NMR signal analysis in the large COMPASS $^{14}NH_3$ target

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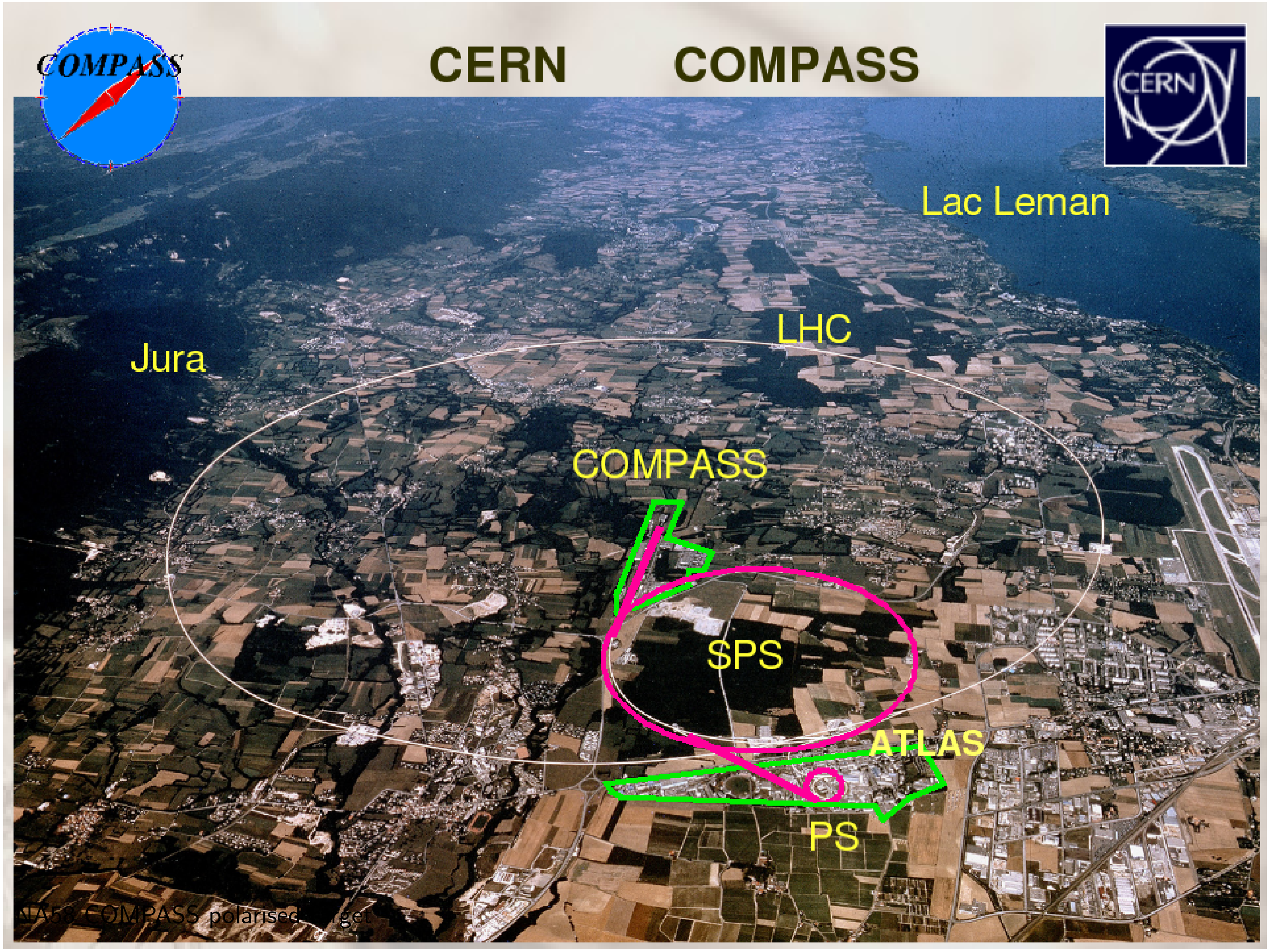
Abstract

COMPASS apparatus, Q-meters, ammonia (nitrogen-14), NMR signals (EPR), dipolar linewidth (quadrupole), nuclear spin thermodynamics, hydrogen bonding


CERN COMPASS
COMPASS
CERN
Lac Leman
LHC
Jura
COMPASS
SPS
ATLAS
PS

COMPASS collaboration wwwcompass.cern.ch

- NIMA **577** (2007) 455-518, *The COMPASS experiment at CERN*
- CERN M2 beam line 160 GeV/c, flux $2 \cdot 10^8/16.8$ s with 4.8 s long spills, -80 % polarized muons, opening angle of 180 mrad
- polarized solid and unpolarized liquid hydrogen targets
- spectrometer magnets SM1 and SM2
- large and small area tracking stations
- RICH, hadron calorimeters

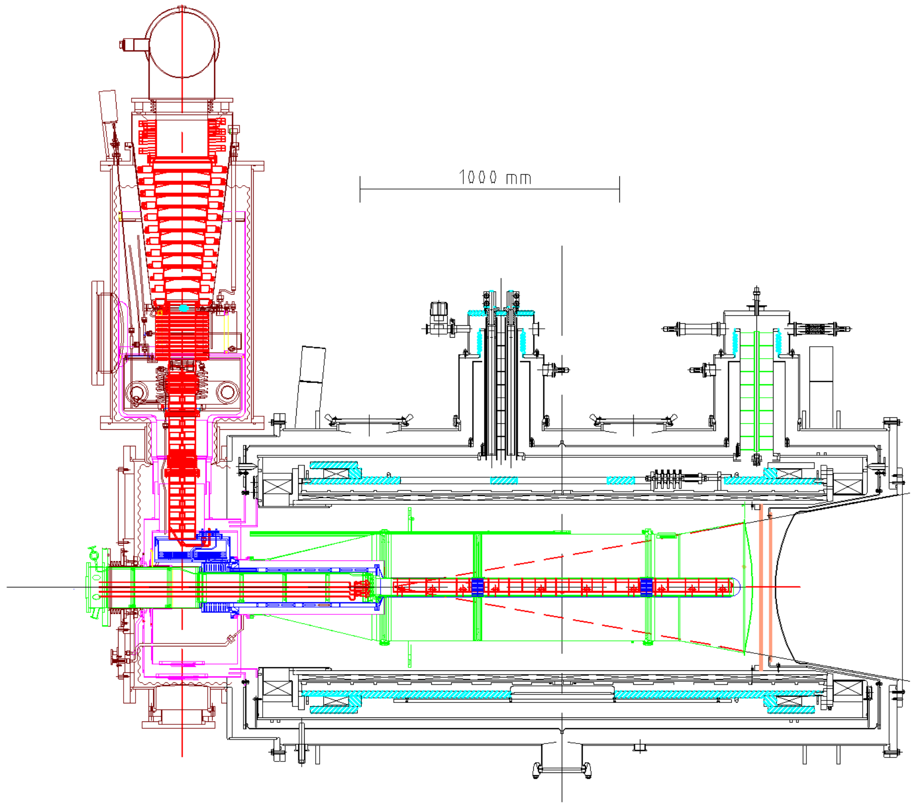
- BMS, iron and concrete walls
- slow control, trigger and DAQ $\sim$ 100 - 250 TB/year
- luminosity $\sim 5 \cdot 10^{32}/\mathrm{s} \cdot \mathrm{cm}^2$

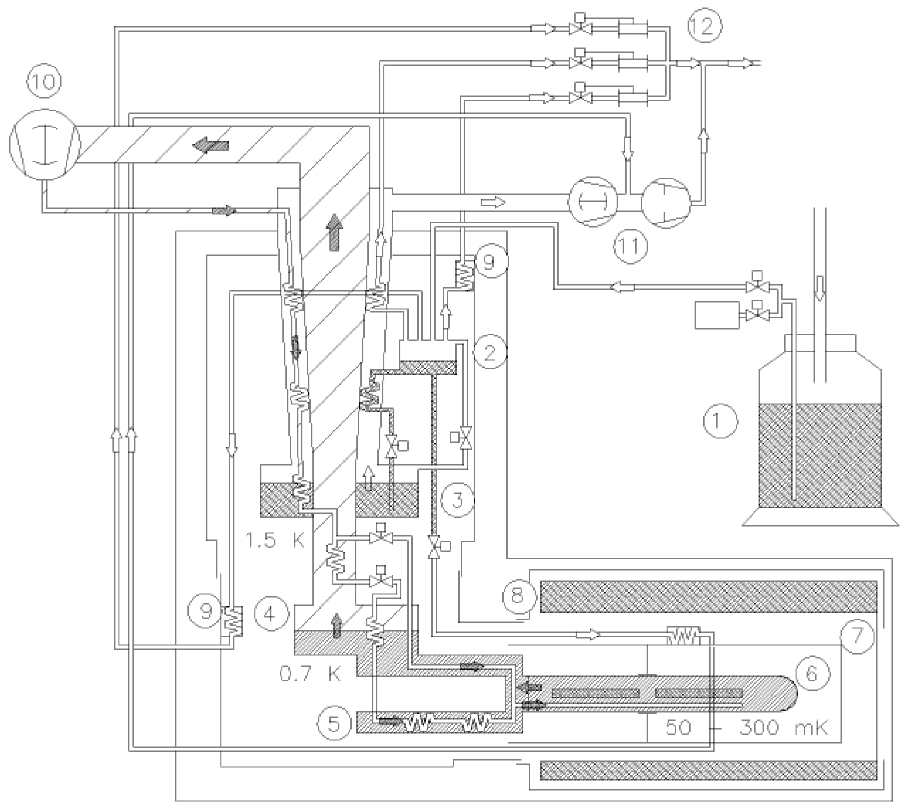
Target materials

- ^{6}LiD deuteron target, color centers in FCC lattice, maximum polarization $\pm$58 %, $f \sim$ 0.5
- NH_3 proton target, $\mathrm{N\dot{H}_2}$ radicals, maximum polarization $\pm$90 %, $f \sim$ 0.176
- granular size of 2 - 5 mm
- DNP $\beta D \simeq \frac{1}{2}\beta_L \omega_S$
- dilution factor f number of polarizable nuclei/all nuclei

