NMR line-shapes in highly polarized ^{6}LiD at 2.5 T

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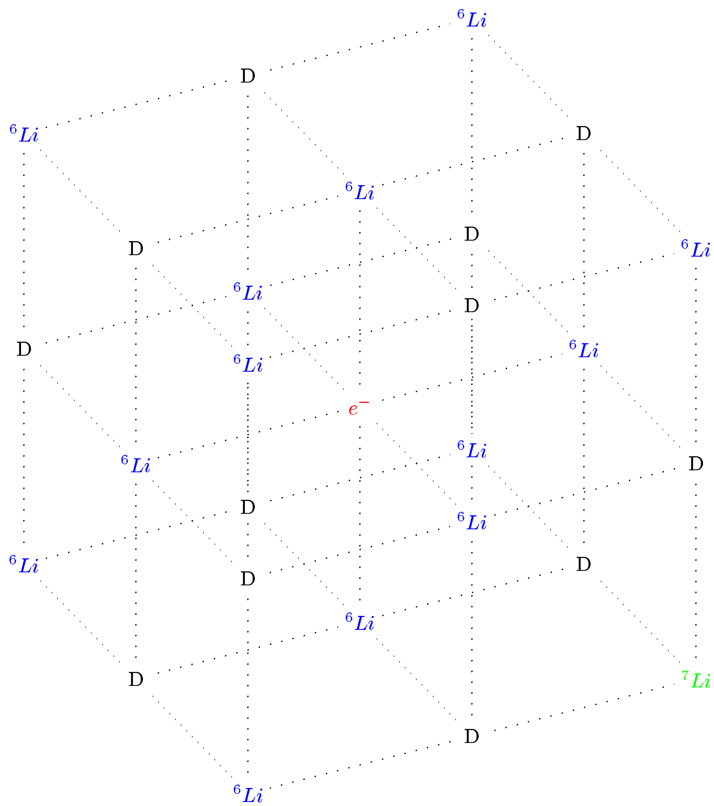
1. ^{6}**LiD target material**
2. **Interactions**
3. **2nd and 4th moments**
4. **Line-shapes**

^{6}LiD target material

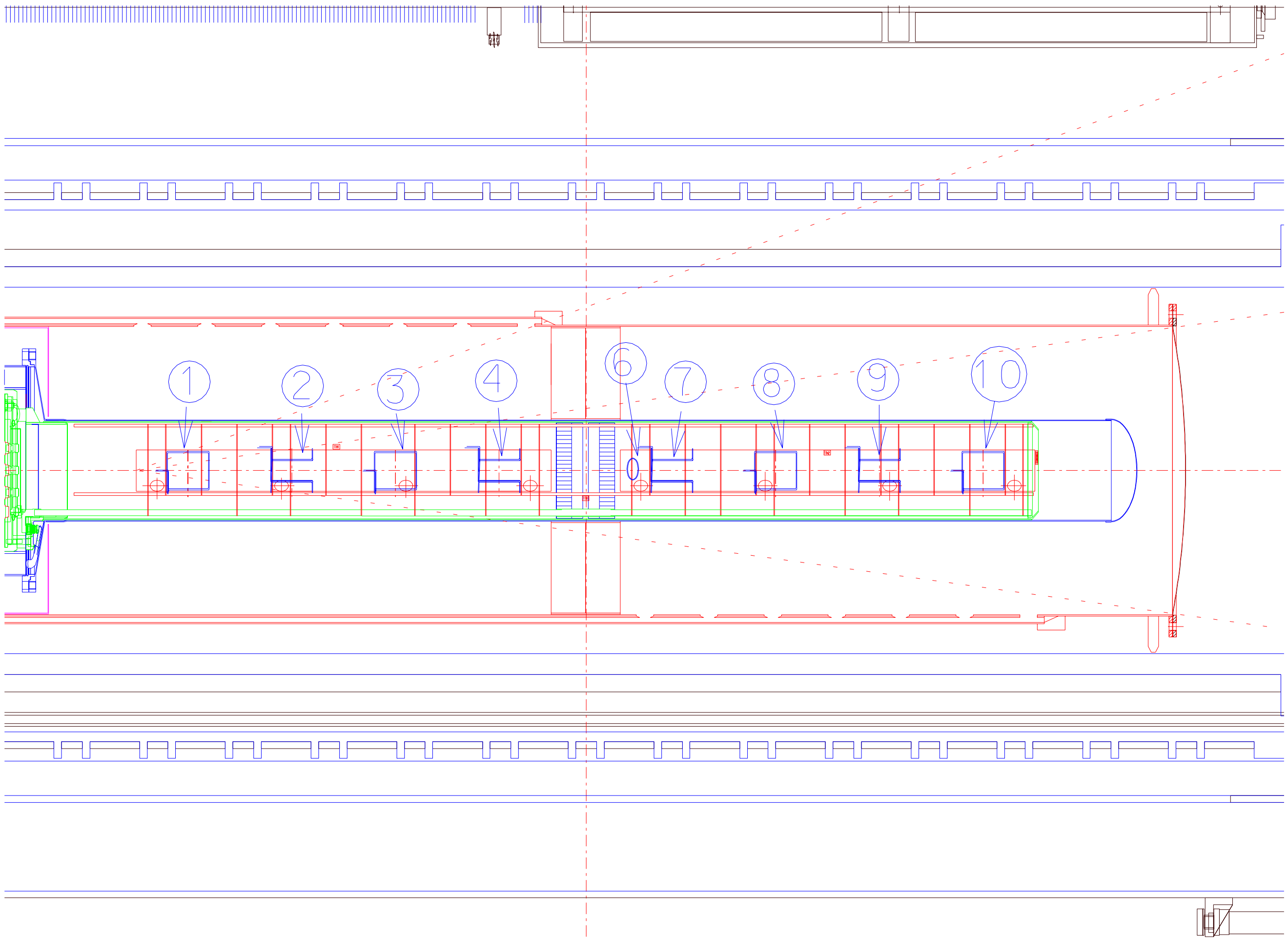
Element	spin	mass [amu]	γ [MHz/T]	[mol]	[%]
^{1}H	1/2	1.00794	42.2957	0.1	0.2
^{2}D	1	2.0140	6.53600	21.4	42.4
^{3}He	1/2	3.0169	32.4343	0.7	1.4
^{4}He	0	4.0026	-	6.8	13.3
^{6}Li	1	6.0151	6.26561	20.6	40.8
^{7}Li	3/2	7.0160	16.5467	0.9	1.8
Total				50.5	100
e-	1/2		27 992.5		

