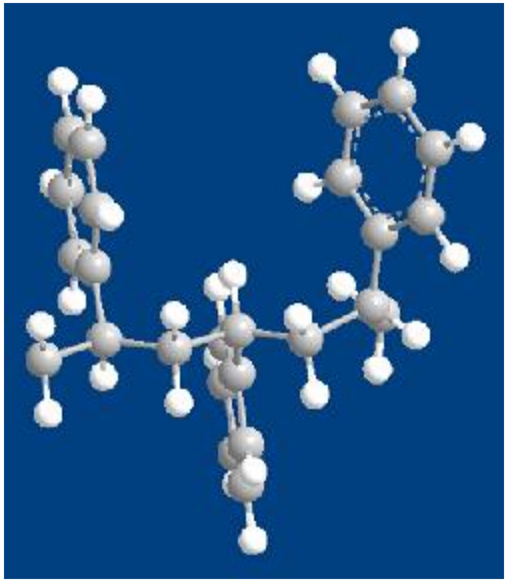


dilution factor

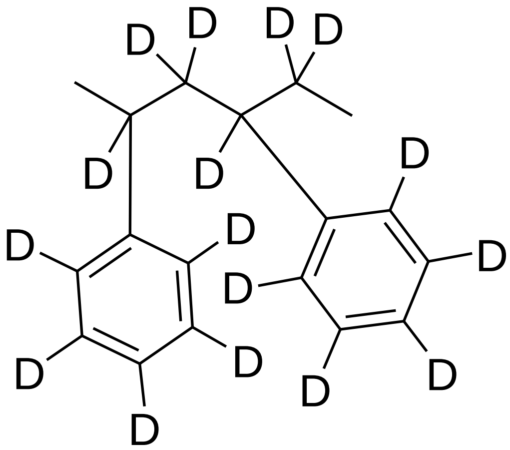
$$f = \frac{8 \text{ from D}}{24 \text{ from C} + 8 \text{ from D}} = 0.25$$



Styrene-D8, polymerized C_8D_8



$$f = \frac{16 \text{ from D}}{96 \text{ from C} + 16 \text{ from D}} = 0.14$$



Motivation to use D-polymer materials

- **Spin physics**
  - Thin targets for scattering experiments at low energies
  - Polarized scintillator targets
- **Merits of CD_2, C_8D_8**
  1. High purity of D 0.98, 0.99
  2. D with spin 1 and C with spin 0
  3. Easy formable to any thickness at room temperature
- **Up to now the maximum polarizations of D-polymer**
  1. D-polyethylene **CD_2** : Paramagnetic Center---Irradiation

     35% at 6.5T/1K

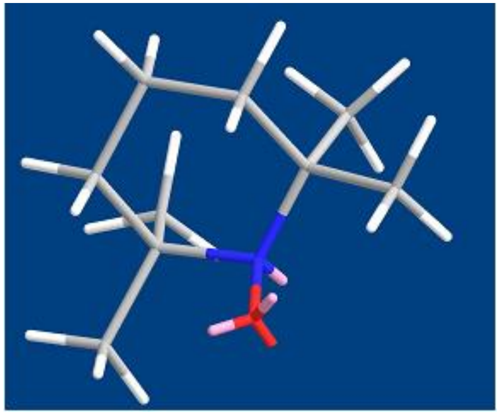
     D.G.Crabb, *Nucl. Instr. and Meth. A* 526, 56 (2004)
  2. D-Polystyrene **C_8D_8** : Paramagnetic Center---D-TEMPO

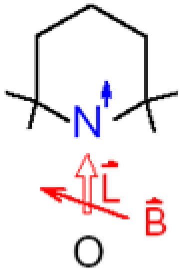
     40% at 2.5 T/100mK

     B.van den Brandt,et al., *Nucl. Instr. and Meth. A* 526, 53 (2004)

Doping methods for DNP

- **Mechanism of Dynamic Nuclear Polarization**
  Paramagnetic centers are needed
- **Chemical (Tempo, Trityl radical) doping**

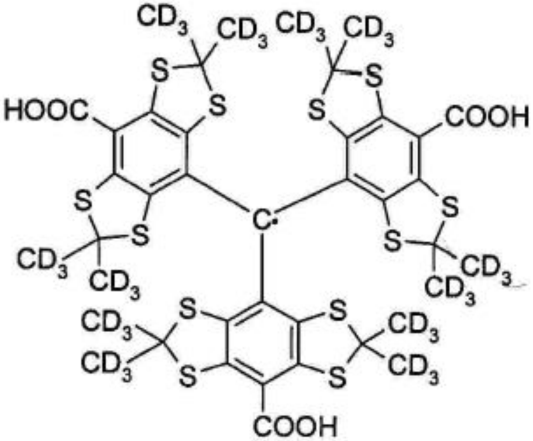




Melting point 36°C

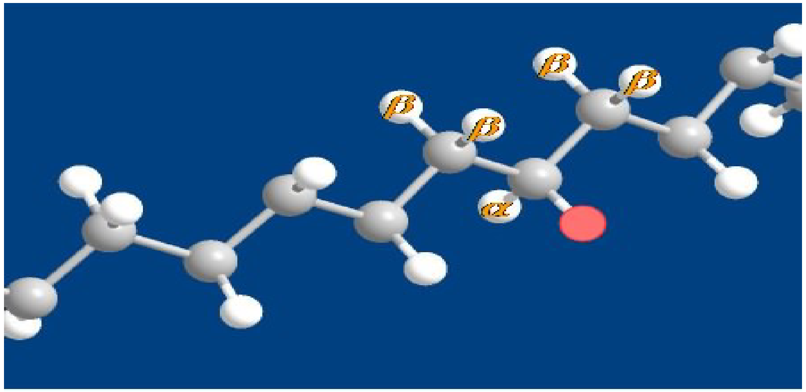
Boiling point 67°C

Tempo (stable free radical)

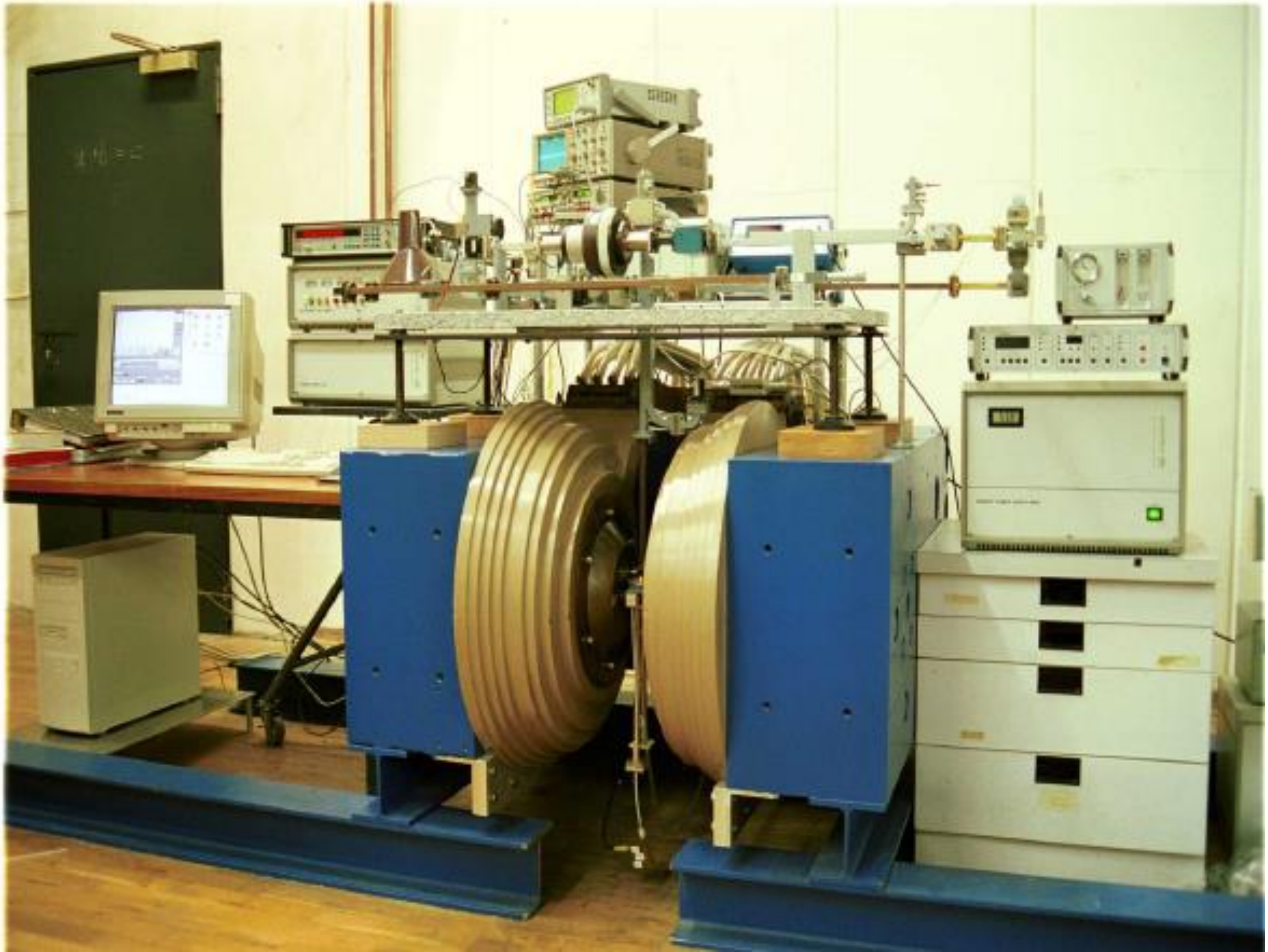


Trityl radicals Finland D36
(stable free radical)