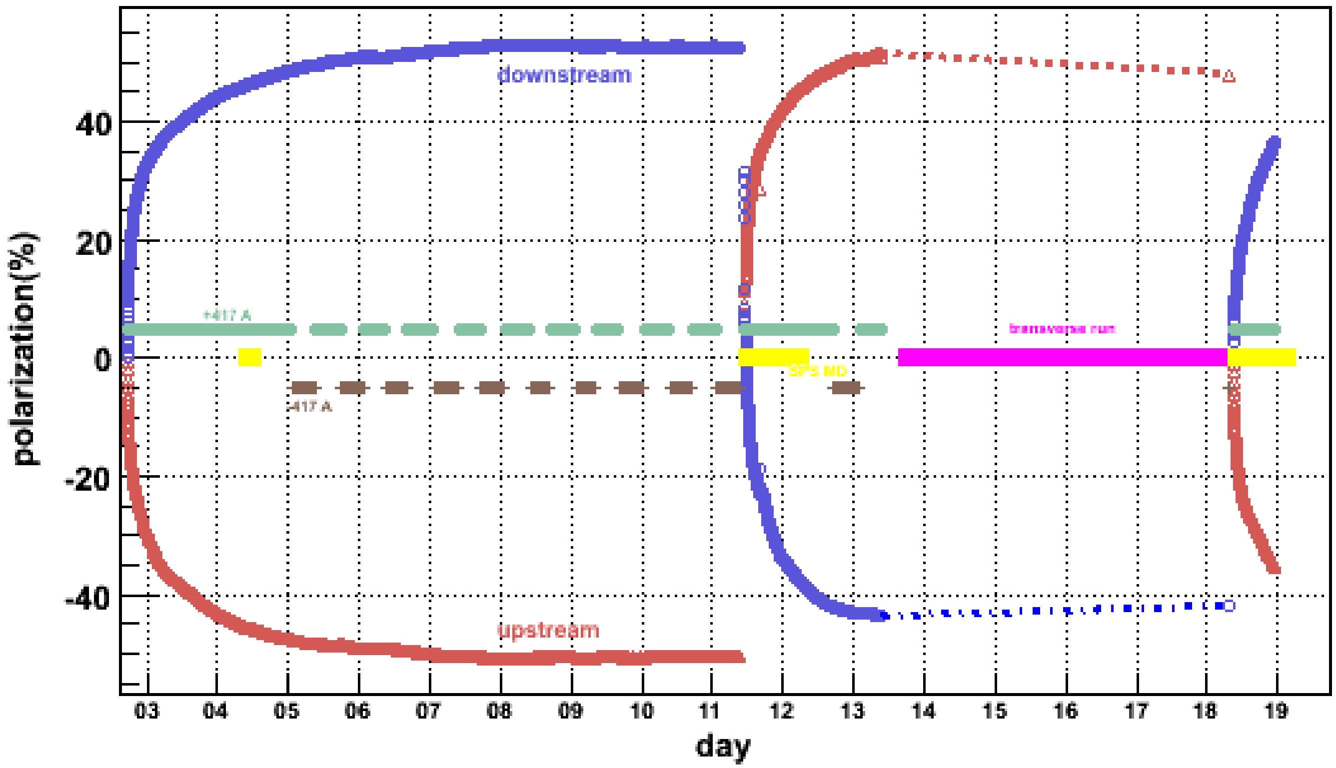
- figure of merit $FOM \sim \rho\kappa(p_b p_T f)^2$
- longitudinal and transverse nuclear spin polarization
- two (60 + 60 cm) or three (30 + 60 + 30 cm) oppositely polarized target cells, diameter 3 cm or 4 cm

Dilution cryostat

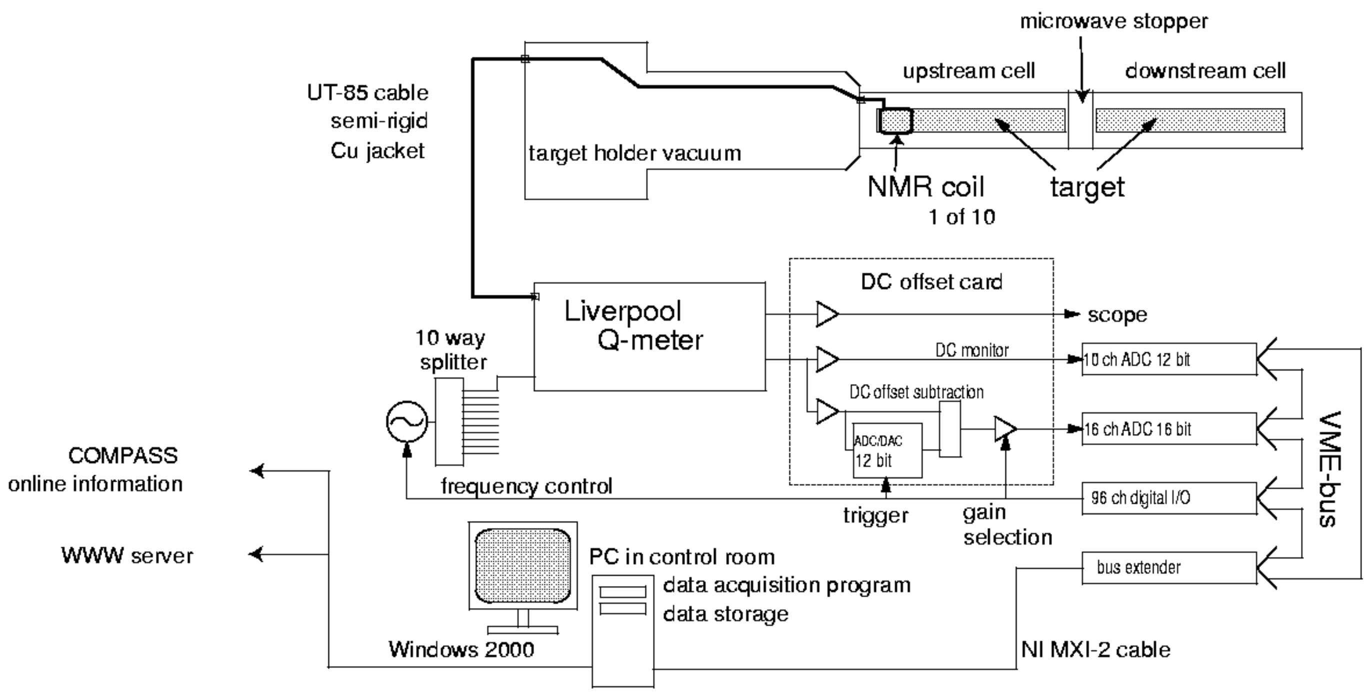



12
10
11
9
2
1
3
1.5 K
8
9
4
7
0.7 K
6
5
50 – 300 mK

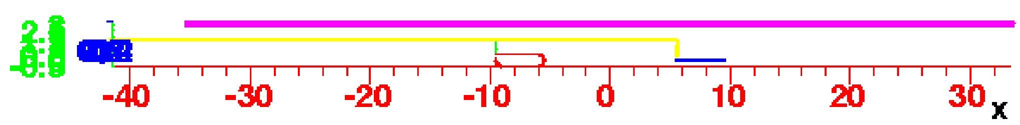
Deuteron polarization physics 2004



10 Q-meter channels



Conducting metals

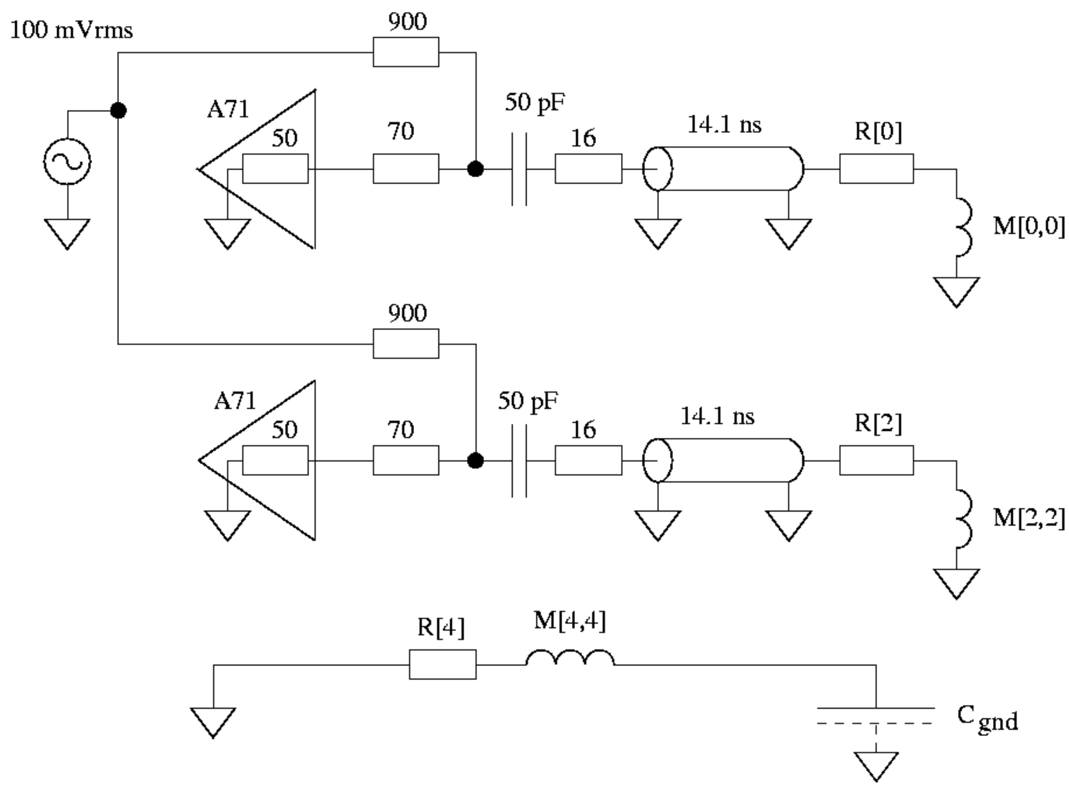


Inductance matrix

$$M[i,j] = \begin{bmatrix} 44.5 & 0.7 & -0.0 & 4.4 & 1.7 \\ 0.8 & 349.4 & -0.0 & 258.6 & 190.0 \\ 0.0 & -0.0 & 43.9 & 0.1 & -0.0 \\ 4.1 & 256.8 & -0.0 & 590.8 & 298.0 \\ 2.4 & 188.7 & -0.0 & 292.9 & 738.8 \end{bmatrix} \text{(nH)}$$

$$R = \begin{bmatrix} 0.313 \\ 0.032 \\ 0.313 \\ 0.047 \\ 0.529 \end{bmatrix} \Omega$$