inside one NMR coil about 15 % $\cdot$ 50.5 mol = 7.8 mol

^{6}LiD target material



NMR coils



Interactions

Dipole-dipole

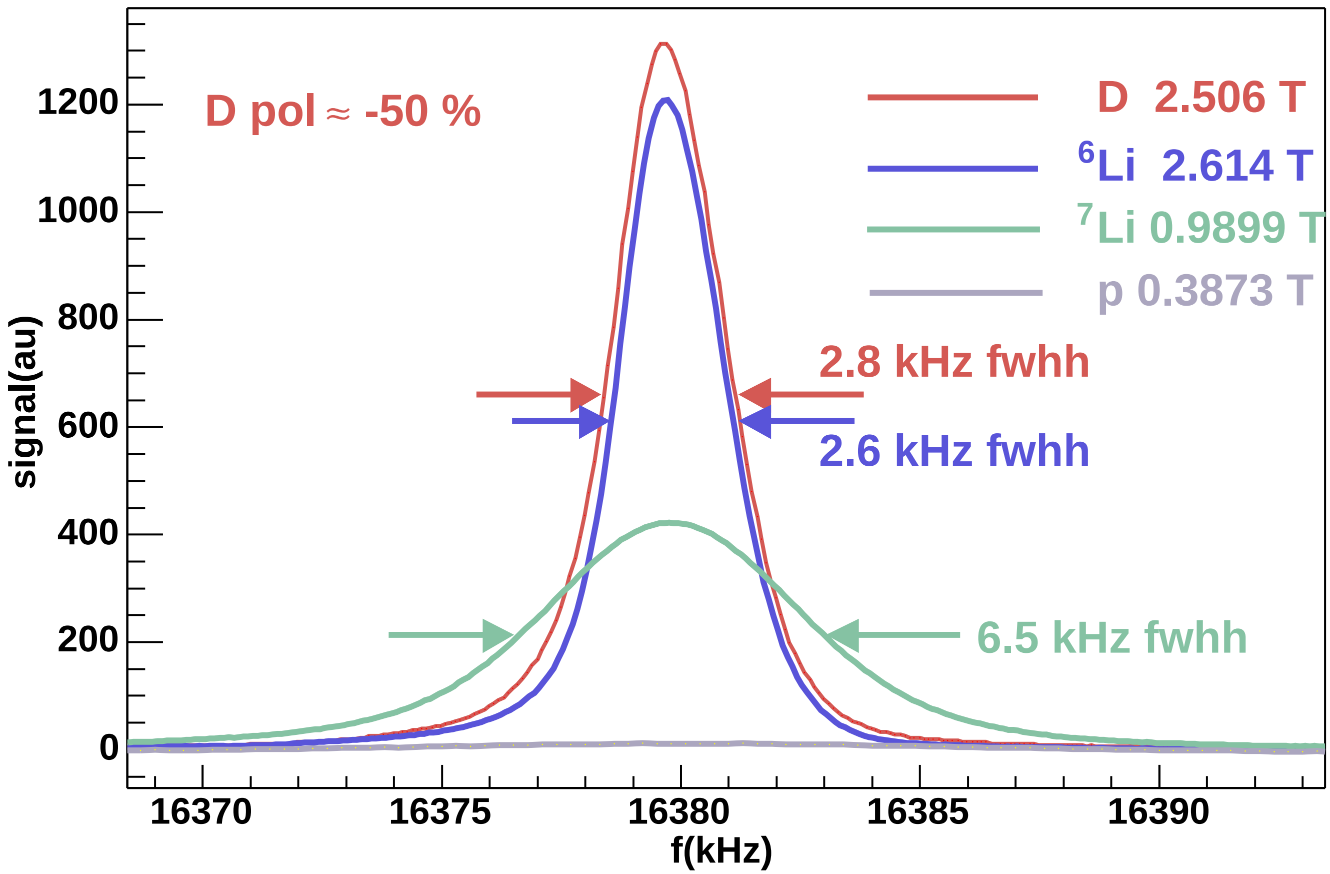
$$D_{zz,jk} = \frac{\mu_0 \hbar \gamma_1 \gamma_2}{4\pi r_{j,k}^3}(1 - 3\cos^2\theta_{j,k})^2 \sim 0 - \pm 1000 \text{ Hz}$$

