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Development of polarized polymer targets

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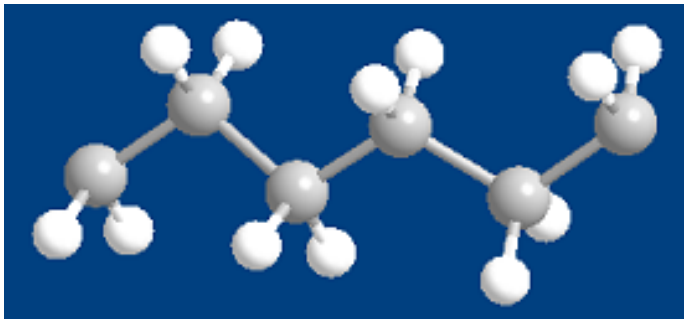
Contents

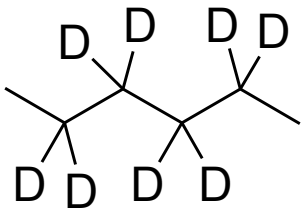
Introduction to both material

Poly(Ethylene-D4) CD_2

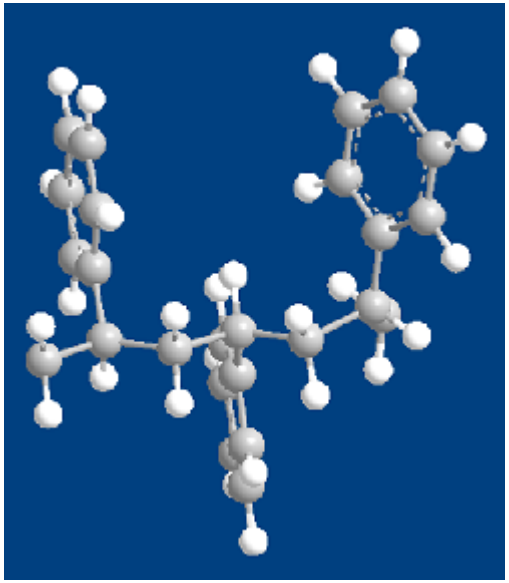


dilution factor

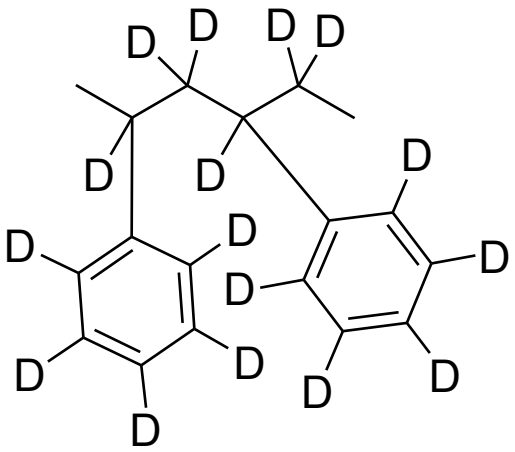
$$f = \frac{8 \text{ from D}}{24 \text{ from C} + 8 \text{ from D}} = 0.25$$



Styrene-D8, polymerized C_8D_8



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



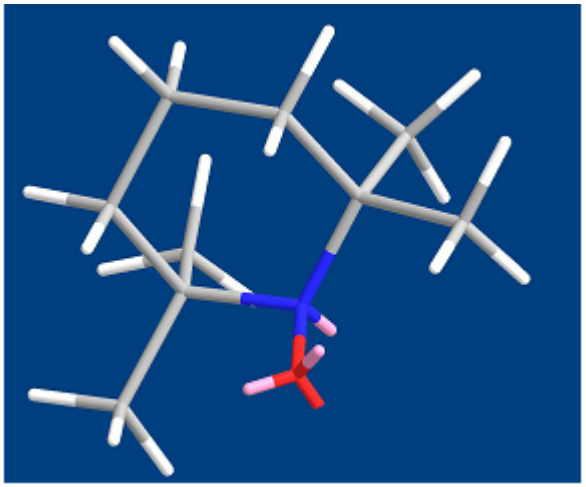
Merits of CD_2, C_8D_8

1. **High purity of D 0.98, 0.99**
2. **D with spin 1 and C with spin 0**
3. **Short polarization build-up time 3-10 hours**
4. **Low radiation damage**
5. **Solid State at room temperature**

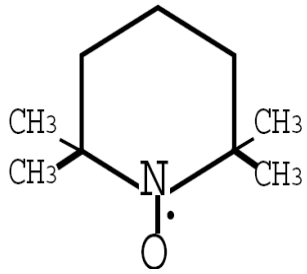
   form thin targets for low-energy experiments

Doping methods for DNP

- Mechanism of Dynamic Nuclear Polarization
  Paramagnetic centers are needed
- Chemical (Tempo radical) doping of CD_2



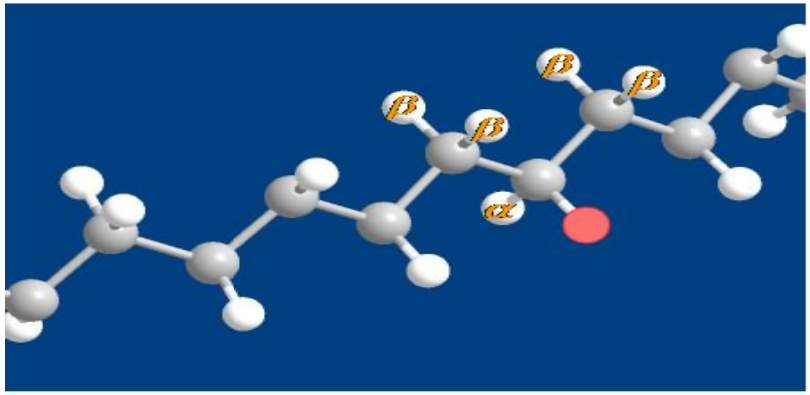
Tempo (stable free radical)