Q-meter simulation

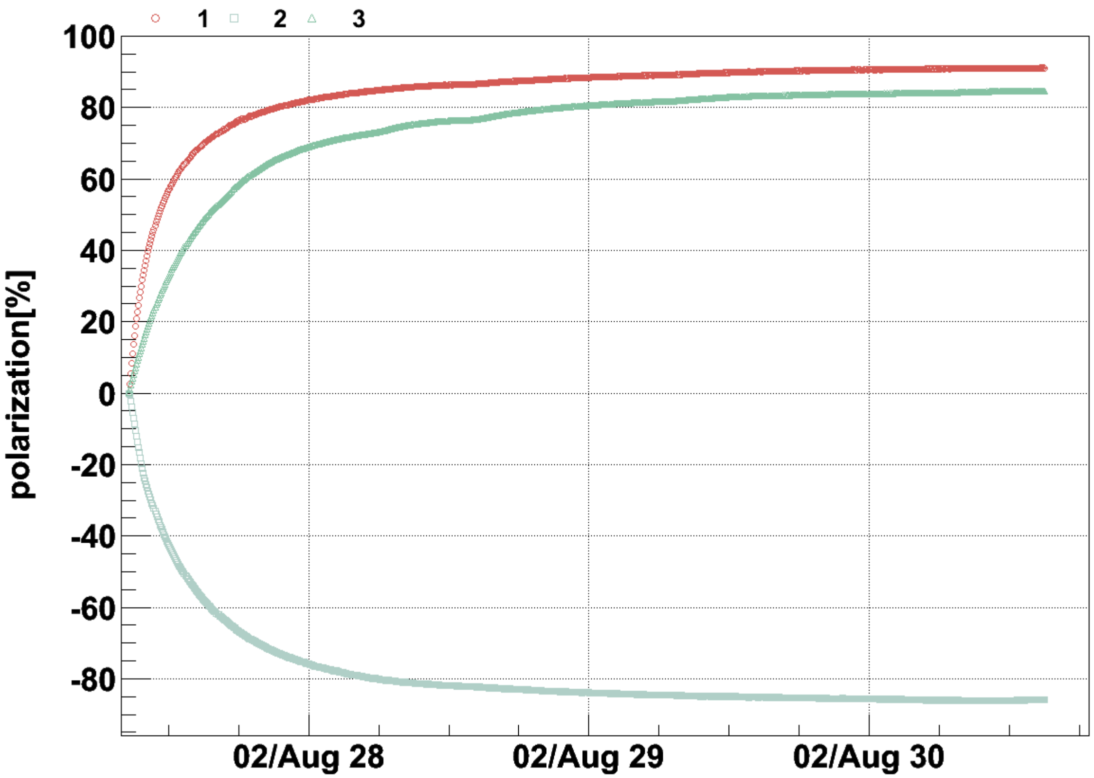


Irradiated ammonia briefly

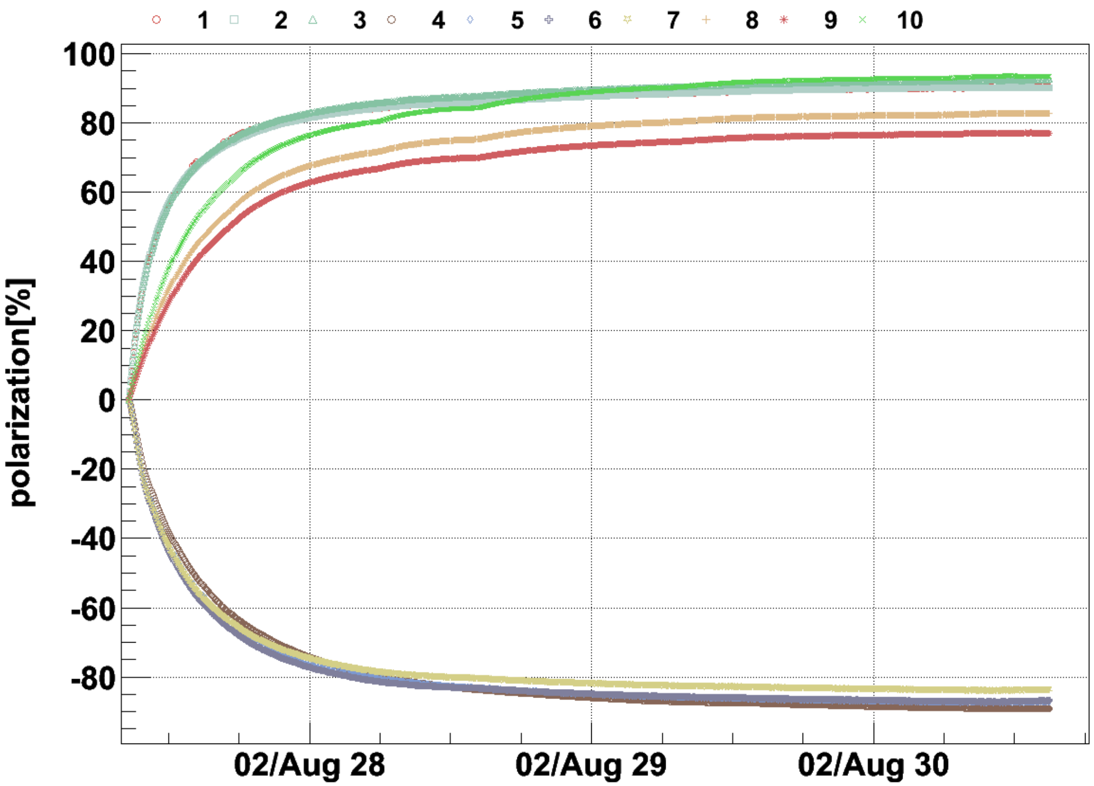
- T.O. Niinikoski, J.-M. Rieubland, *Dynamic nuclear polarization in irradiated ammonia below 0.5 K*, Phys. Lett. A **72** (1979) 141-144
- D.G. Crabb et al., *Observation of a 96% Proton Polarization in Irradiated Ammonia*, Phys. Rev. Lett. **64** (1990) 2627-2629 (1 K and 5 T)
- W. Meyer, *Ammonia as a polarized solid target material - a review*, Nucl. Instr. Meth. A **526** (2004) 12-21
- $+$ SMC papers (nitrogen-14)

- typically $10^{-4} - 10^{-3}$ free electrons/nucleus, here $\mathrm{N\dot{H}_2}$ radicals
- polarizations up to $\pm$ 91 - 96 %
- density 0.853 g/ccm at 77 K
- thermal equilibrium polarization 0.25 % at 2.5 T and 1.0 K