- **Irradiation with electron beam**

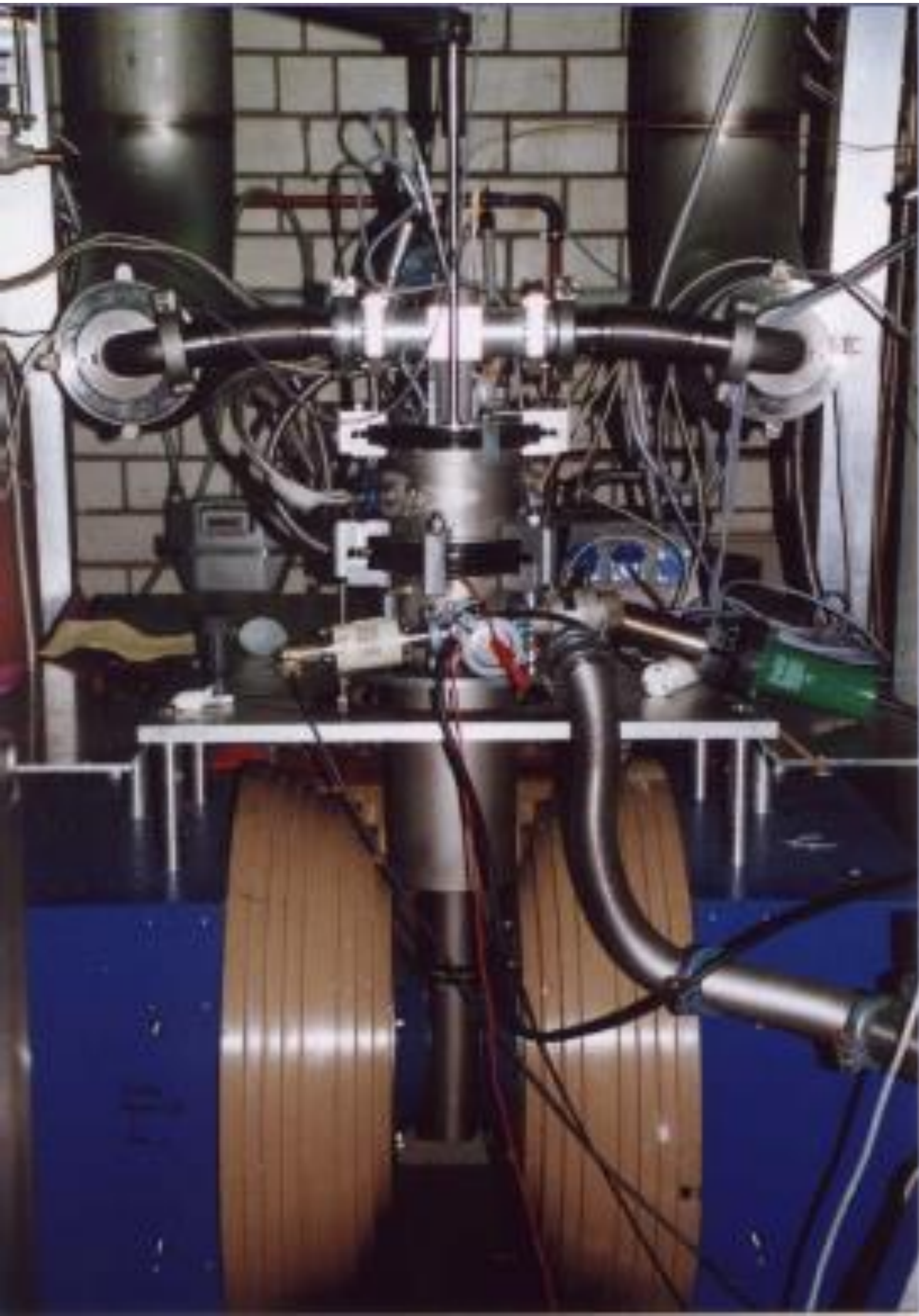


The Bochum EPR Apparatus

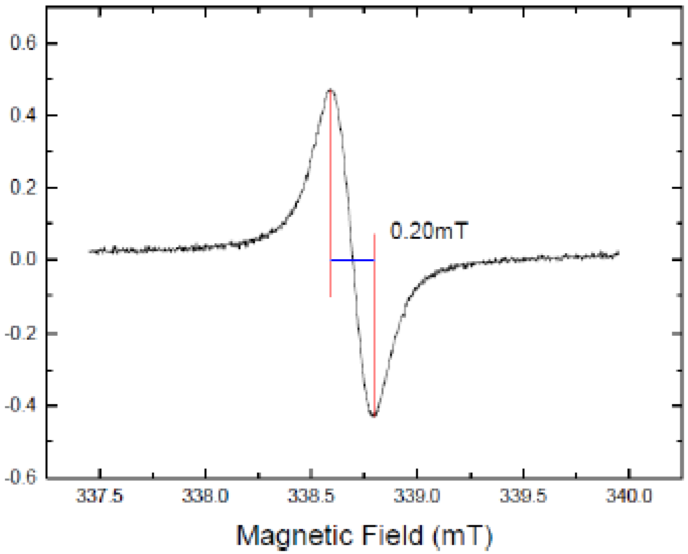


The Bochum DNP Apparatus

Magnet+cryostat

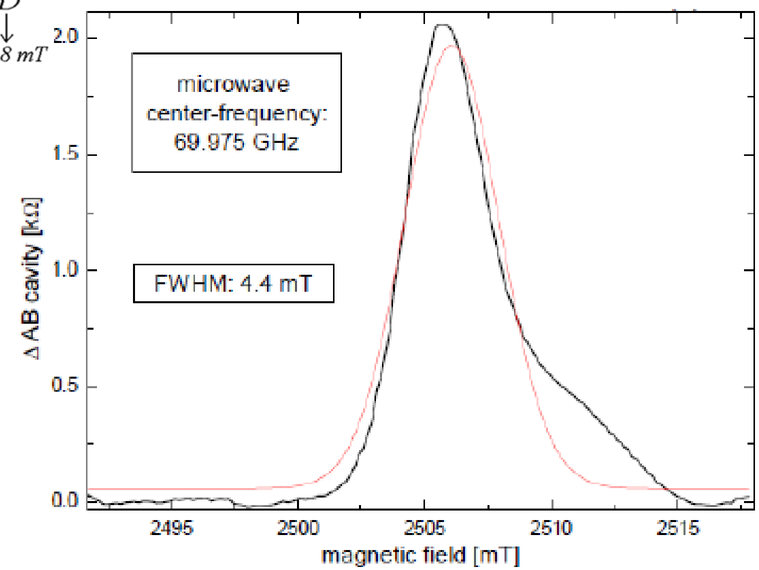


Preparation of trityl radical in CD_2

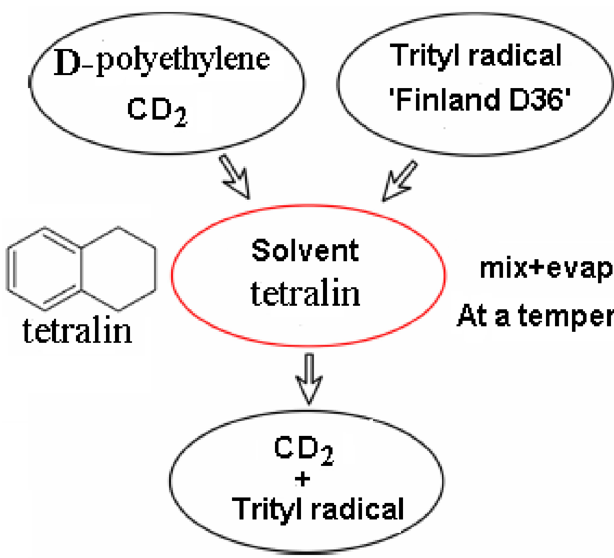


Deuteron $h\omega_I \le g_e u_B D$

$B = 2.5\ T$: 16.4 MHz 0.58 mT

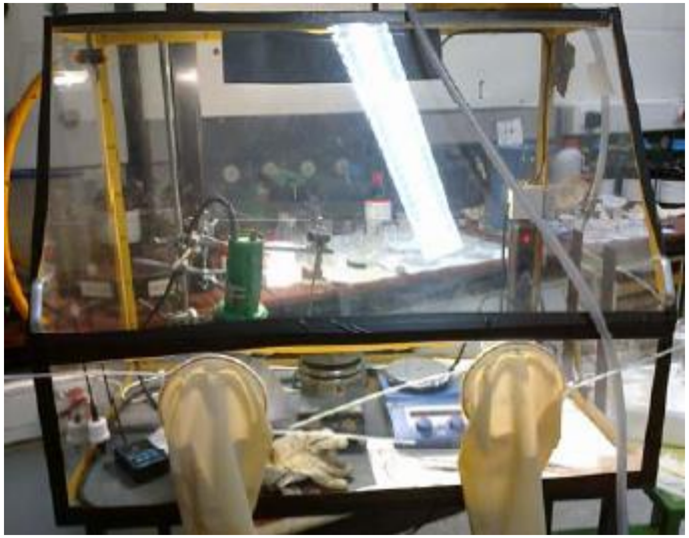


- Introduce Finland D36 Radicals in CD_2