Melting point 36°C
Boiling point 67°C

(2,2,6,6-tetramethyl-piperidine-1-oxyl)

- Irradiation with electron beam



'aramagnetic center for DNP

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. ⟶ Diplo-Diplo interaction ⟶ between electrons

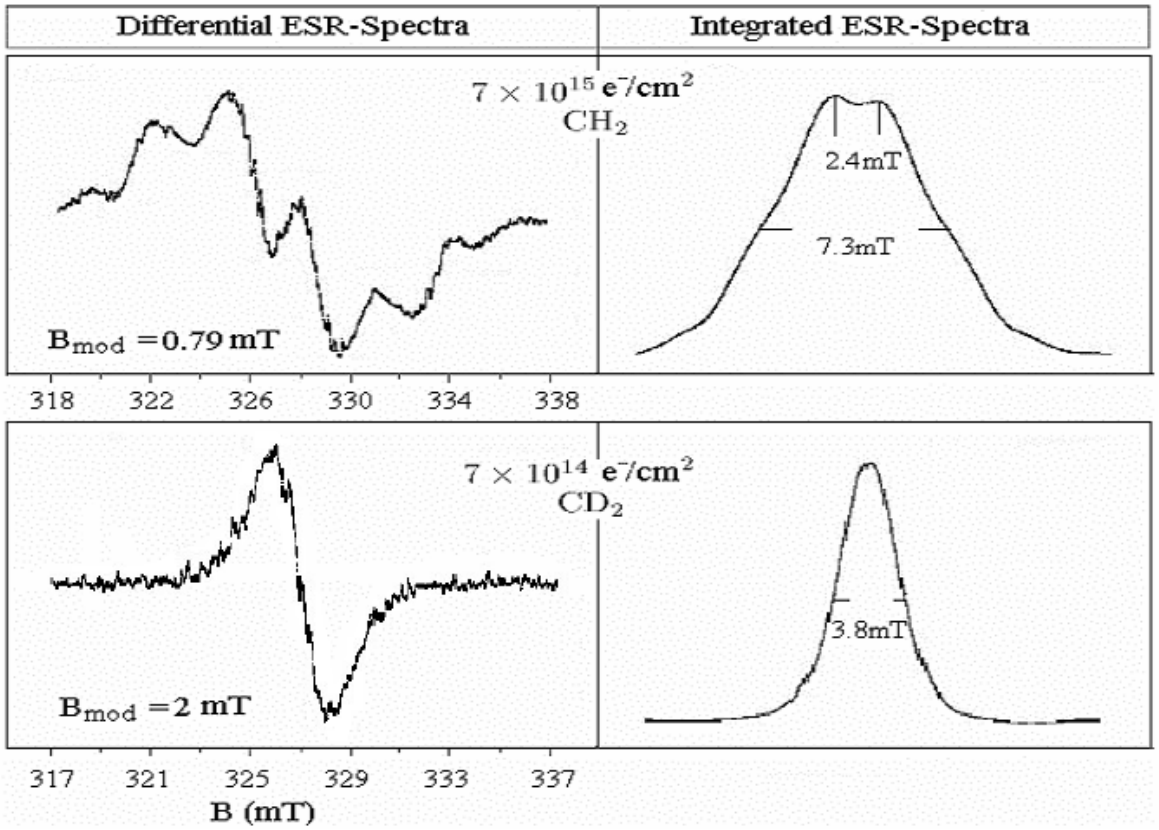
Inhom. ⟶ Hyperfine interaction ⟶ magnetic nuclei ⟶ indep. of B_0

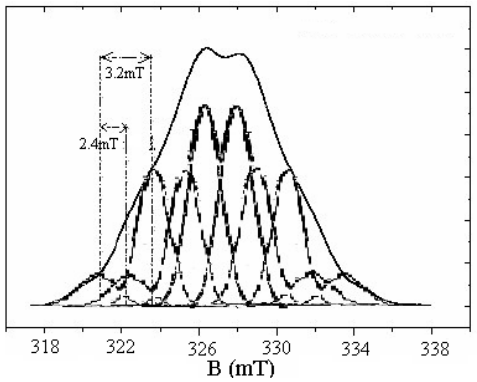
Inhom. ⟶ g-factor anisotropy ⟶ crystal field ⟶ dep. of B_0

- Polarization at 2.5T/0.3K Electron: 99.9% Deuteron: 0.17%
- Transfer high electron polarization to deuteron polarization