Quadrapole

$$\omega_Q = \frac{3eQ}{2I(2I-1)\hbar}\partial_{xy}V(x,y)$$

lattice a $= 4$ Å, $Q_D = 2.82 \cdot 10^{-31}\text{m}^2$.

NMR signals


D pol ≈ -50 %
D 2.506 T
6Li 2.614 T
7Li 0.9899 T
p 0.3873 T
2.8 kHz fwhh
2.6 kHz fwhh
6.5 kHz fwhh
signal(au)
0
200
400
600
800
1000
1200
16370
16375
16380
16385
16390
f(kHz)

Moments from text book

$$M_2 = g_S \sum_k (\frac{\mu_0 \hbar \gamma_1 \gamma_2}{4\pi r^3_{j,k}}(1 - 3\cos^2\theta_{j,k}))^2 = g_S \sum_k (D_{zz,jk})^2.$$

$$g_S = \frac{S(S+1)}{3} \quad \text{unlike spins}$$

$$g_I = \frac{3I(I+1)}{4} \quad \text{like spins}$$

$$M_4 = -\frac{g_I^2}{5}\sum_k (D_{zz,jk})^4[8 + \frac{3}{2I(I+1)}]$$

$$+3[g_I \sum_k (D_{zz,jk})^2]^2$$

$$-\frac{g_I^2}{3N} \sum_{j,k,m\neq j,k} (D_{zz,jk})^2[D_{zz,jm} - D_{zz,km}]^2$$

Moments from text book

$$M_4 \propto (H_{II})^4 + (H_{IS})^4 + (H_{II})^2(H_{IS})^2 + (H_{SS})^2(H_{IS})^2$$

$$\gamma_I^8 \quad \gamma_I^4\gamma_S^4 \quad \gamma_I^6\gamma_S^2 \quad \gamma_I^2\gamma_S^6$$

$$\frac{M_4}{M_2^2} \propto (\frac{\gamma_S}{\gamma_I})^2$$

$$\text{D and } ^7\text{Li } (\frac{\gamma_{^7Li}}{\gamma_D})^2 \approx 6.4$$

Calculations

- 6 unlike neighbors for D, ^{6}Li, ^{7}Li and proton at $r = 2$ Å
- 12 like neighbors at $r = 2.828$ Å
- 0.4 % of D is proton and 4.4 % of ^{6}Li is ^{7}Li
- ignore paramagnetic centers
- 1500 crystals inside NMR coil with random crystal orientation
- average 100 randomly chosen samples inside NMR coil

elements	M_2 [kHz^2]
D $\leftrightarrow$ 6 $\times$ ^{6}Li/^{7}Li + 12 $\times$ D/p	1.0 - 1.6
^{7}Li $\leftrightarrow$ 6 $\times$ D/p + 12 $\times$ ^{6}Li/^{7}Li	5.1
p $\leftrightarrow$ 6 $\times$ ^{6}Li/^{7}Li + 12 $\times$ D	35