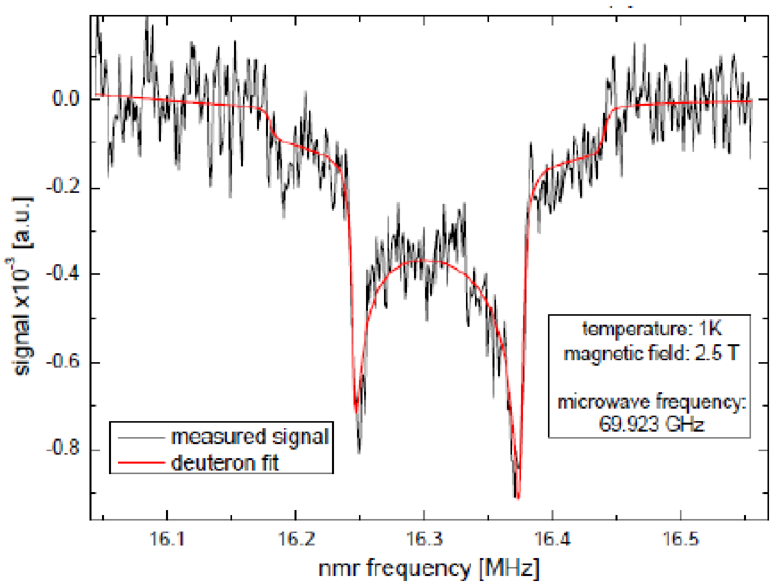


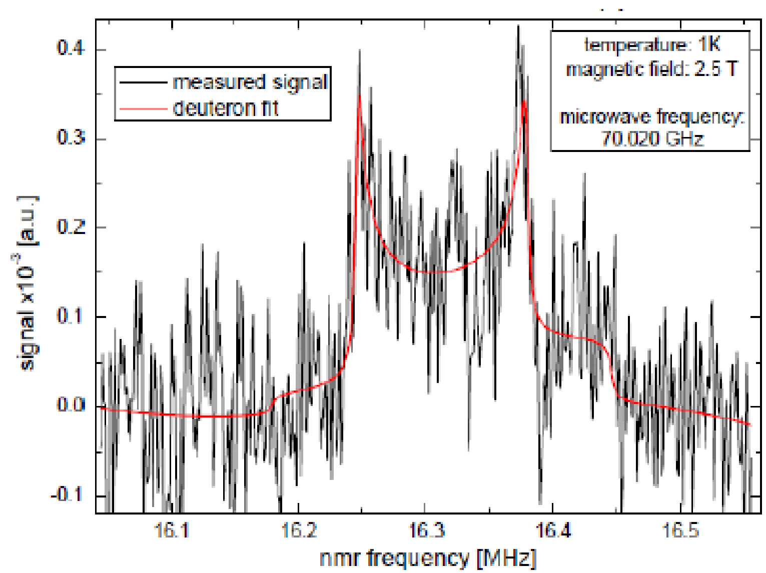
mix+evaporate in Nitrogen Box

At a temperature of 190 degree

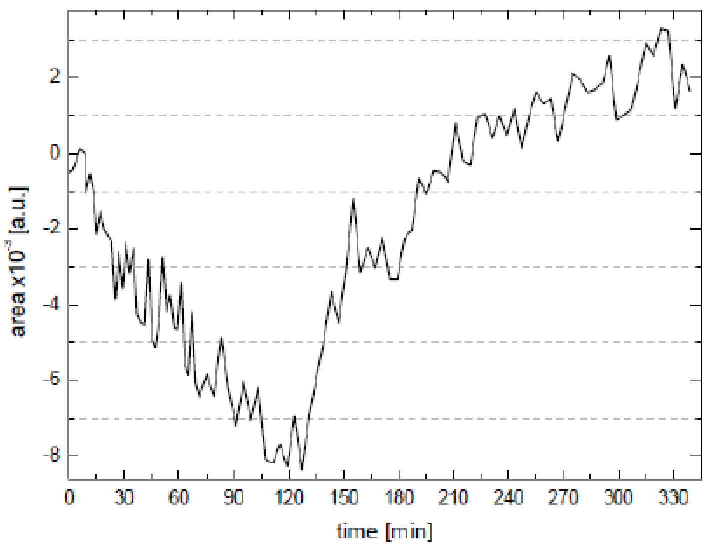


Polarization of Finland D36-doped CD_2

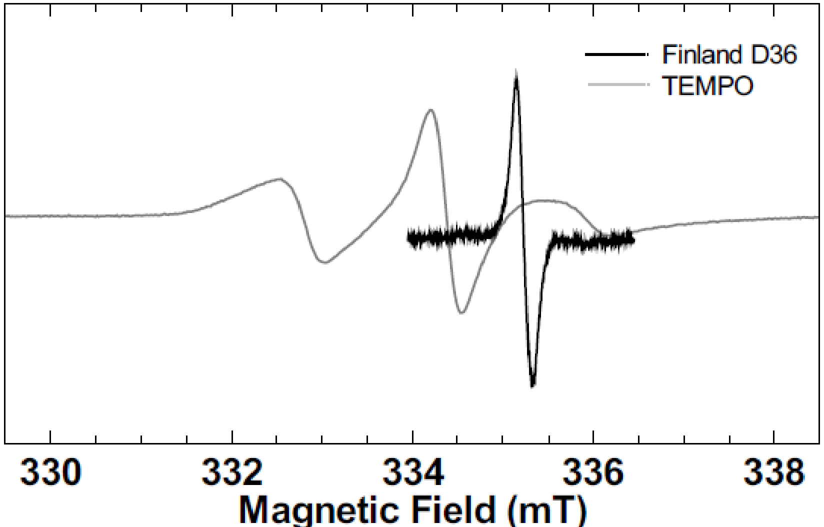


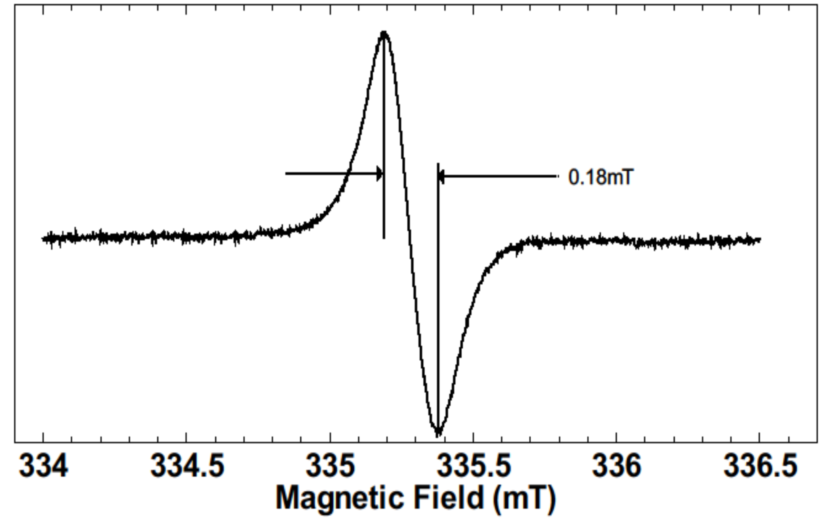


◆ The build-up curve shows that the unpaired electrons of the radicals are not well coupled with the CD_2 ,which leads to a low polarization.