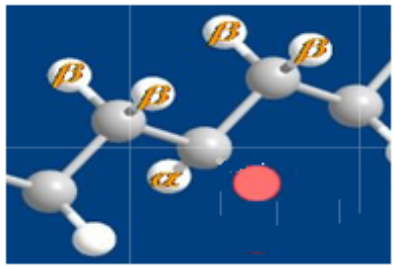
$$\Delta E_{HFS} : \Delta E_D$$

EPR spectra of irradiated CH2 and CD2 at 77K





Alkyl-radical

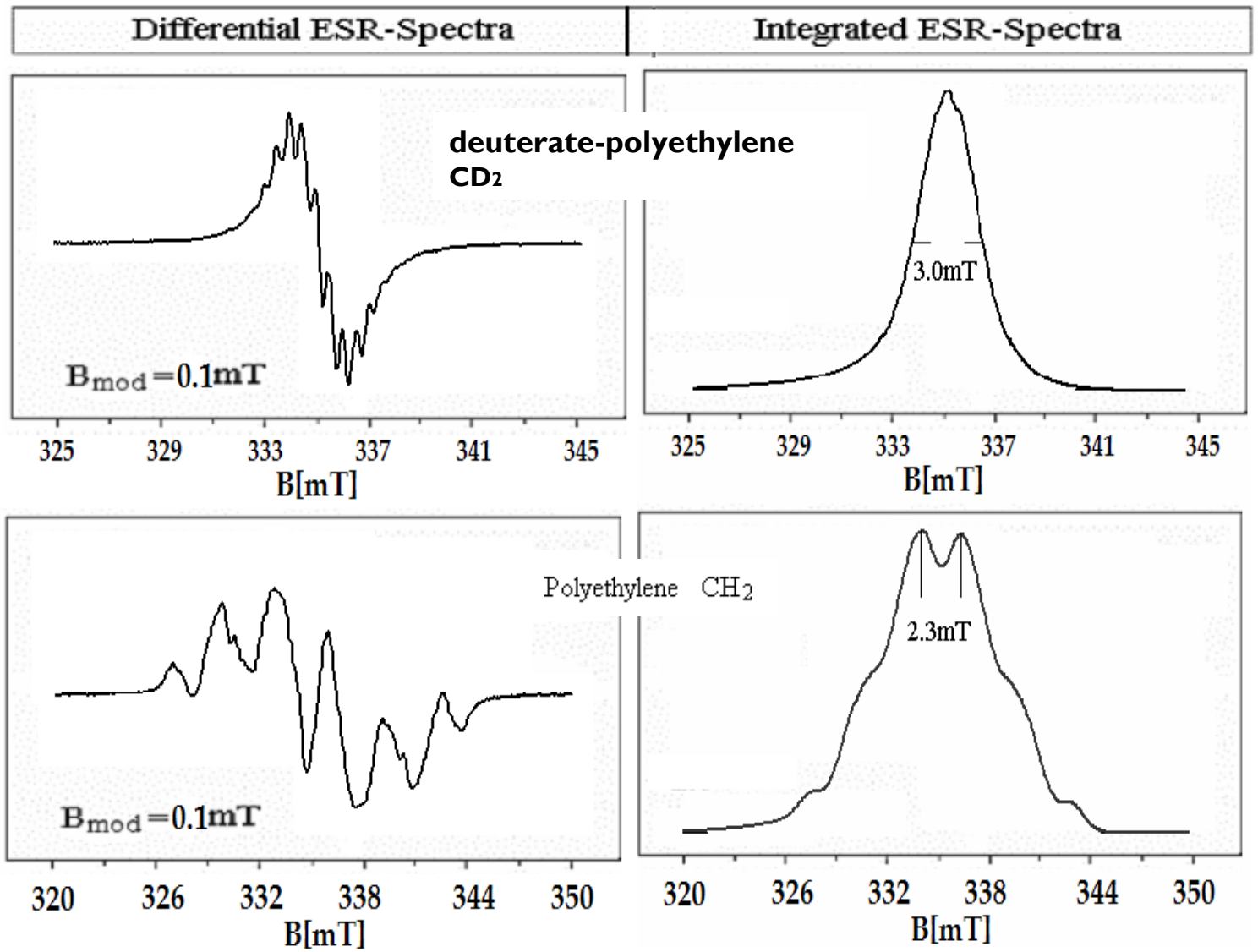


$r_{C-C} = 1.54 \times 10^{-10}$ m

$r_{C-H} = 1.11 \times 10^{-10}$ m

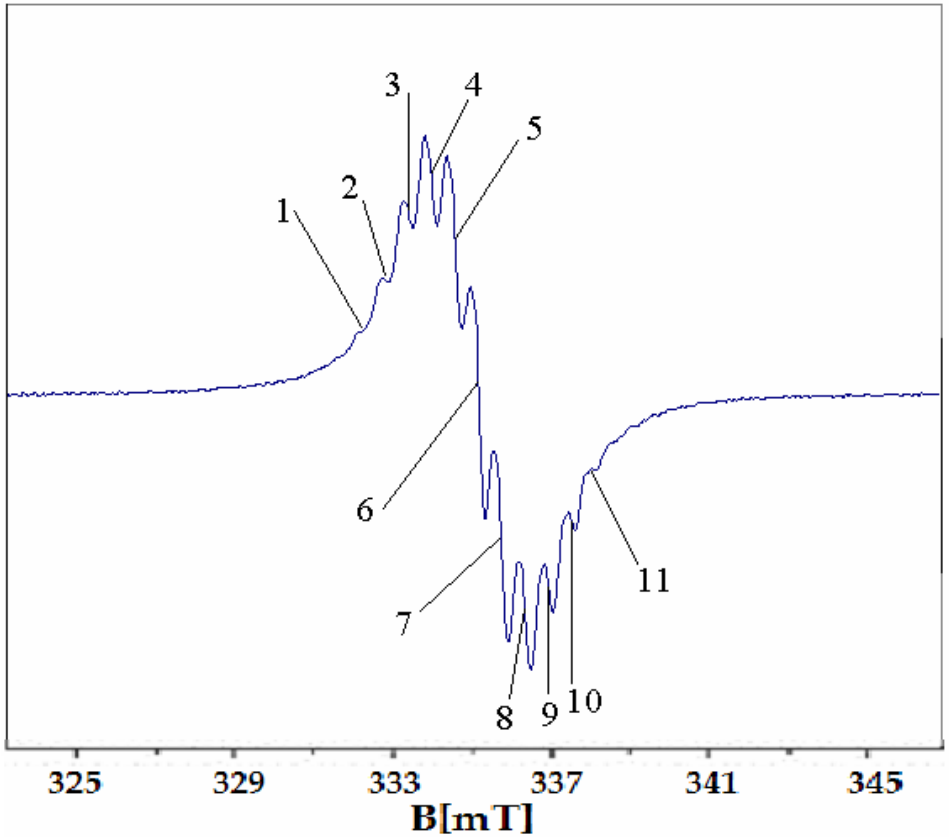
- According to HFS, 6-line pattern conresponds to 5 adjacent H, m= ٥/٢, ٣/٢, ١/٢ ... ٥/٢
- 2.4mT splitting of HFS interval belongs to Hα
- Splitting broadening 1.56mT mainly belongs to electron dipolar-dipolar interaction