Gaussian vs memory

- Gaussian

$$G(f) = A \cdot exp(-\frac{(f-f_0)^2}{2M_2}),\ M_4/M_2^2 = 3$$

- Memory function (solution of FID integro-differential equation)

$$M(f) = A \cdot \frac{K'(f-f_0)}{(2\pi(f-f_0) - K''(f-f_0))^2 + (K'(f-f_0))^2}$$

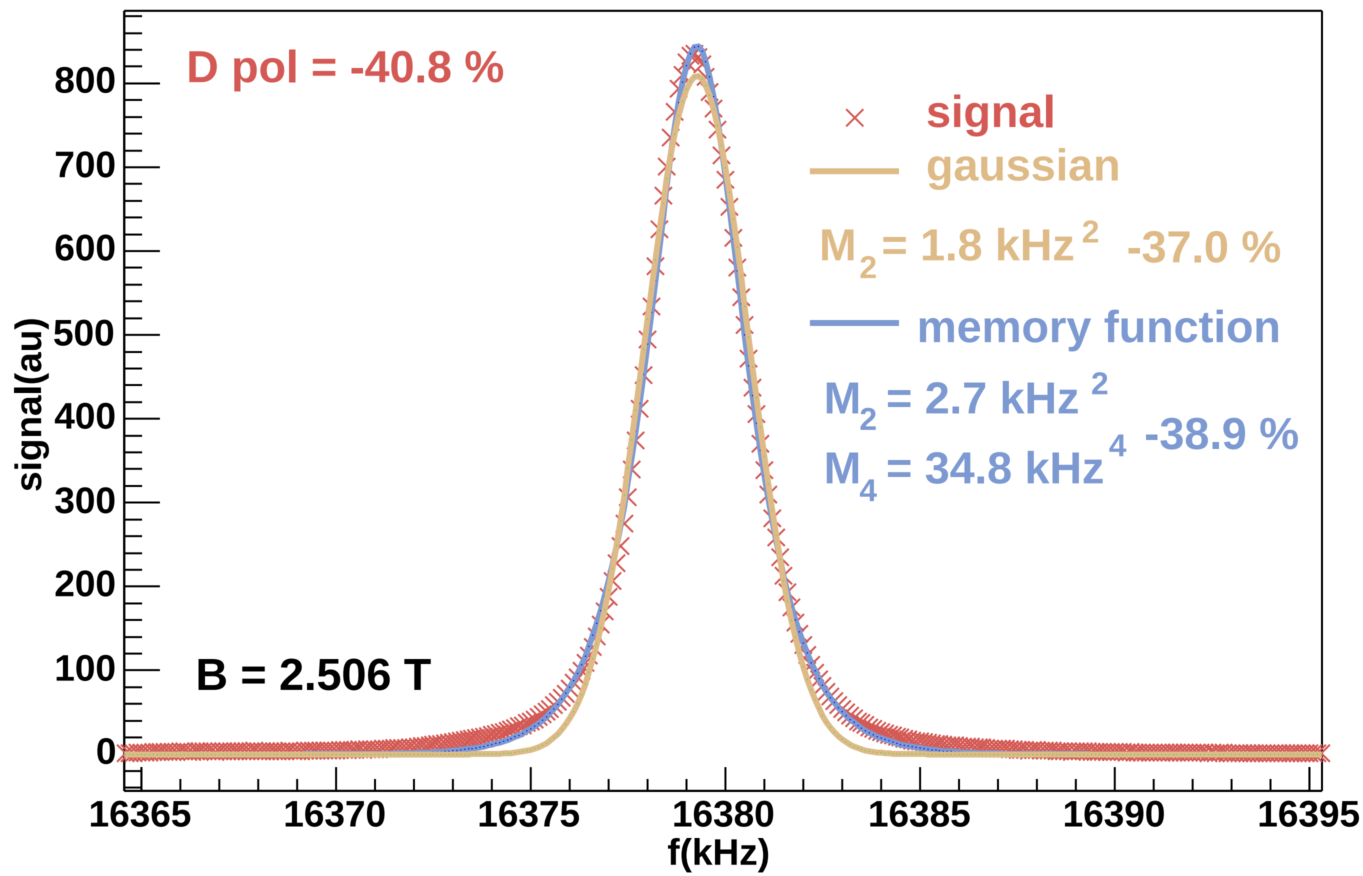
$$K'(f) = \frac{4\pi^2 M_2 \sqrt{\pi}}{\sqrt{2N_2}} exp(-\frac{2\pi^2 f^2}{N_2})$$

$$K''(f) = \frac{8\pi^3 M_2 f}{N_2} exp(-\frac{2\pi^2 f^2}{N_2}) F(1/2, 3/2, 2\pi^2 f^2/N_2)$$