Polarization buildup 2007

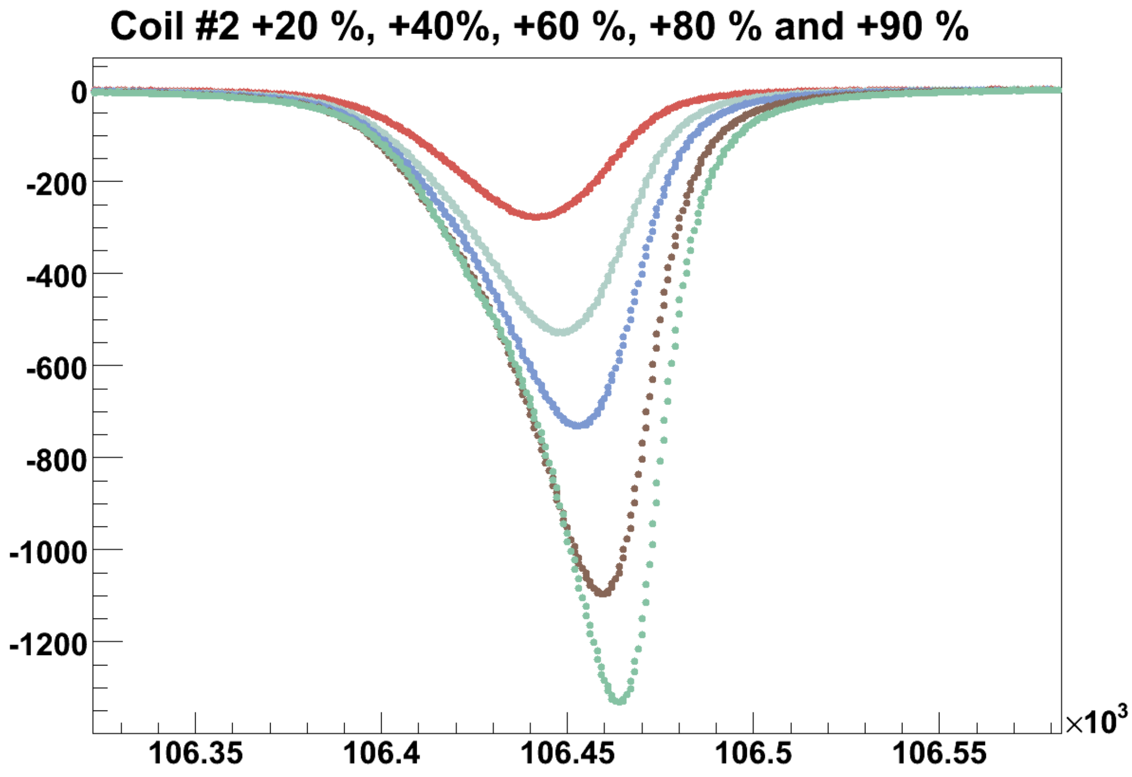


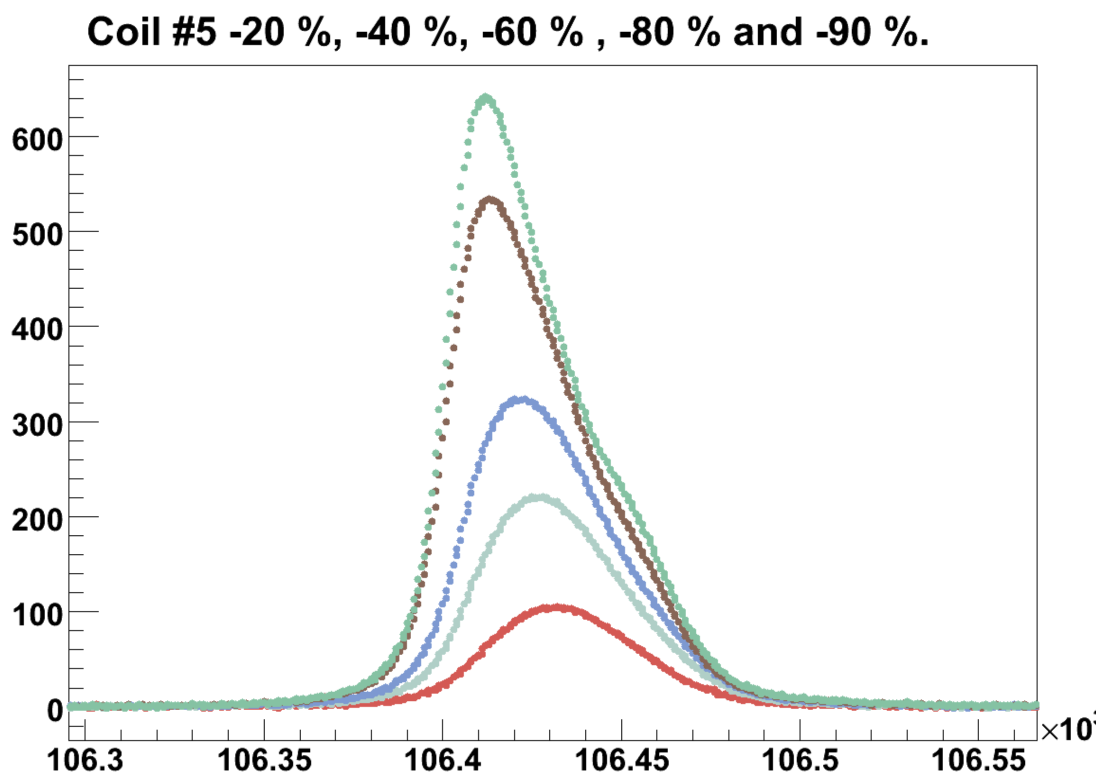
Polarization buildup 2007



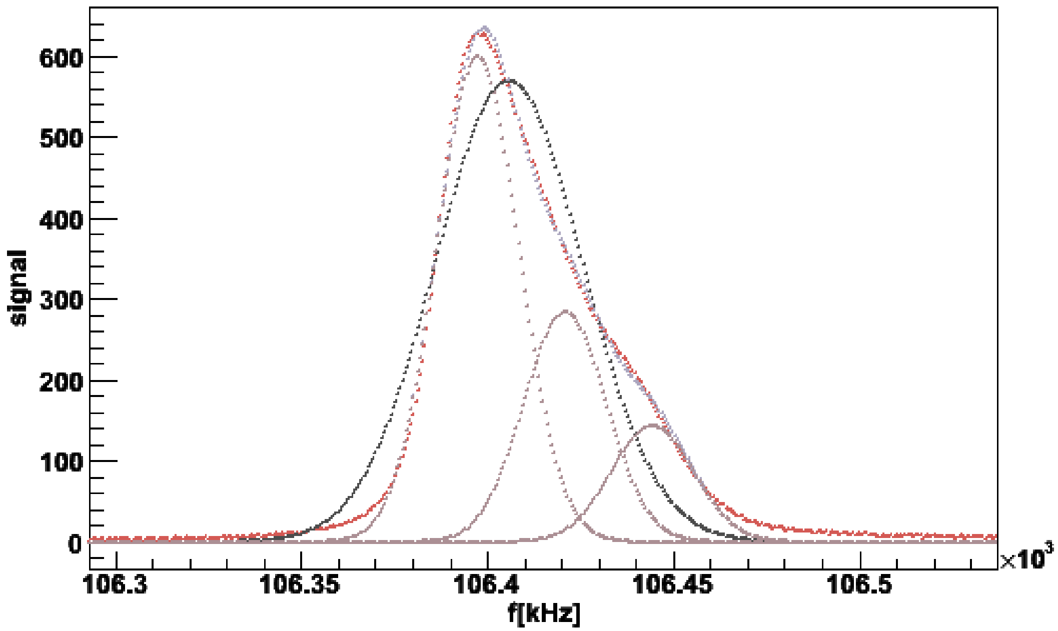
- 2007 build up with helium-3 flow 60 - 70 mmol/s and still heater 12 V
- in three cell configuration up- and downstream cells do not polarize equally
- polarization is not homogeneous along the target

Polarized proton signals



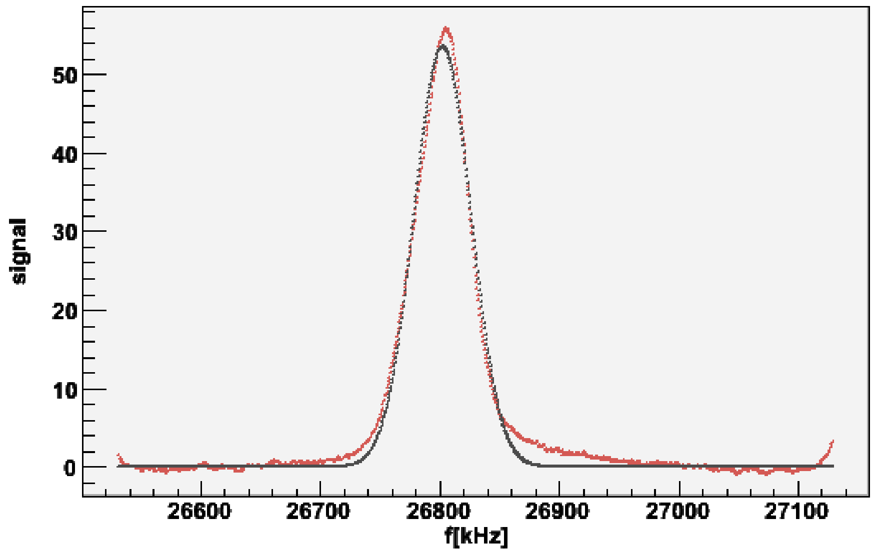

Coil #5 -20 %, -40 %, -60 % , -80 % and -90 %.
600
500
400
300
200
100
0
106.3
106.35
106.4
106.45
106.5
106.55
×10^3

Polarized proton signals



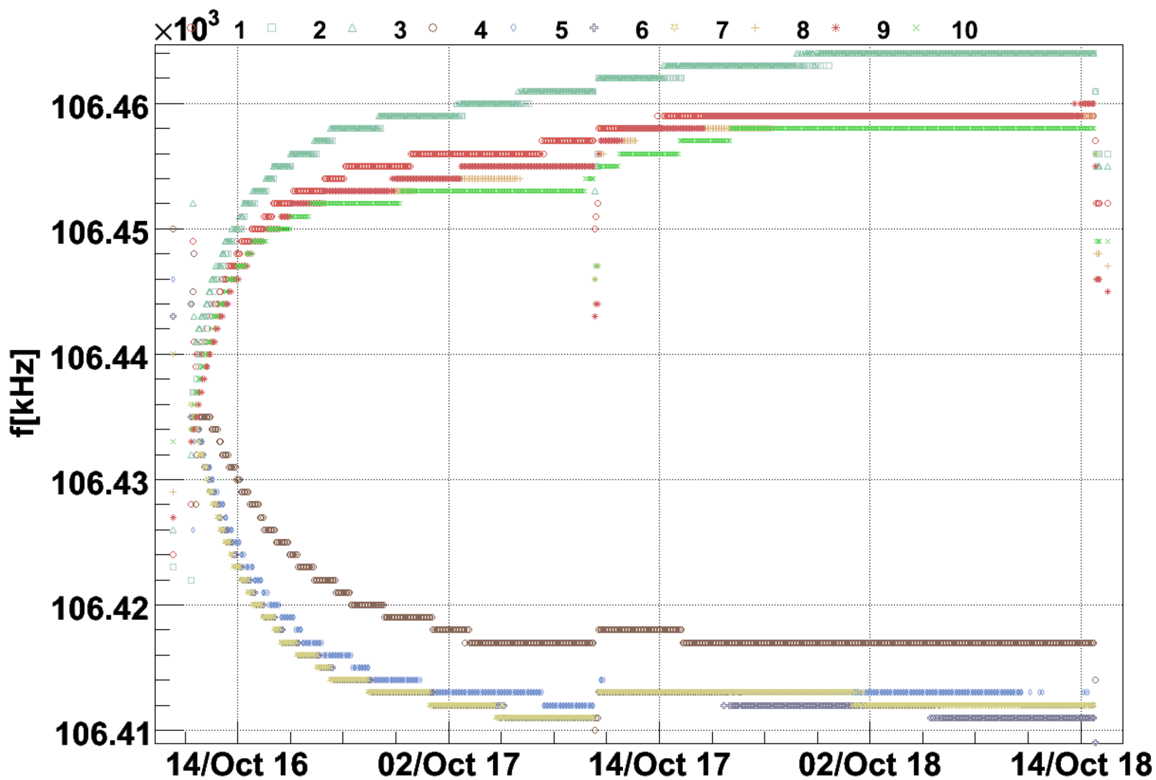
three gaussians with 25 kHz separation: $M_2 =$ 350 - 550 kHz^2 or 100 - 200 kHz^2 for each proton