Irradiated CD2 and CH2 spectra



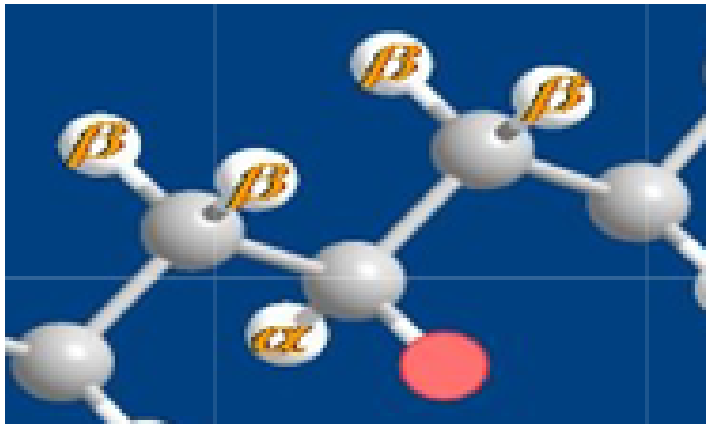
Bochum Group (2002)

EPR spectra of Radiation-doped CD_2

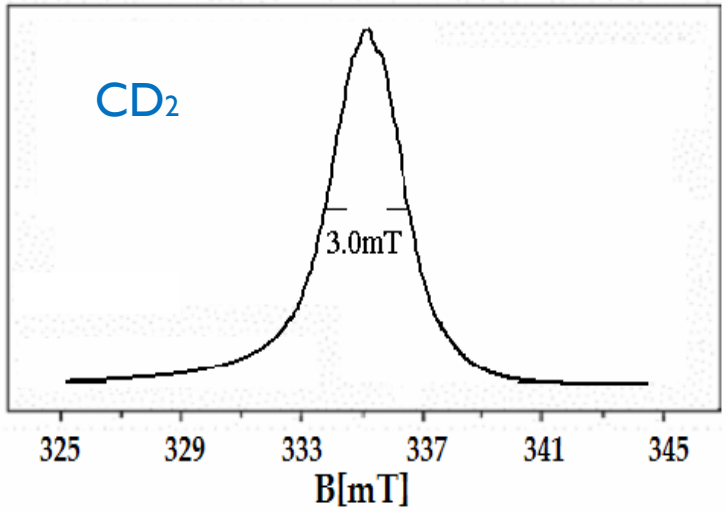


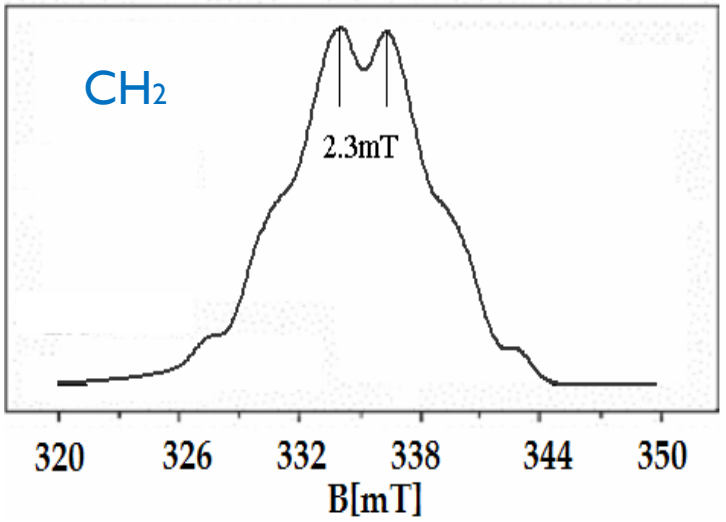
- According to HFS, 11-line pattern corresponds to 5 adjacent D, $m = 5, 4, 3 \cdots -5$