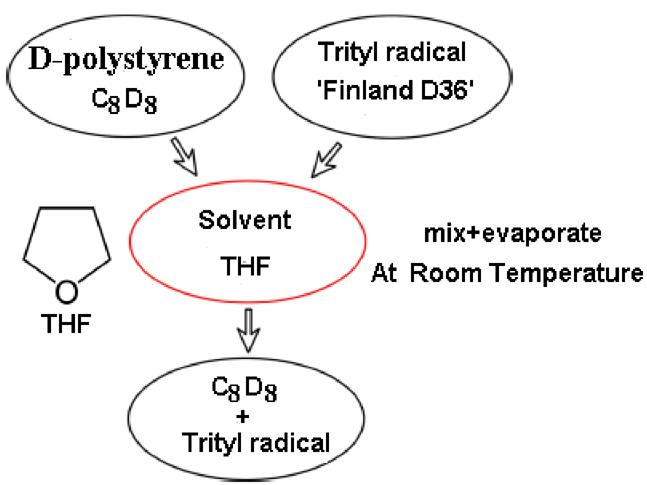
Preparation of trityl radical in C_8D_8





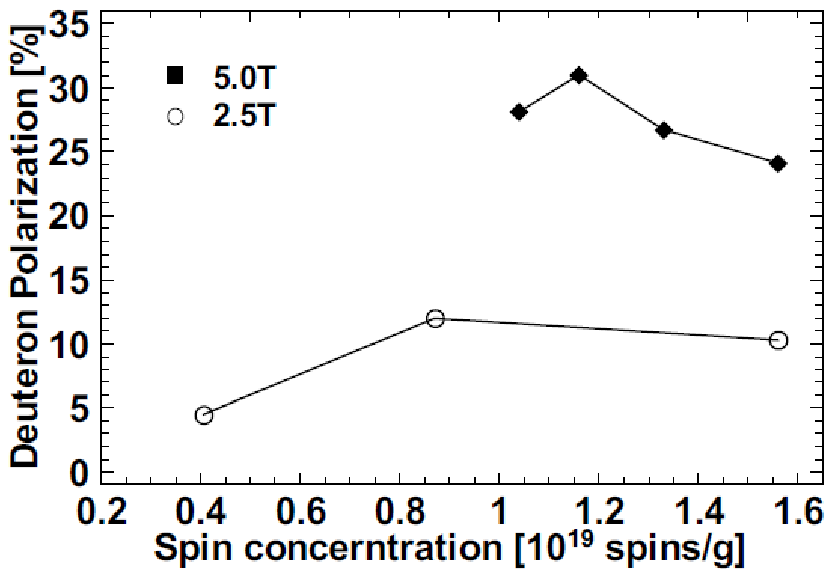
g-factor anisotropy: $\frac{\Delta g}{g} \square 3.0\times10^{-4}$

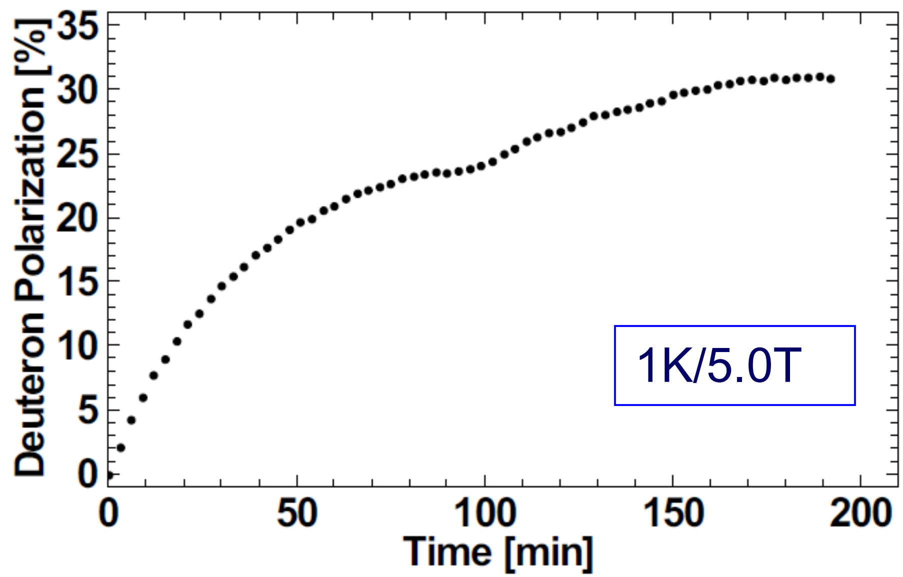
- Introduce Finland D36 Radicals in C_8D_8



Homogenous and transparent
A thin foil (70μm)

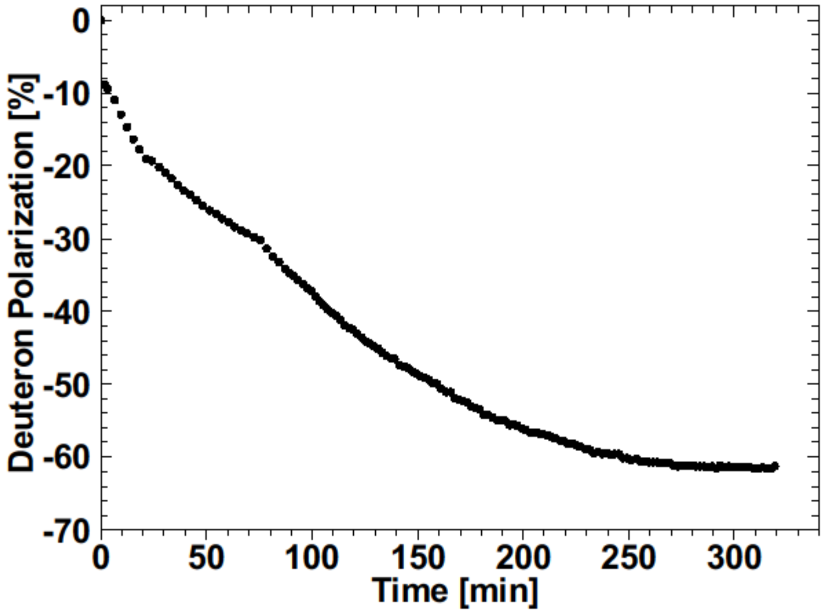
Polarization of Finland D36-doped C_8D_8

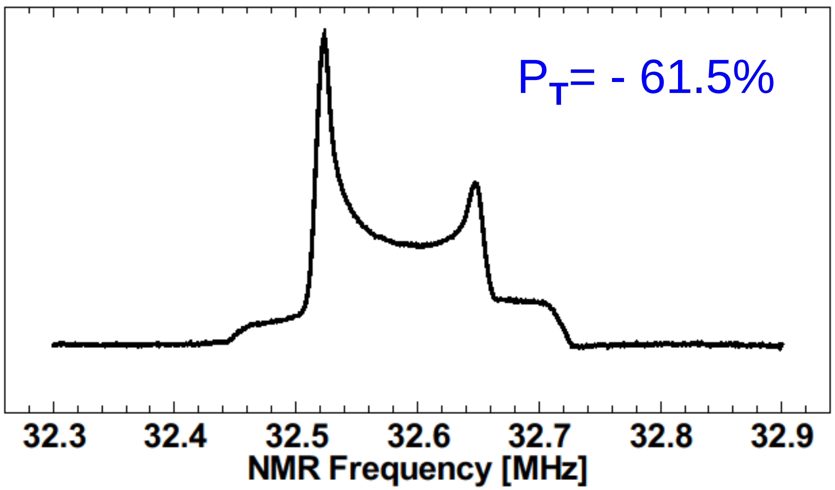




Spin conc. (spins/g)	Mag. Field (T)	$T_{build-up}$ (min)	$T_{1,d}$ (min)	Microwave Freq. (GHz)	d-pol. (%)	f^+-f^- (MHz)
0.87×10^{19}	2.5	76	80(T=1.01K)	69.877	+10.2	56
				69.933	-12.5	
1.16×10^{19}	5.0	47	139(T=0.99K)	139.736	+29.5	92
				139.828	-31.0	

Polarization of Finland D36-doped C_8D_8





Temperature = 400mK   Magnetic field= 5.0 T

Sample	MW (GHz)	d-pola. (%)	$T_{l,d}$ (min)	$T_{build-up}$ (min)
d-PS(98%-d)	139.723	+56.1	863	100
+Finland D36	139.825	-61.5		

$f_{d,NMR}$=32.6MHz

Li Wang, et al., NIM A 729 (2013) 36

Deuteron Polymer Polarizations

Material	Doping	Magnetic field(T): 2.5	5	Temperature	$T_{l,d}$	FWHM-bolometric
		Polarization(%)			(min)	(mT)
CD_2	Irradiation (8.0×10^{15} e^-/cm^2)	+21.1 -31.1		150mK		
CD_2	Tempo (3.0×10^{19} spins/cm^3)	+11.1 -9.3		330mK		
C_8D_8	Tempo (2.3×10^{19} spins/g)	+7.3 -7.7		1 K	12	6.73 *(2.5T)*
C_8D_8	Trityl (1.16×10^{19} spins/g)	+11.8 -12.3		1 K	24	1.87 *(2.5T)*
C_8D_8	Trityl (1.16×10^{19} spins/g)		+29.5 -31.0	1 K	139	3.06 *(5.0T)*
C_8D_8	Trityl (1.16×10^{19} spins/g)		-61.5 +56.1	400mK	863	

Conclusion & Outlook

1 Concerning CD_2 material, chemical doping method with TEMPO or Trityl Finland D36 , there are no remarkable polarization values obtained. The problem of Finland D36 seems to be its solubility into the solvent.