Transverse polarized signal 82 % 0.63 T

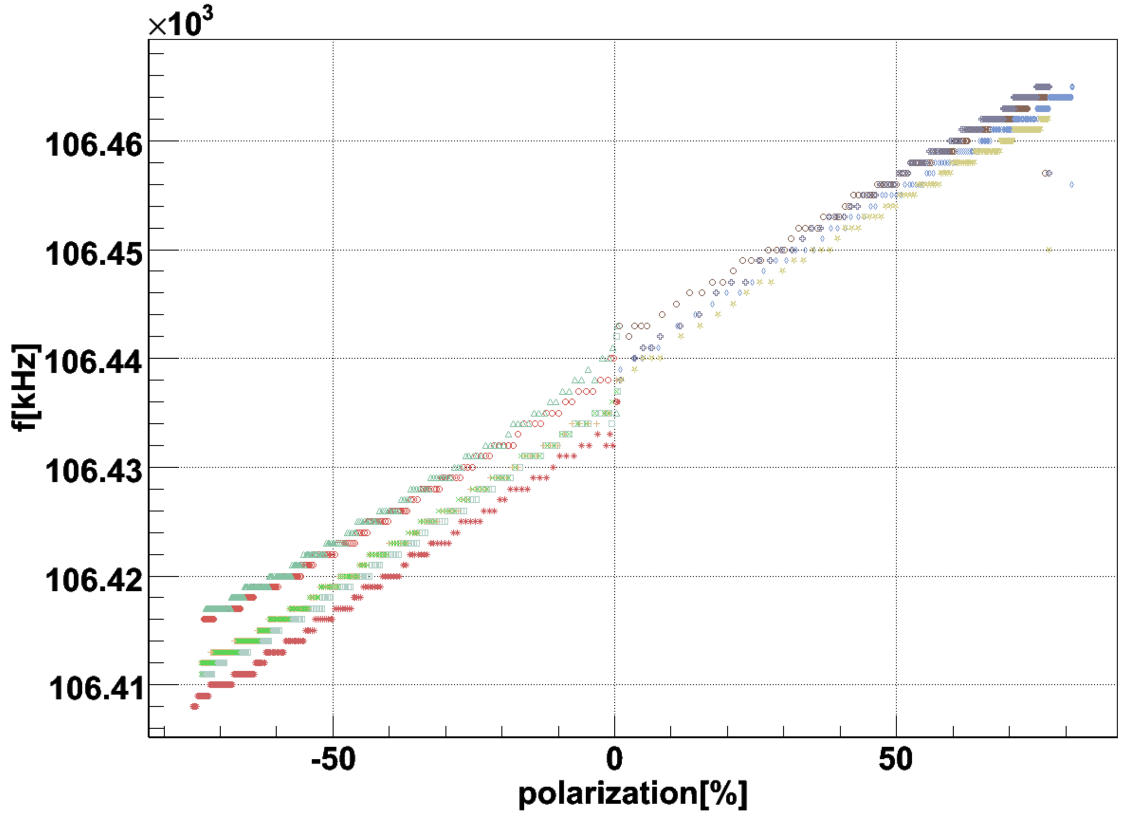


- phase correction about 1.5 rad
- $M_2 = 564$ kHz^2

Peak shift vs. polarization



NMR frequency shifts



Nuclear spin Hamiltonian

$$H = H_z + H_{dip} + H_{quad} + H_{hf} + H_{RF}$$

- D in ^{6}LiD at 2.5 T CW NMR: 16.4 MHz + 1 kHz + 0 + 0 + 0
- H in NH_3 at 2.5 T CW NMR : 106 MHz + 25 kHz + 0 + 0 + 0
- for spin thermodynamics only zeeman term needed
- $T_s \sim h \cdot f / k_B \sim$ 0.8 mK (57 %) for D and $\sim$ 5 mK (47 %) for H at 2.5 T (possible anisotropy)

Proton NMR linewidth calculation in NH_3

model	**H-N-H[deg]**	$\mathbf{r}_{NH}$**[Å]**	**H** $\mathbf{M_2}$**[kHz^2]**	**N** $\mathbf{M_2}$**[kHz^2]**
neutron powder diffraction 2 K	107.5	1.012	690 ± 13	37 ± 1
Dunitz, Seiler weight scheme	109.0	1.010	662 ± 13	38 ± 1
"fit" to measured width	109.5	1.055	501 ± 10	29 ± 1

- ideal sp3 hybridization of nitrogen 109.5 deg
- motional averaging of dipole term due to hydrogen movement?

Highly polarized nuclear spins

- J. H. Van Vleck, Phys. Rev. 1168–1183 **74** (1948)
- dipole interaction: odd moments vanish resulting in a symmetric lineshape, lineshape independent of polarization or sample shape
- A. Abragam et al., *Absorption Lineshape of Highly Polarized Nuclear Spin Systems*, J. Magn. Res. **10** (1973) 322–346
- spherical sample of one species of nuclear spins coupled by pure dipole interaction: $M_2(p) = M_2(0)[1 - p^2]$

Proton level populations in NH_3

$+3/2 \mid \uparrow\uparrow\uparrow>$ +100 %, $+1/2 \mid \uparrow\uparrow\downarrow>$ + 33 %,

$-1/2 \mid \uparrow\downarrow\downarrow>$ -33 %, $-3/2 \mid \downarrow\downarrow\downarrow>$ -100 %

Polarization 81.1 % one of the possible solutions

$E_{+3/2}$ —— $n_{+3/2}$ 0.01

$I_{+3/2\leftarrow\rightarrow+1/2}$ 0.067

$E_{+1/2}$ —— $n_{+1/2}$ 0.063

$I_{+1/2\leftarrow\rightarrow-1/2}$ 0.081

$E_{-1/2}$ —— $n_{-1/2}$ 0.127

$I_{-1/2\leftarrow\rightarrow-3/2}$ 0.852

$E_{-3/2}$ —— $n_{-3/2}$ 0.8

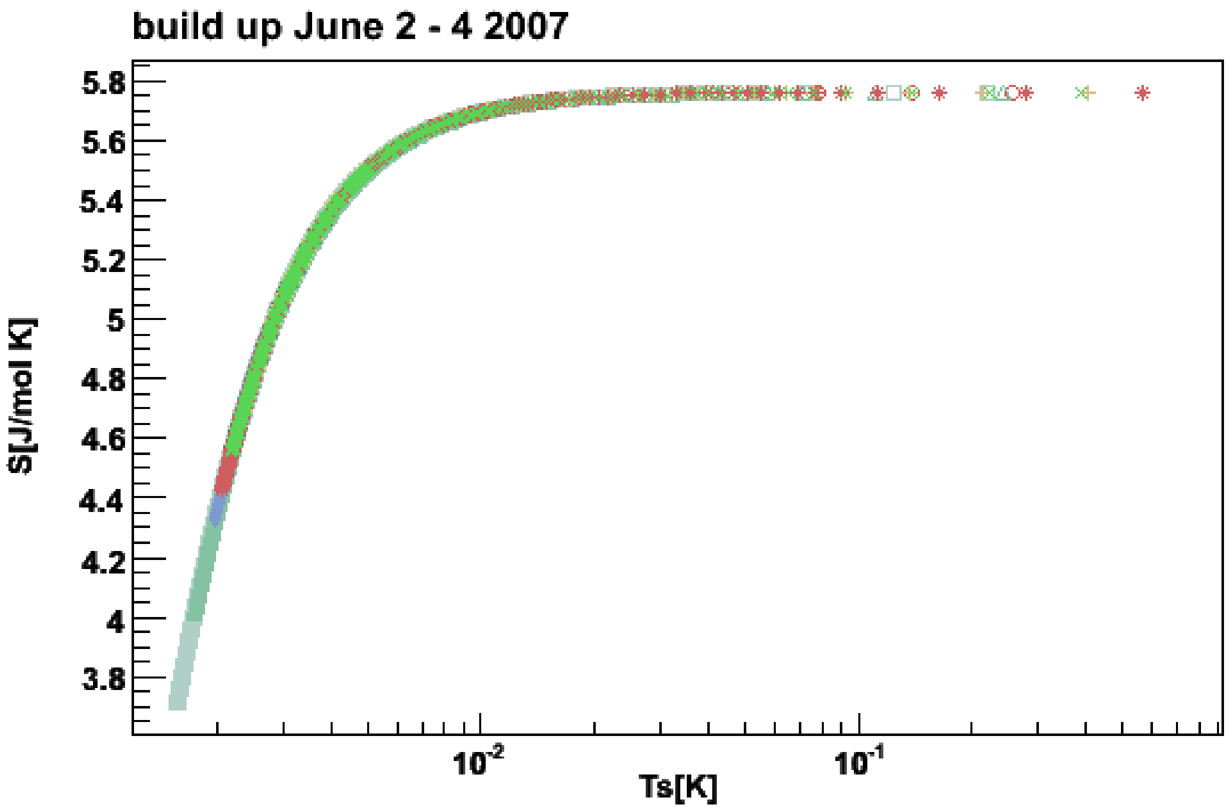
Dipolar spin flips allowed only for

$+1/2 \mid \uparrow\uparrow\downarrow> +$ 33 % and

-1/2 $\mid \uparrow\downarrow\downarrow>$ -33 %.

Frustrated spin system? Probably not since zeeman energy is dominating.