EPR spectra of Radiation-doped CH_2



Integrated EPR lines



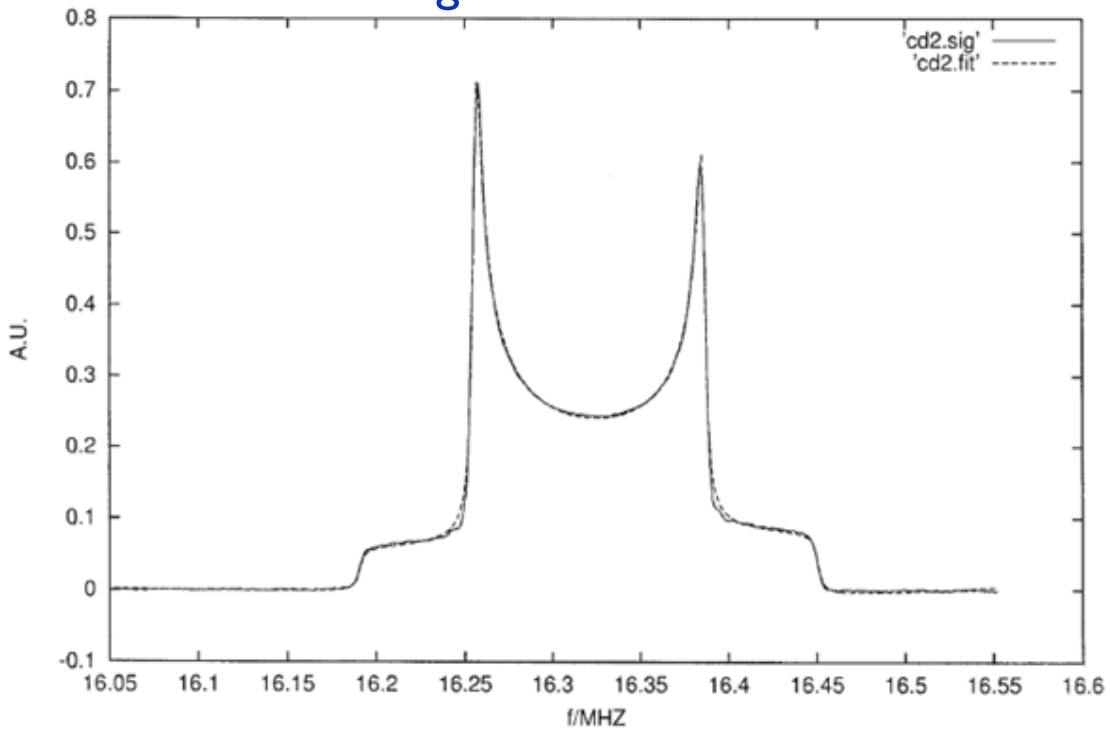


- The unpaired electron interacts with the one hydrogen on α- site stronger

  than the four hydrogen on β- site

Polarization of radiation-doped CD_2

NMR Signal of Deuteron

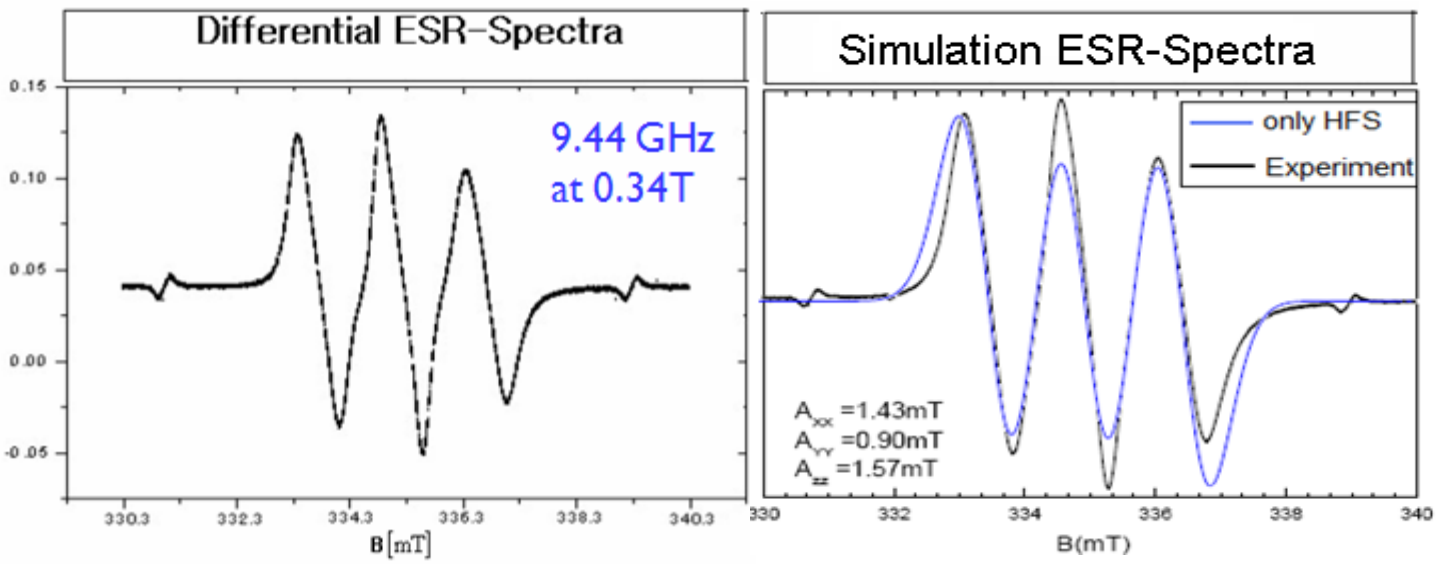


dose $[e^-/\mathrm{cm}^2]$	spin concentrantion[e/g]	irradiation Temp. [K]	positive Pol[%]	negative Pol. [%]
2.4×10^{16}	6.3×10^{19}	90 (liquid argon)	-	-
1.2×10^{16}	4.0×10^{19}	90 (liquid argon)	~ 16	~ -25
6.0×10^{15}	2.3×10^{19}	90 (liquid argon)	~ 17	~ -30
8.0×10^{15}	3.2×10^{19}	77(liquid nitrogen)	~ 20	~ -30
4.0×10^{15}	1.9×10^{19}	77(liquid nitrogen)	~ 20	~ -27