2 Chemically doped C_8D_8 with trityl radical can be polarized to more than 30% at 5.0T/1K and more than 60% at 5.0T/400mK with potential to values higher than 80%. But the dilution factor is much lower than that of C_8D_8.

3. A new approach for C_2D_2 with trityl radical doping is needed.

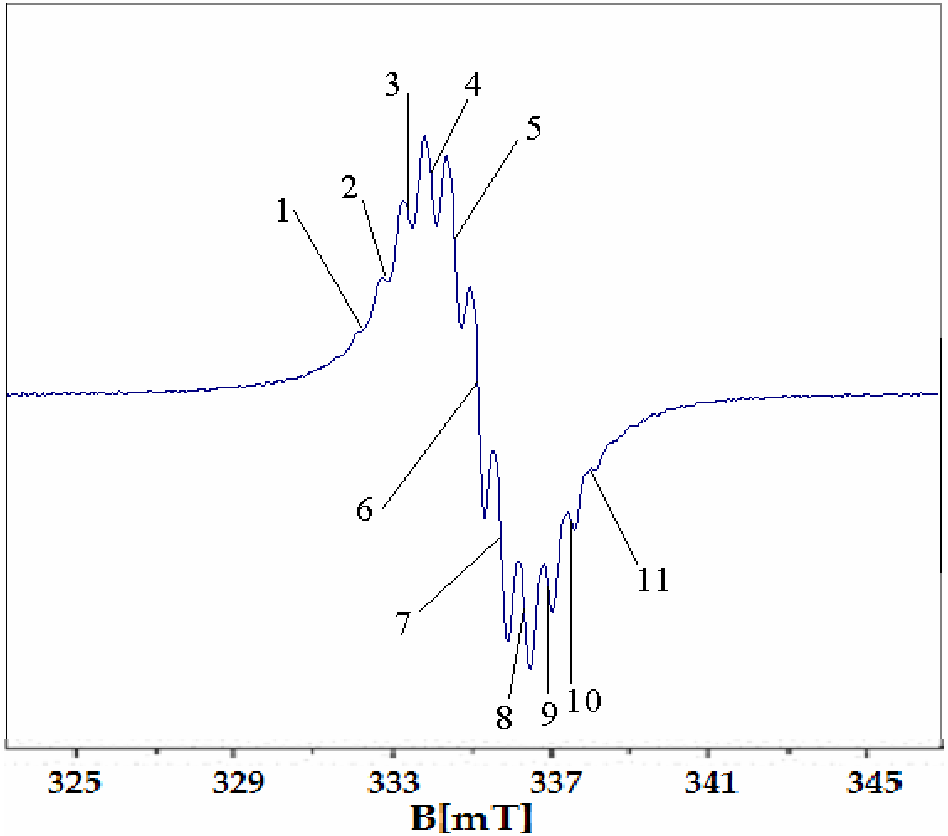
a new method called “mechanical doping”

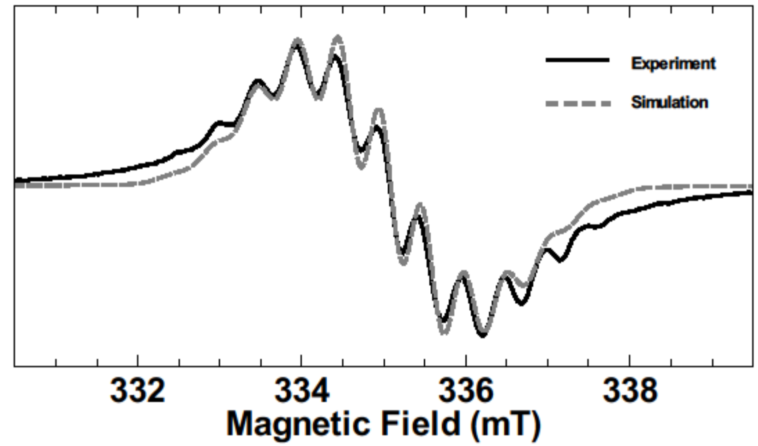
nano - level

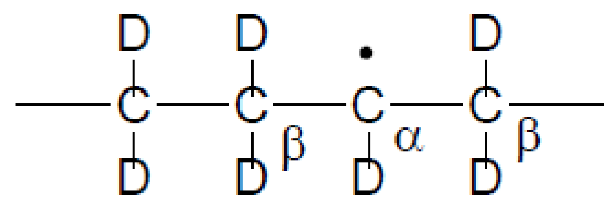
Ball mill P7
made by
Fritsch

Thanks for your attention!

EPR spectra of Radiation-doped CD_2







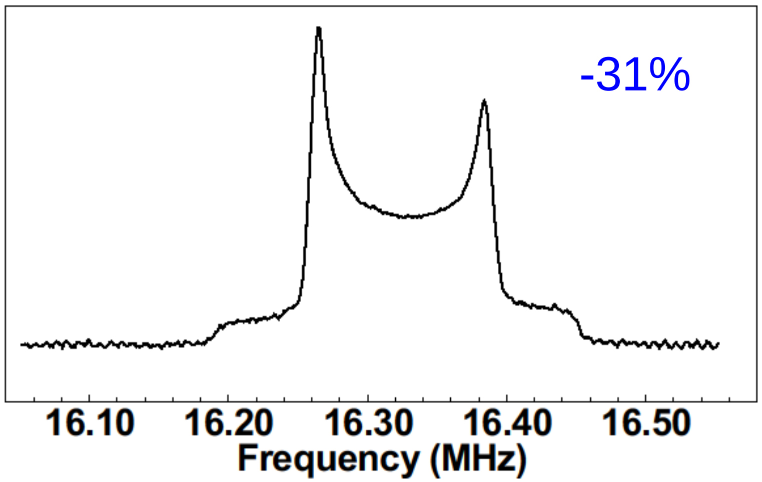
D_α =0.485 mT(1D);
D_β =0.480 mT(4D)
D(FWHM)=3.0±0.2 mT

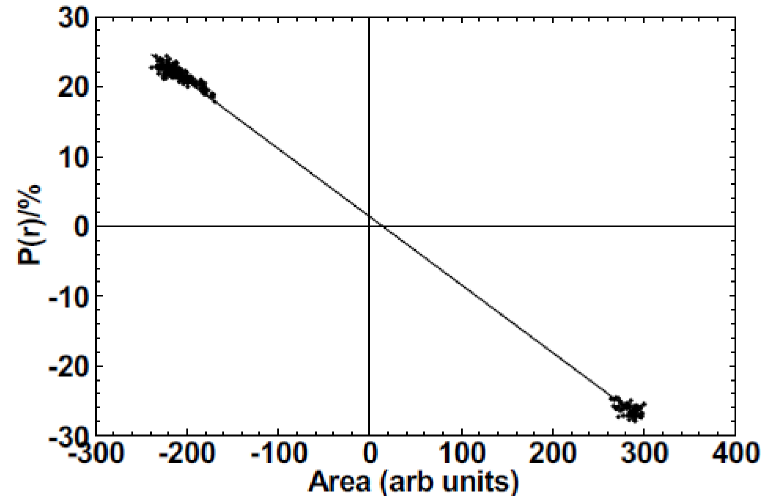
- According to HFS, 11-line pattern corresponds to 5 adjacent D,