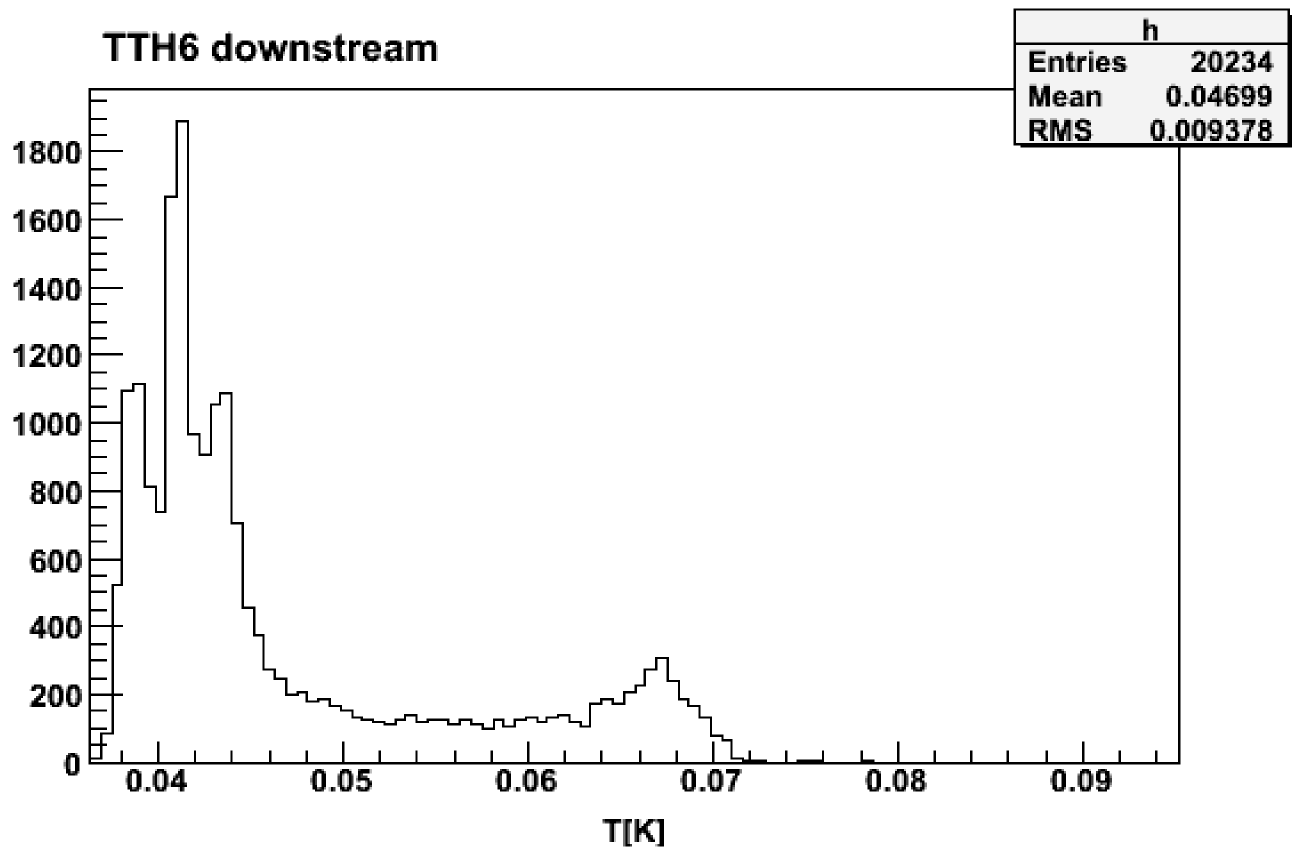
Entropy vs. spin temperature



Minimum entropy densities

coil	S[J/mol K]	ρ_n / $\rho_{\overline{n}}$ [%]
1	4.01	+2.56
2	3.71	-5.11
3	4.01	+2.56
4	4.555	-0.08
5	4.33	-5.02
6	4.67	+2.44
7	4.68	+2.44
8	4.53	+0.53
9	4.43	-1.69
10	4.558	+1.15

Helium temperature in transverse run



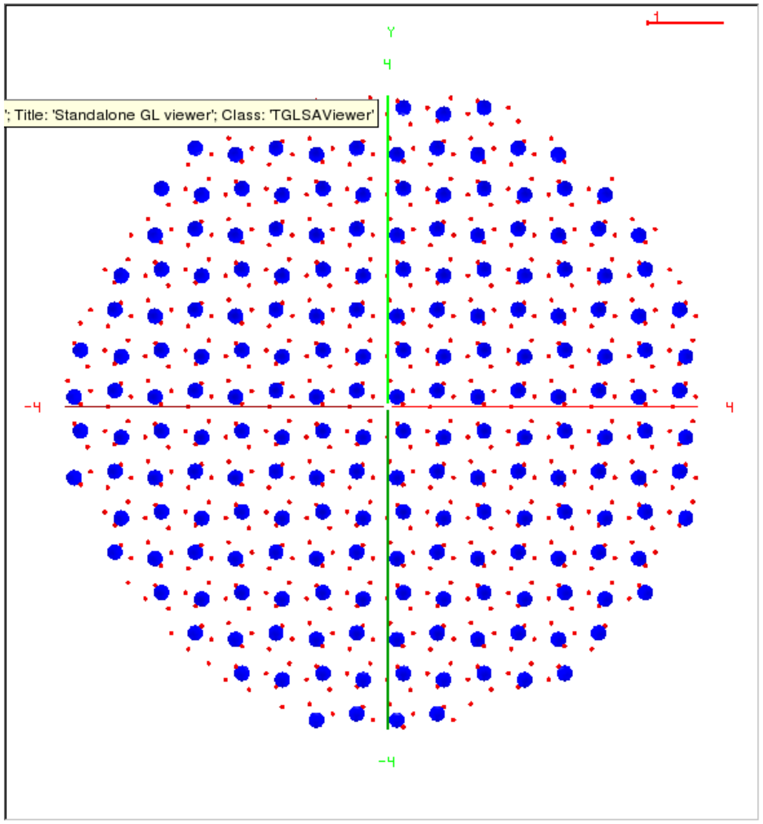
Transverse relaxation summary

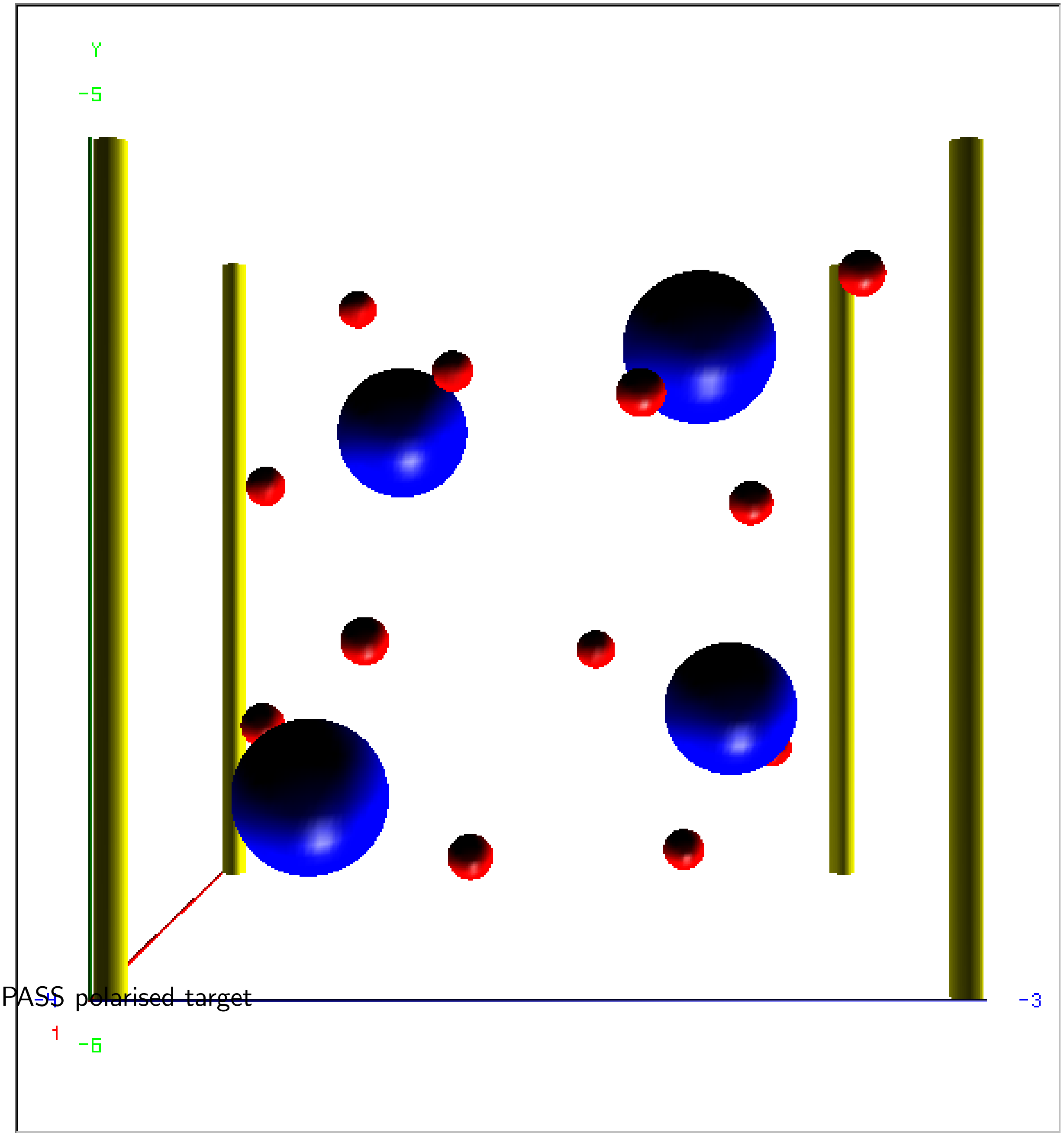
- deuteron target 0.4 - 1 %/day or 100 - 230 pW/mol to frozen spin system 0.42 T
- proton target 2007 0.4 - 0.7 %/day or 180, 170 and 230 pW/mol 0.63 T
- mean helium temperatures 62.2 mK, 51.5 mK and 47.0 mK