$T_{DNP} = 0.13 \sim 0.15\mathrm{K}$

Bochum Group (2002)

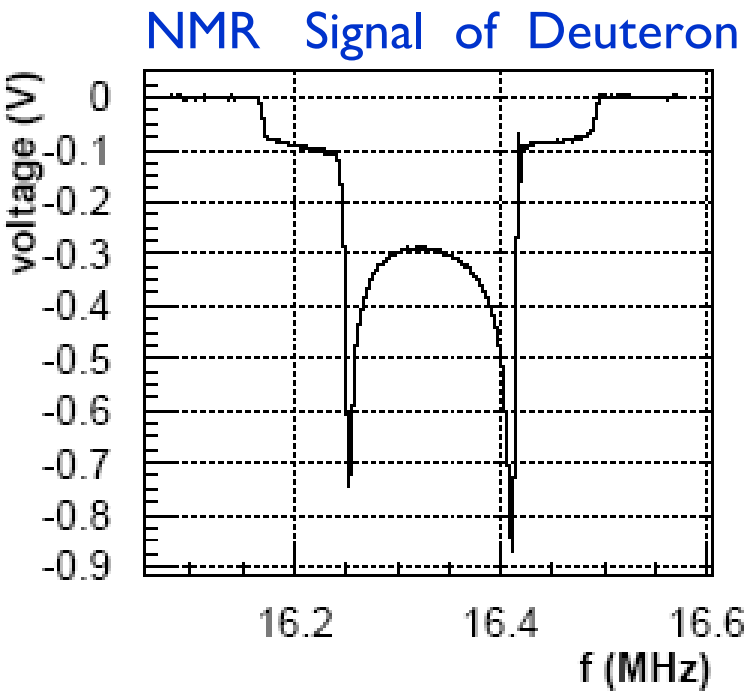
EPR spectra of TEMPO-doped CD_2

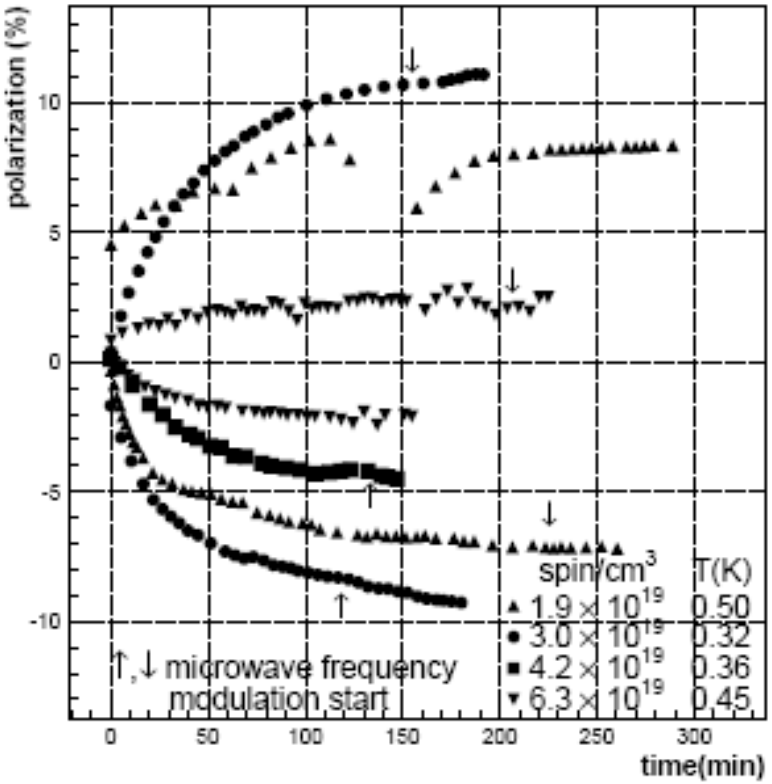


- Introduce TEMPO Radicals in CD_2
  - Tempo and CD_2 foil into a vessel without toching each other
  - 80°C diffusion from TEMPO vapour

Structure of Polyethylene CD_2

Polarization of TEMPO-doped CD_2



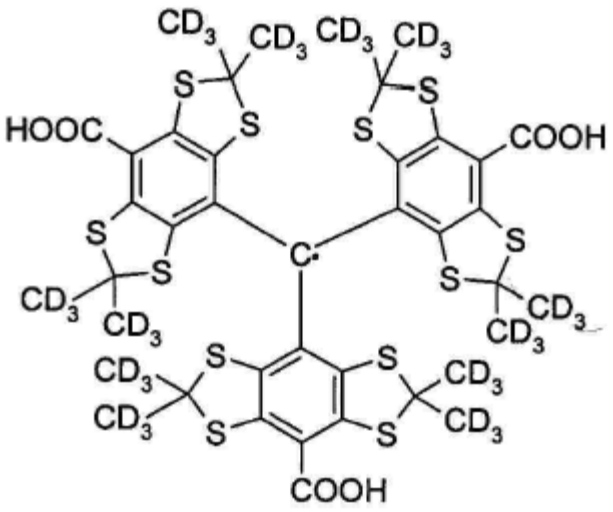


CD_2 mass (g)	spin concentration (spin/cm^3)	Temp. (K)	Polarization (%)	Microwave (GHz)
1.190	$(1.9 \pm 0.2) \times 10^{19}$	0.57	$+8.3 \pm 1.1$	69.97
		0.54	-7.2 ± 0.9	70.29
1.180	$(3.0 \pm 0.2) \times 10^{19}$	0.33	$+11.1 \pm 1.6$	69.97
		0.33	-9.3 ± 1.3	70.30
1.017	$(4.2 \pm 0.2) \times 10^{19}$	0.36	-4.5 ± 0.6	70.28
1.418	$(6.3 \pm 0.2) \times 10^{19}$	0.45	$+2.8 \pm 0.3$	69.97
		0.45	-2.4 ± 0.3	70.28