  $m = 5, 4, 3 \cdots - 5$

Polarization of radiation-doped CD_2

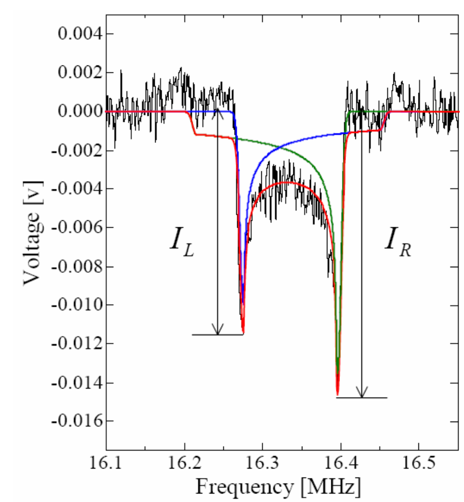
NMR Signal of Deuteron





Temperature = 150mK *Magnetic field=2.5T*

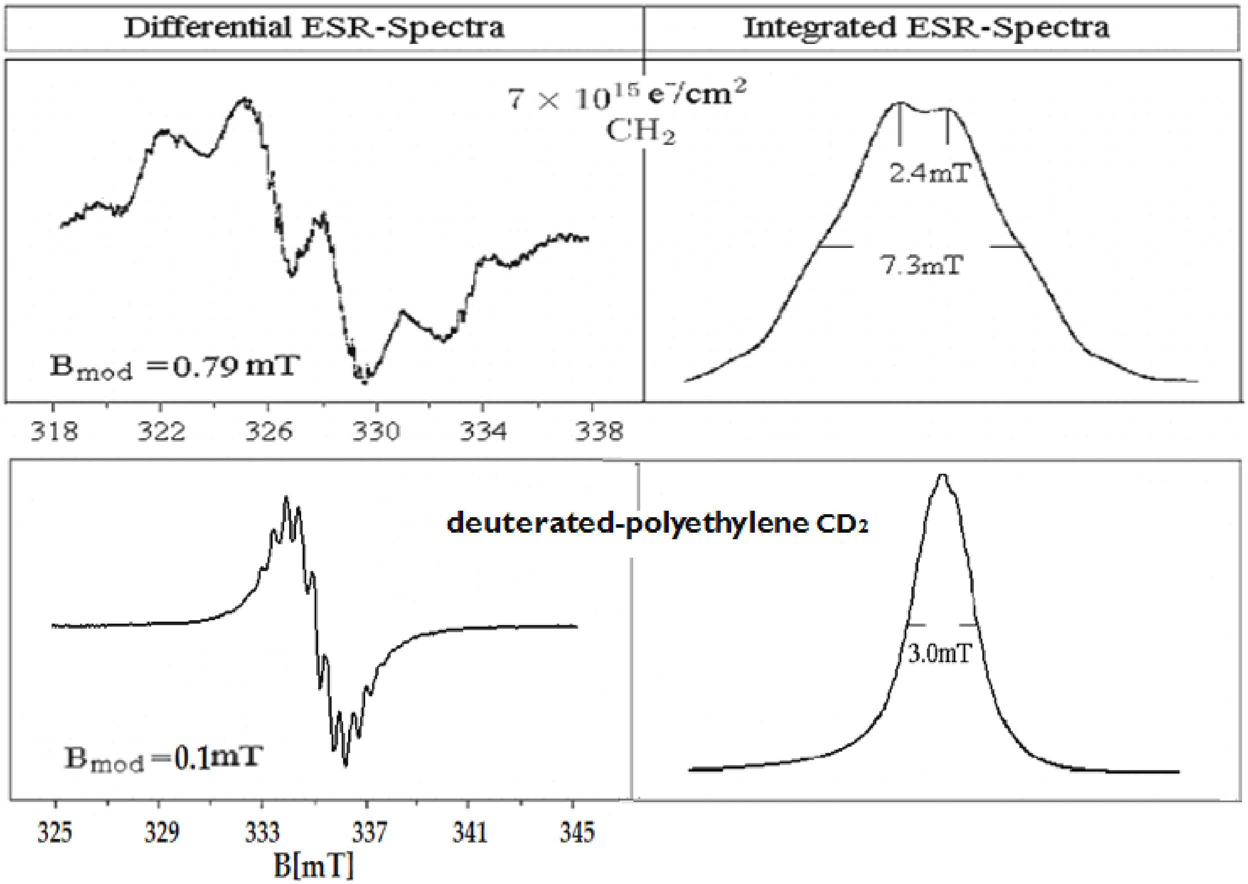
Dose [e^-/cm^2]	DNP Temp.[mK]	f_{mw}[GHz]	d-Pol[%]	$T_{build-up}$[min.]	f^+-f^- [MHz]
6.0×10^{15}	150	69.860	+21.0	110	215
		70.075	-31.0		



$$P = \frac{r^2 - 1}{r^2 + r + 1}, \quad r = \frac{I_R}{I_L}$$

*The large difference of positive and negative polarization values is still not understood.

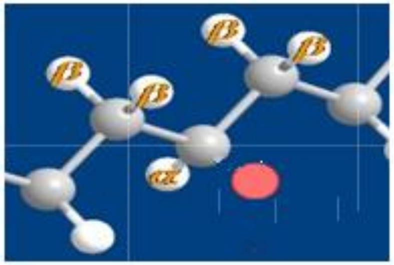
EPR spectra of irradiated CH_2 and CD_2 at 77K



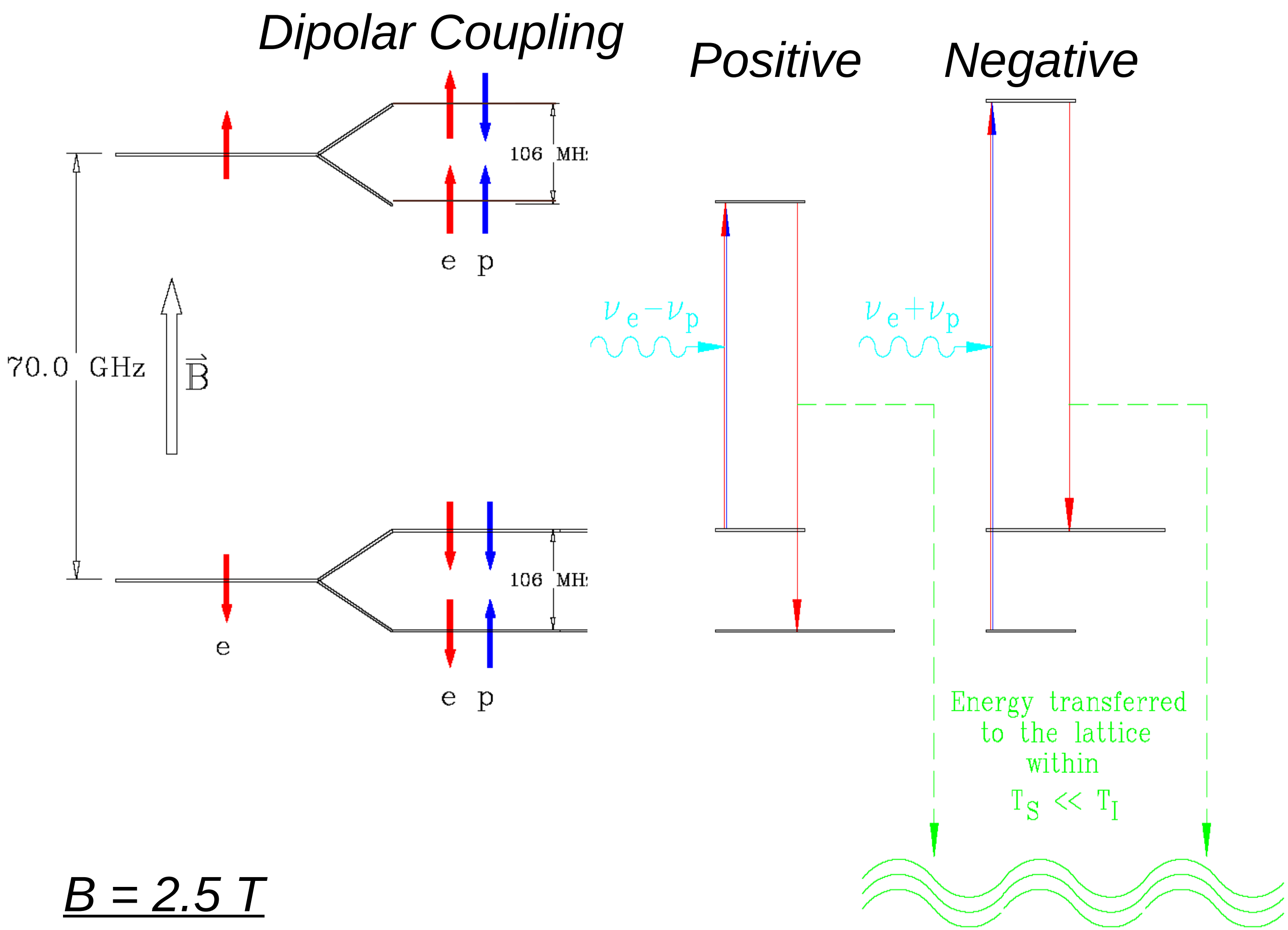
- According to HFS, 6-line pattern corresponds to 5 adjacent H,