Hydrogen bonding

- acceptors and donors
- residual entropy in water ice
- J-coupling frequency shifts fraction of Hertz
- http://en.wikipedia.org/wiki/J-coupling
- http://en.wikipedia.org/wiki/Hydrogen_bond

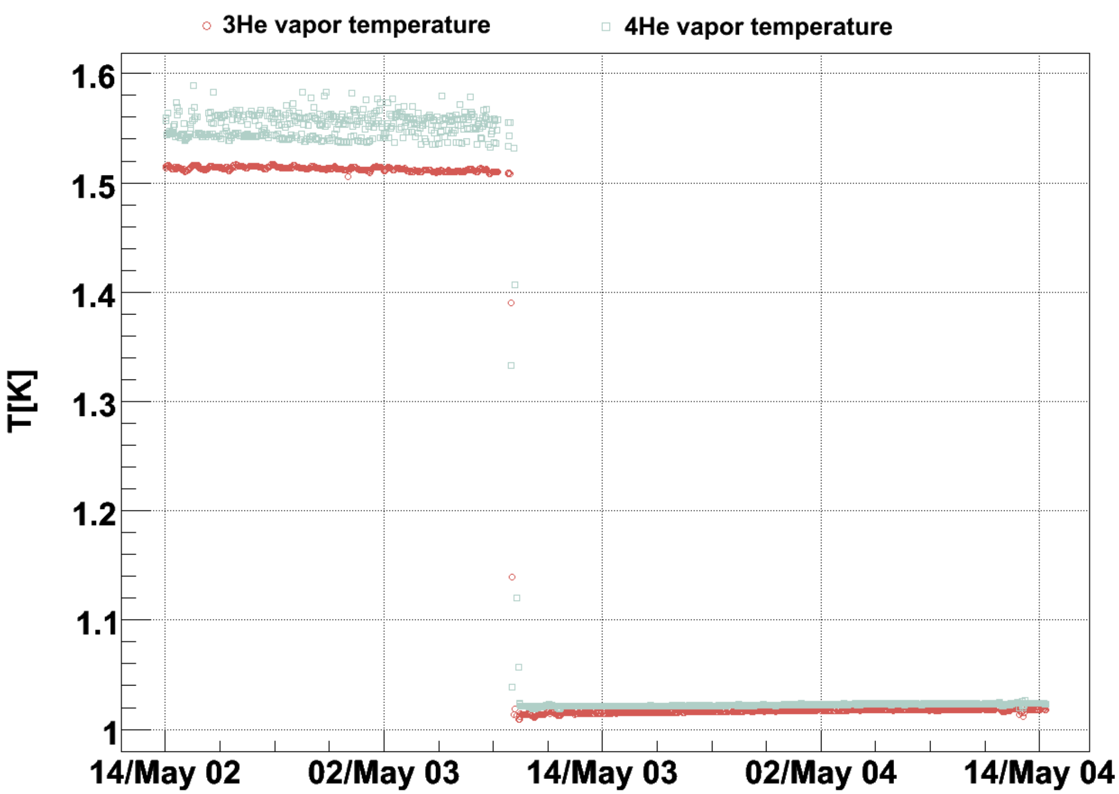
Possible P$2_1$3 cubic crystal symmetry



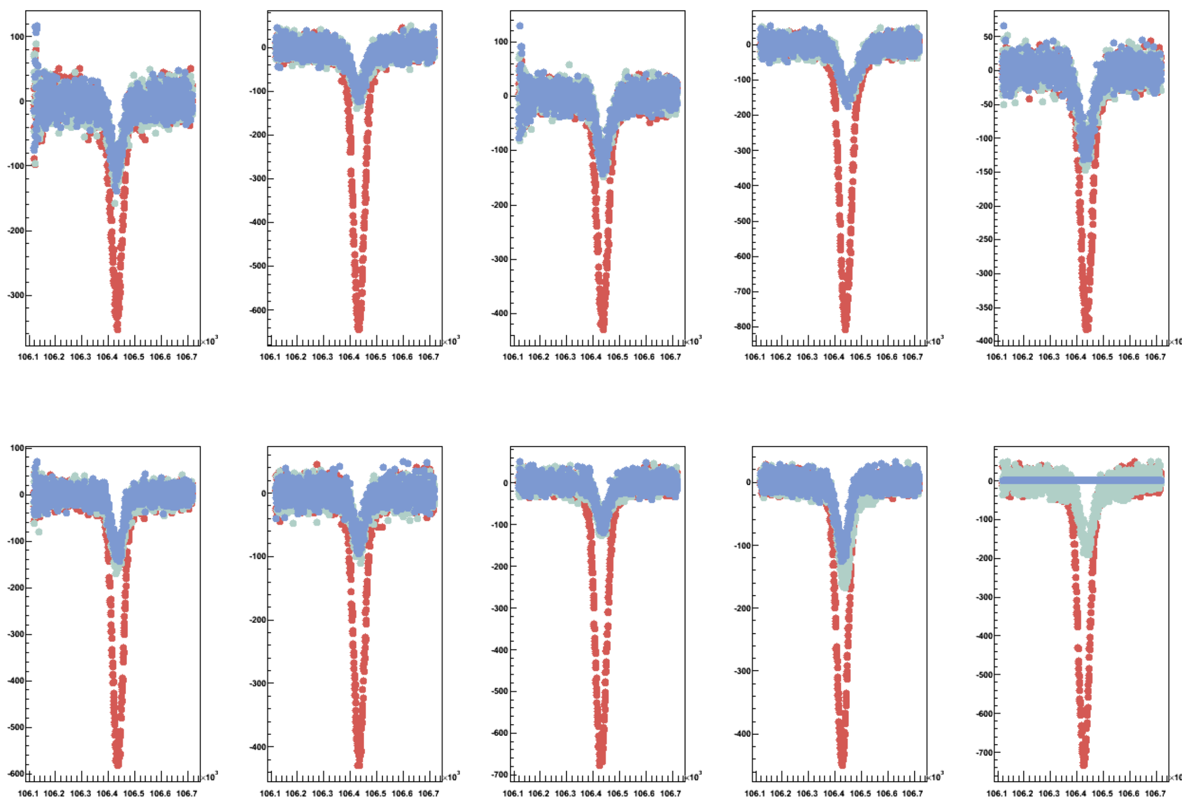

Y
-5
-3
1
-6

- assuming cubic P$2_1$3 symmetry: a=5.1305 Å, r_{NH}=1.0099 Å, r_{NN}=3.3769 Å, and H-N-H bond angle of 107.5 - 109.0°
- density 0.838 g/cm^3
- calculated NMR-line second moment $M_2 = 890$ kHz^2, static spherical sample with radius of 4 unit cells
- polarized dipole shifts: two peaks in histogram $\pm$13 and $\pm$15 kHz
- with polarization negative/positive dipole shifts suppressed, probable reason for asymmetric line shape