Nagoya Group (1998)

Current Research

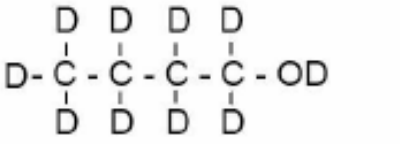
- Try Trityl radical as dopant for C_8D_8

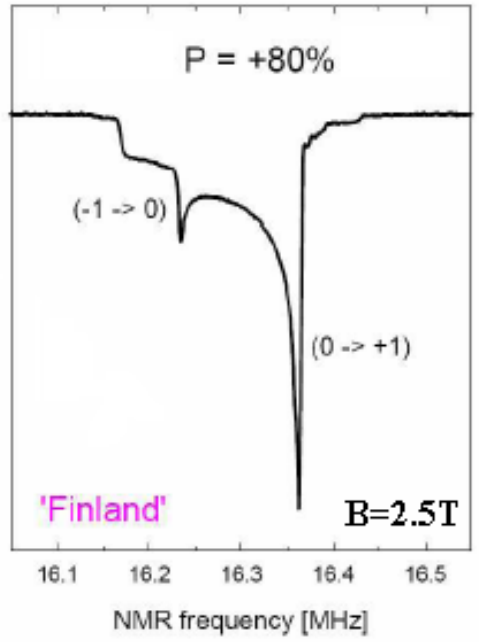


Trityl radicals Finland D36

Boiling point
>200°C

D-Butanol :



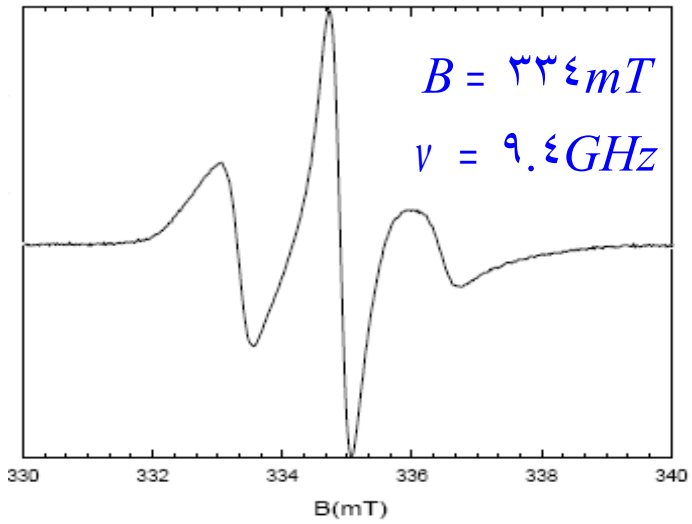


Bochum Group (2003)