$$m=\frac{5}{2},\frac{3}{2},\frac{1}{2}\cdots-\frac{5}{2}$$

Alkyl-radical



The Solid State Effect



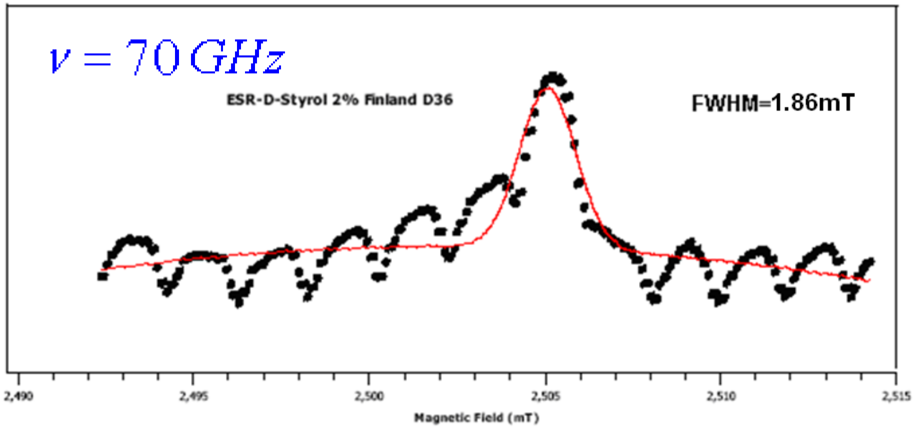
B = 2.5 T

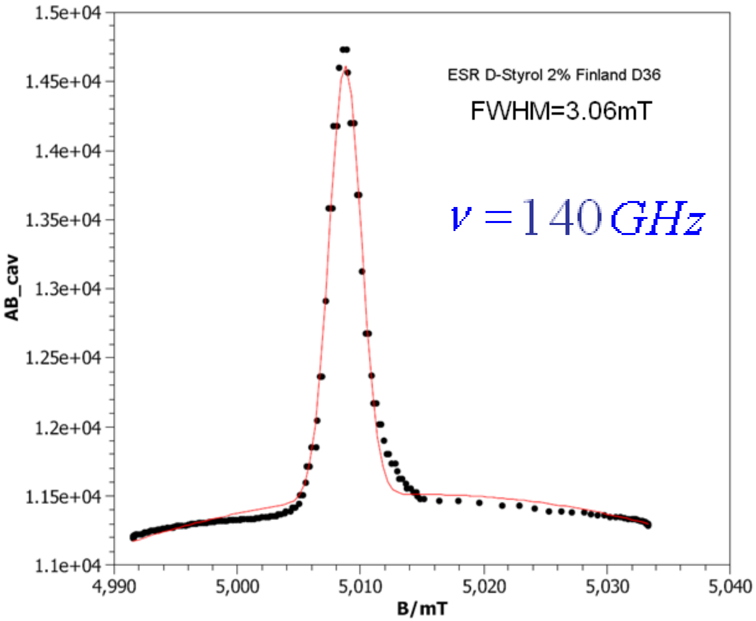
EPR spectra of Finland D36-doped C_8D_8

X-band

$\nu = 9.4 GHz$

Bolometric





➢ Introduce Finland D36 Radicals in C_8D_8

1. dissolve **C_8D_8** polymer in toluene
2. dissolve Finland D36 in isobutanol
3. mix and evaporate solvents

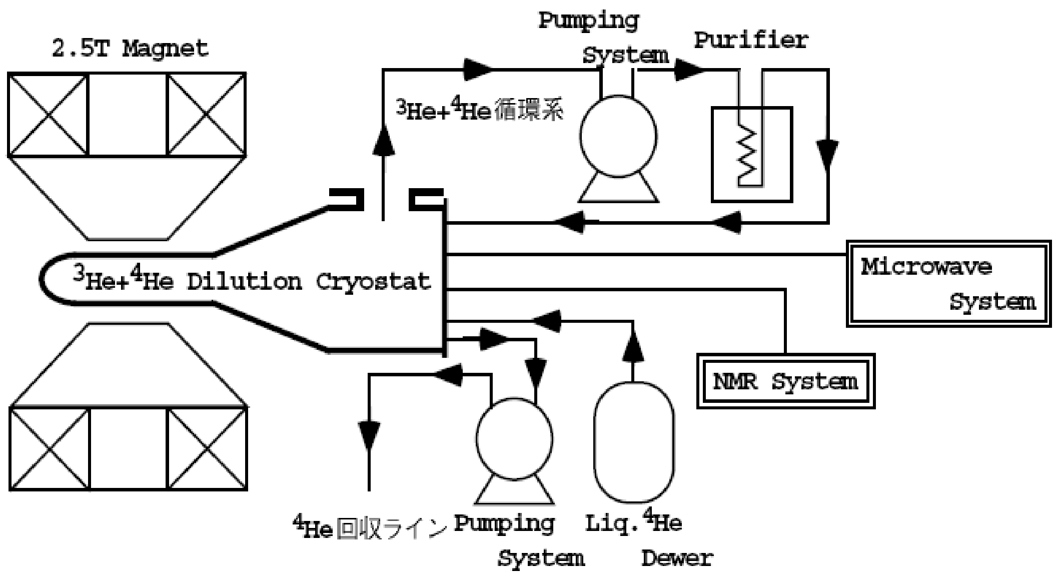
Polarized target system

- Cooling system ~ 100mK
- Magnet system 2.50T

C-yoke normal conduction magnet
(JM-611made by JEOL)

homogeneity:

2×10^{-4} (ø70mm×25mm)



- Microwave system 70GHz

Oscillator: 68.5GHz-71.5GHz 150mW

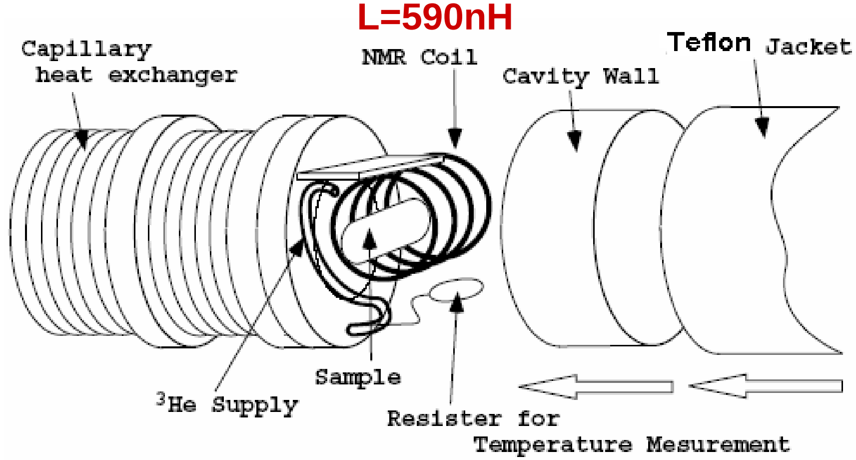
(IMPATT- 47134H-1115 made by HUGHES)

- NMR measurement system

Larmor frequency of D: 16.35MHz

Digital Synthesizer: 1MHz-250MHz
Accuracy: 0.1MHz

(PTS250 made by PTS inc.)