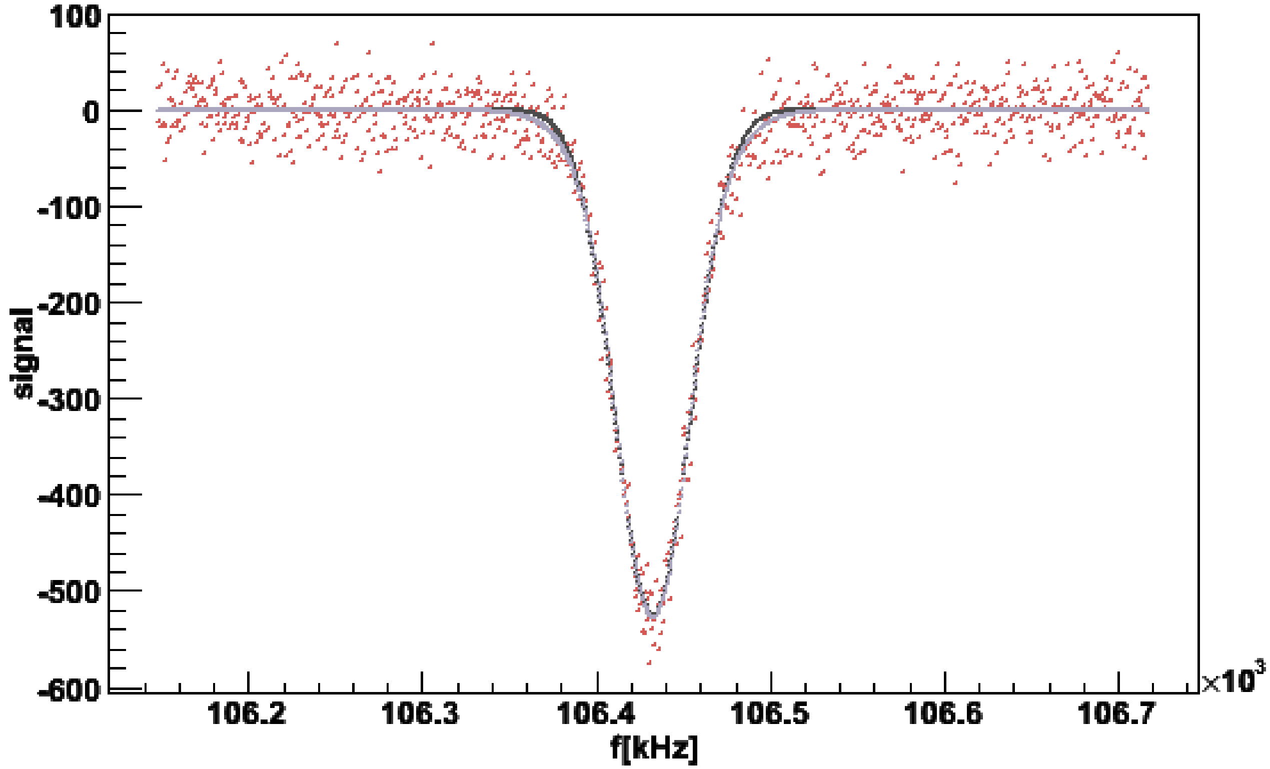
Thermometry in TE-calibration



Thermal equilibrium signals and background 1.3 K

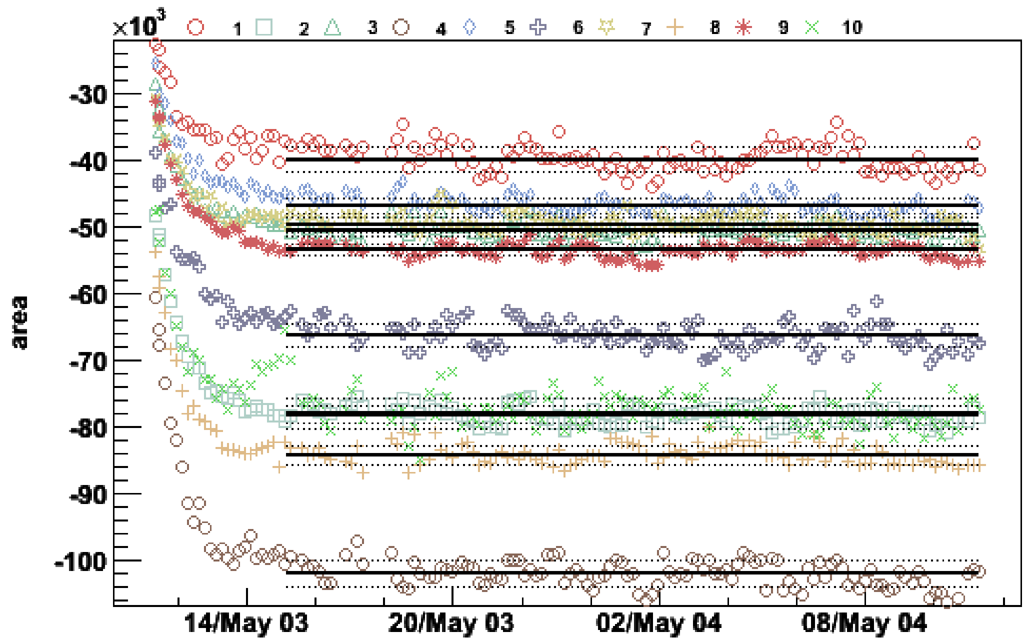


Thermal equilibrium signal 1.0 K



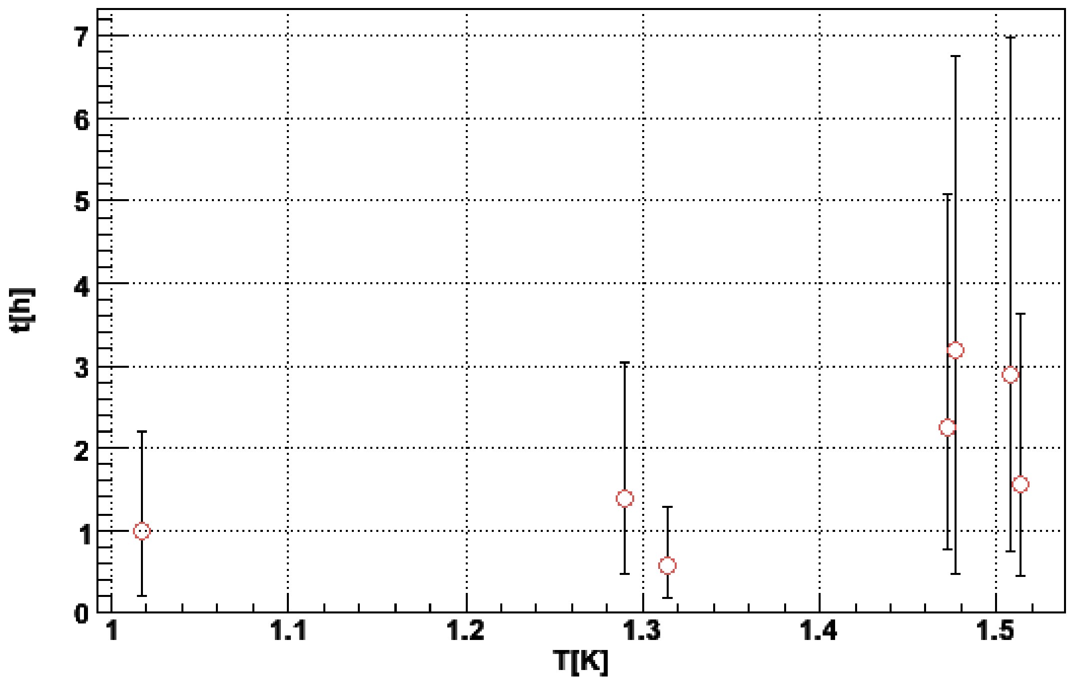
- correction with Kronig-Kramers dispersion relations -0.038 - $+$ 0.027 rad (about 2 degree)
- residual error in imaginary part less than 0.24 %
- $M_2 =$ 520 - 650 kHz^2
- $M_4 =$ 1.0 - 1.7 $\cdot 10^6$ kHz^4
- $\mu = M_4/M_2^2 \sim$ 3.8 - 4.0 (5.0 - 5.5 ^{6}LiD)
- $A_m/A_{raw} =$ -1.4 - -4.5 %
- relaxation time 1 - 3 hours and 1.5 - 4 hours for background protons
- background protons 700 - 4000 kHz^2, $\mu \sim$ 4.1 - 11.6

Robust time cuts to TE-areas



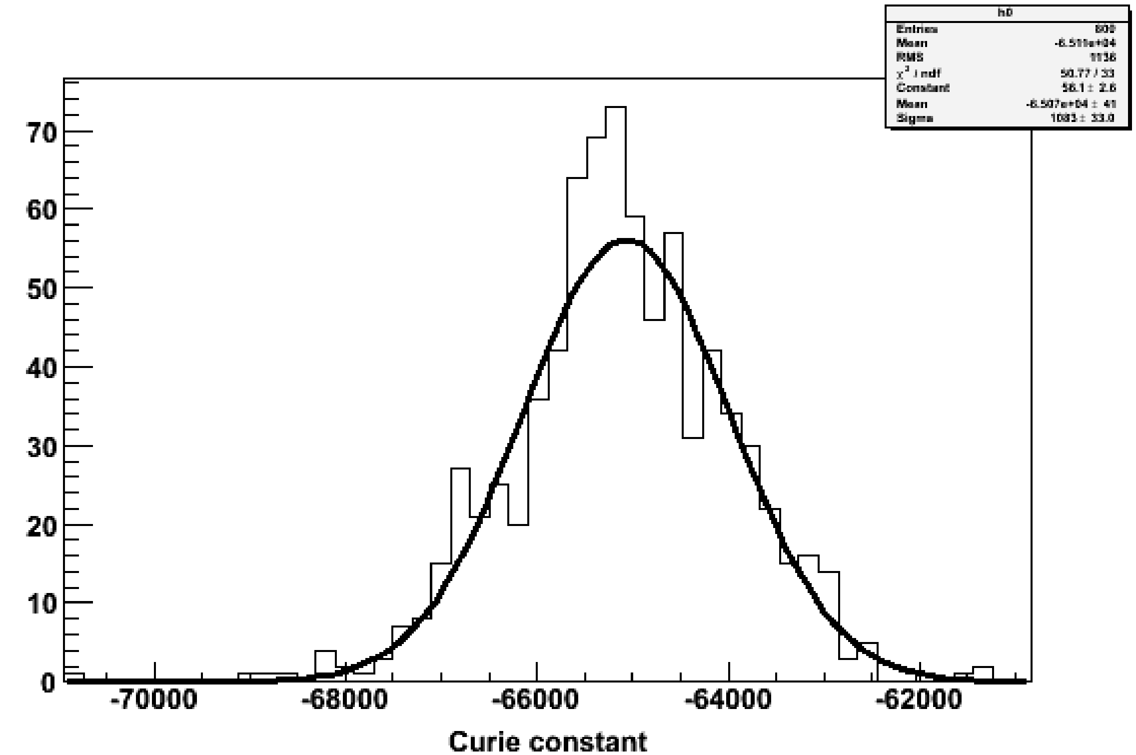
- median and 18 % and 82 % quantiles are used as robust estimate

TE relaxation times



Simulating TE-calibrations

- for real error estimate the thermal equilibrium calibration should be repeated N times
- not practical, would take too long and is expensive
- use computers to simulate the TE-calibration: produce similar set of NMR signal with same S/N ratio and analyze this set N times
- example: Gaussian background noise and uncertainty in temperature for coil #6 N =800 calibrations gives an error 1.67 %, 5.21 % N =700 first empty cell calibration and 6.23 % N =700 second empty cell calibration


h0
Entries 800
Mean -6.511e+04
RMS 1136
χ² / ndf 50.77 / 33
Constant 56.1 ± 2.6
Mean -6.507e+04 ± 41
Sigma 1083 ± 33.0
70
60
50
40
30
20
10
0
-70000
-68000
-66000
-64000
-62000
Curie constant

Summary

- dipolar frequency shifts 22 - 27 kHz indicate close to maximum nuclear polarizations in NH_3
- spin Hamiltonian too simple, probably some excitations (amorphous) present (cf low temperature dielectric constant)
- new computer tools developed for solid state targets, better control of polarization results

Software

- LabVIEW for DAQ and signal analysis
- 2001 - 2007 NMR data about 23 GB
- ptnmr on ROOT libraries at CERN CVS http://svnweb.cern.ch/world/wsvn
- 19436 lines of C++ and Makefiles
- compiled code and testing programs
- unix shell login: data and analysis accessible from anywhere
- http://wwwcompass.cern.ch/compass/detector/target/NMR/Ntoolsdoc/index.h