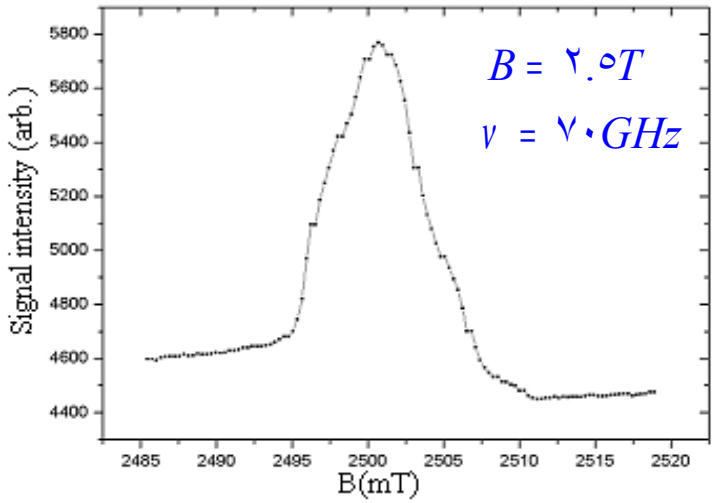
EPR spectra of TEMPO-doped C_8D_8

- Try different radical concentration in TEMPO-doped C_8D_8

X-band

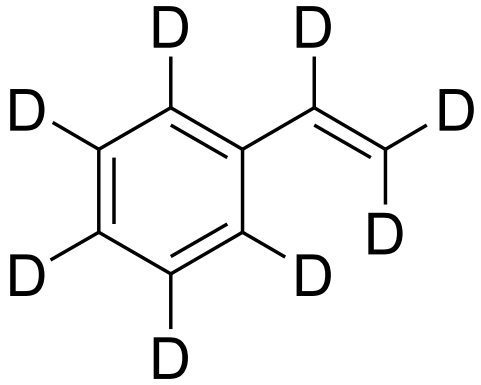


V-band



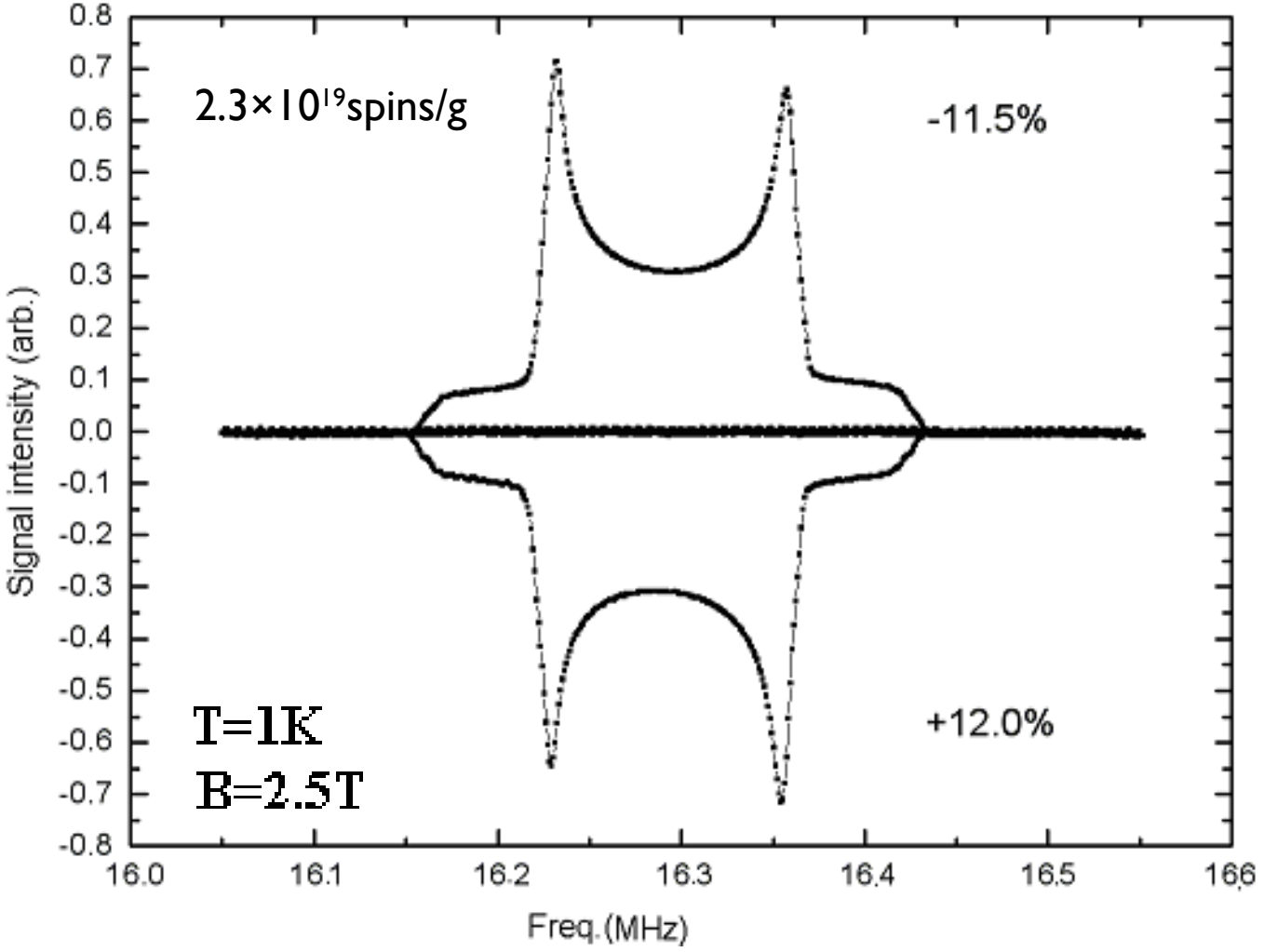
- IntroduceTEMPO Radicals in C_8D_8

1. dissolve **C_8D_8** polymer in toluene
2. add free radical
3. let the toluene evaporate at RT



Styrene-D8, polymerized C_8D_8

Polarization of TEMPO-doped C_8D_8



Sample	f_{mw} (GHz)	d-pol (%)	$T_{1,d}$ (s)
Styrene-d8 +TEMPO	69.850 70.050	+11.5% -12.0%	603

$f_{d,NMR}$ =16.4 MHz

$T_{build-up}$ = ٣٤٦S

Summary

1. Deuterated Polyethylene CD_2 and Styrene-D8, polymerized C_8D_8 can be successfully polarized under DNP conditions.
2. The maxium polarization of deuterated Polyethylene is 30% with irradiation of 8×10^{15} e^-/cm^2 and 11% with chemical (Tempo) doping.
3. Due to EPR spectra,unpaired electrons produced by irradiation have Hyperfine interaction with 5 adjacent D nuclei .
4. The first measurement of Styrene-D8 polymerized C_8D_8 was successful with 12% polarization at 2.5T/1K

outlook

Material	Doping	Polarization	Temperature
CD_2	Irradiation	30%	150mK
C_8D_8	Irradiation	?	?
CD_2	Tempo	11%	330mK
C_8D_8	Tempo	12%	1K
CD_2	Trityl	×	×
C_8D_8	Trityl	?	?

- Irradiate Styrene-D8, polymerized C_8D_8 ?
- Find an optimal radical concentration and magnetic feild of Tempo-doped C_8D_8
- Find a good solvent for Trityl-doped C_8D_8

Acknowledgement

Prof. Naoaki Horikawa
Prof. Takahiro Iwata
Prof. Werner Meyer
Dr. Gerhard Reicherz

Thank you very much !

G 因子は外部により加える磁場方向によってそれぞれ異なるためであり、これをｇ因子の異方性という