ESR linewidth and shape

- Zeeman Energy of a free electron

$$E_Z = -g_e \mu_B \vec{S} \cdot \vec{B}$$

- Contributions to the Electron Zeeman linewidth

$$\Delta E_{tot} = \underbrace{\mu_B(\vec{S} \cdot \hat{g} \cdot \vec{B}) + (\vec{S} \cdot A \cdot \vec{I})}_{in\,\mathrm{hom}} + \underbrace{E_D}_{\mathrm{hom}}$$

Hom. ⟶ Dipol-Dipol interaction ⟶ between electrons

Inhom. ⟶ Hyperfine interaction ⟶ magnetic nuclei ⟶ indep. of B_0

Inhom. ⟶ g-factor anisotropy ⟶ crystal field ⟶ dep. of B_0

- Try to minimize the energy spread ΔE_{tot}
  - Find a suitable doping method ⟶ $\Delta E_{HFS} \sim \Delta E_D$
  - Try radiation doping if only low μ nuclei present

DNP Mechanism $CW\&B \leq 5T$

- Depend on the relationship of δ, Δ and ω_{0I}

Solid Effect (SE) $\delta, \Delta < \omega_{0I}$

Cross effect (CE) $\delta < \omega_{0I}, \Delta > \omega_{0I}$

Thermal mixing (TM) $\delta \approx \omega_{0I}$

δ a homogeneous EPR linewidth

Δ an inhomogeneous EPR linewidth

ω_{0I} the nuclear Larmor frequency

- **Contributions to the Electron Zeeman linewidth**

$$\Delta E_{tot} = \underbrace{\mu_B(\vec{S} \cdot \hat{g} \cdot \vec{B}) + (\vec{S} \cdot A \cdot \vec{I})}_{in\,\text{hom}\ \Delta} + \underbrace{E_D}_{\text{hom}\ \delta}$$

Hom. → Dipol-Dipol interaction → between electrons

Inhom. → Hyperfine interaction → magnetic nuclei → indep. of B_0

Inhom. → g-factor anisotropy → crystal field → dep. of B_0

The Spin Temperature Theory

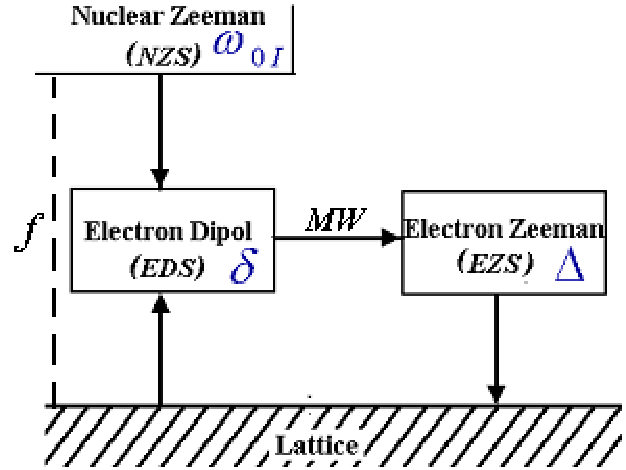
- Deuteron with rather small gyromagnetic ratio

Thermal Mixing is DNP mechanism for deuteron enhancement

Nucleus	γ/2π (MHz.T^{-1})
^{1}H	42.576
^{2}H	6.536
^{3}He	-32.434
^{7}Li	16.546
^{13}C	10.705
^{14}N	3.077
^{15}N	-4.316
^{17}O	-5.772
^{19}F	40.053
^{23}Na	11.262
^{31}P	17.235
^{129}Xe	-11.777

Three spin exchange process:

EZS-EDS-NZS



$$P_{I,\max} = \mathrm{B}_{iI}\left(I\beta_L \omega_e \frac{\omega_I}{2D} \frac{1}{\sqrt{\eta(1+f)}} \right)$$

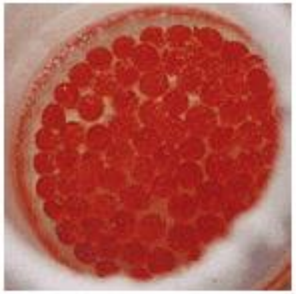
$$\beta_L = \hbar / kT_L$$

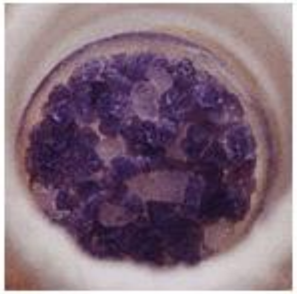
$$h\delta = g_e \mu_B D \qquad \eta = t_z / t_D \qquad f: \text{ a leakage factor}$$

The smaller EPR linewidth , the higher polarization

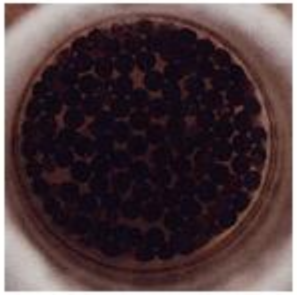
Polarized Deuteron Targets Materials

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


Butanol with Porphyrexide


Ammonia


^{6}LiD

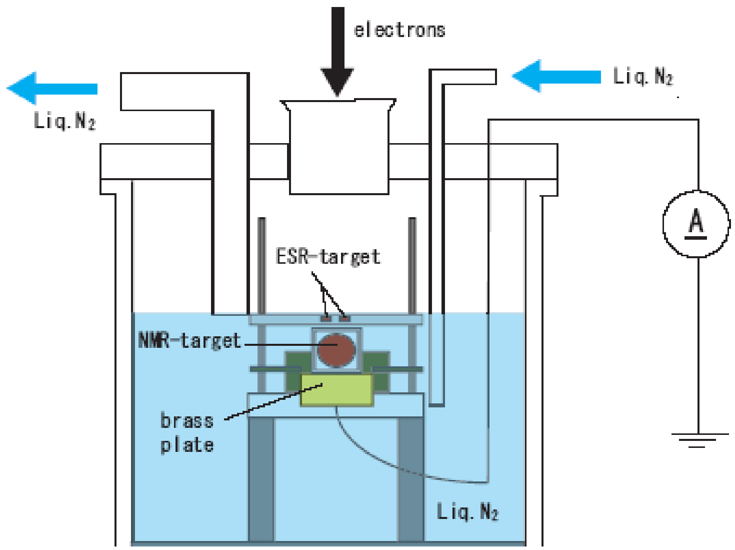

Butanol with CrV

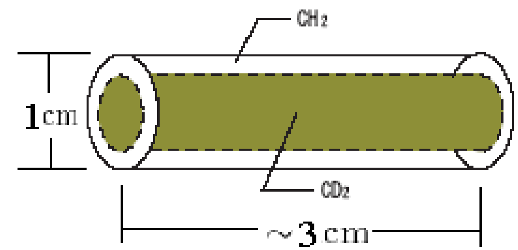
- 13 C

Radiation-doping of CD_2 foil

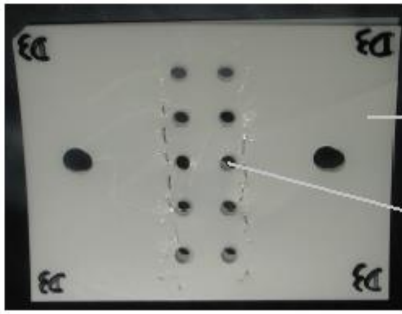
Find an optimal radiation dose

- 7MeV electron beam (Osaka Uni.)
  beam spot **ø60mm×20mm**
- Irradiation dose ~10^{14} - ~10^{17} e^-/cm^2
- Irradiation at liquid Nitrogen 77K
- CD_2 foil thickness 40 μm
  density 0.93 g/cm³





Sample	[e^-/cm^2]	Spin density [e^-/g]	Irradiation temp. [K]
a	3.0×10^{14}	1.8×10^{18}	77
b	7.0×10^{14}	2.7×10^{18}	77
c	4.0×10^{15}	1.9×10^{19}	77
d	6.0×10^{15}	2.3×10^{19}	90
e	8.0×10^{15}	3.2×10^{19}	77
f	1.0×10^{16}	3.6×10^{19}	77
g	1.2×10^{16}	4.0×10^{19}	90
h	5.0×10^{16}	2.3×10^{20}	77
i	1.0×10^{17}	1.4×10^{21}	77

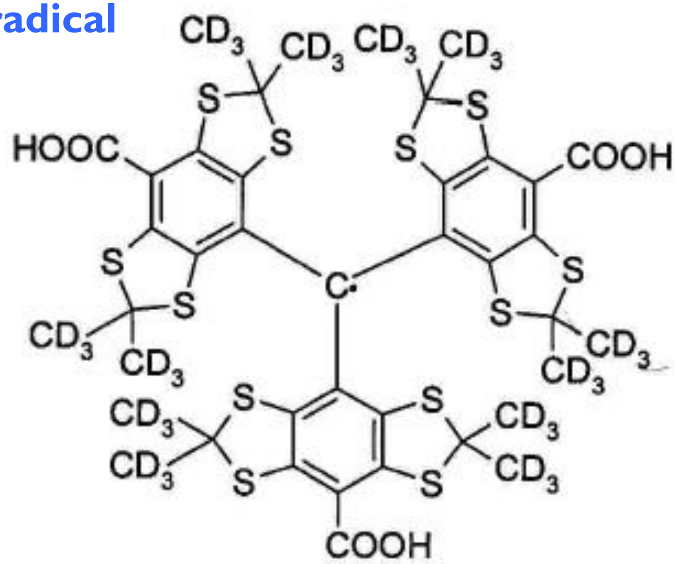


Introduce Trityl radical

- Trityl radical as dopant for D-Butanol

Boiling point >200°C

Very stable radical



Trityl radicals Finland D36

Weak g-factor anisotropy in D-Butanol