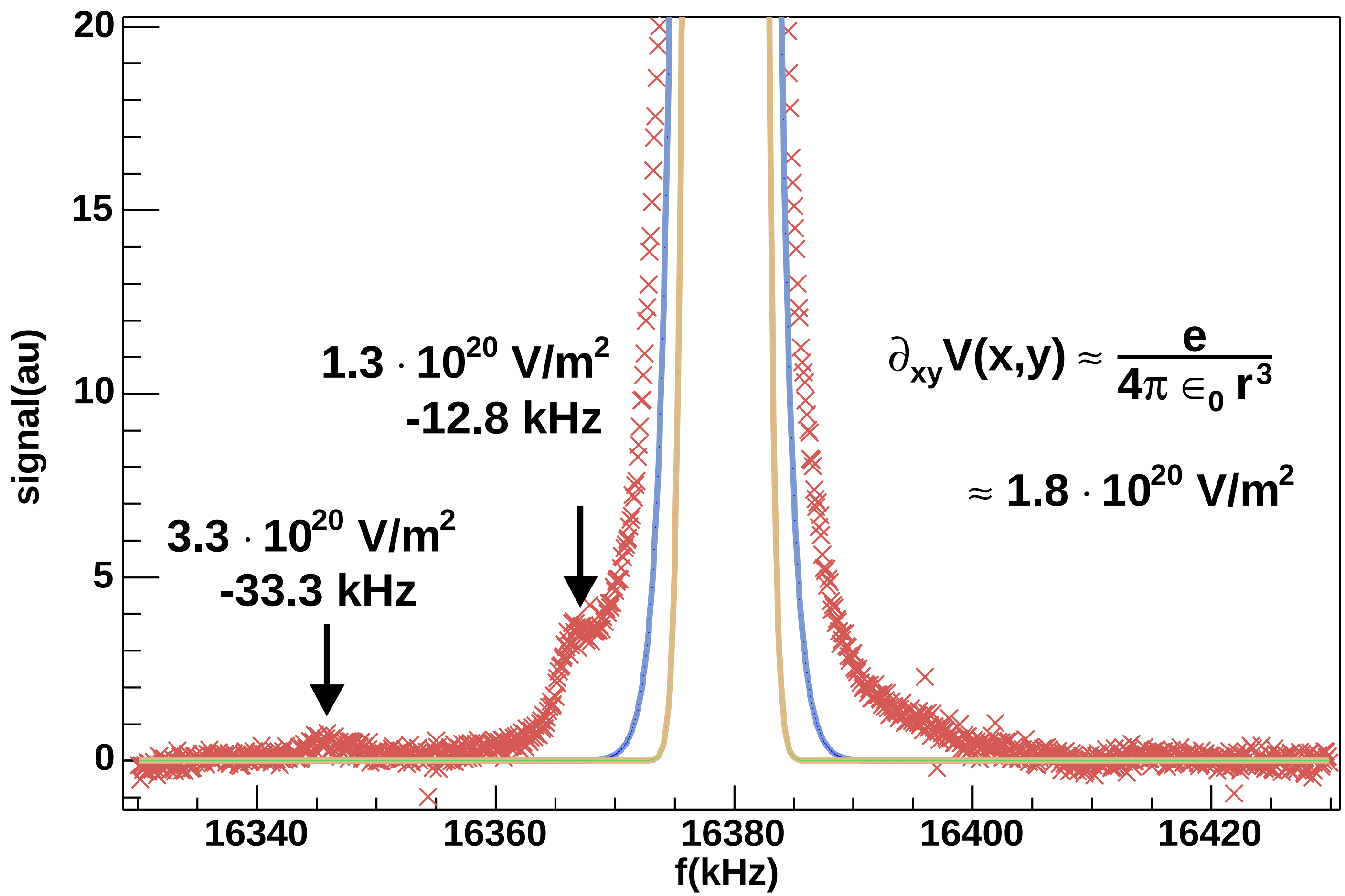
$$N_2 = M_2(M_4/M_2^2 - 1)$$

- also possible: modified Lorentzian, Abragam function

Gaussian vs memory

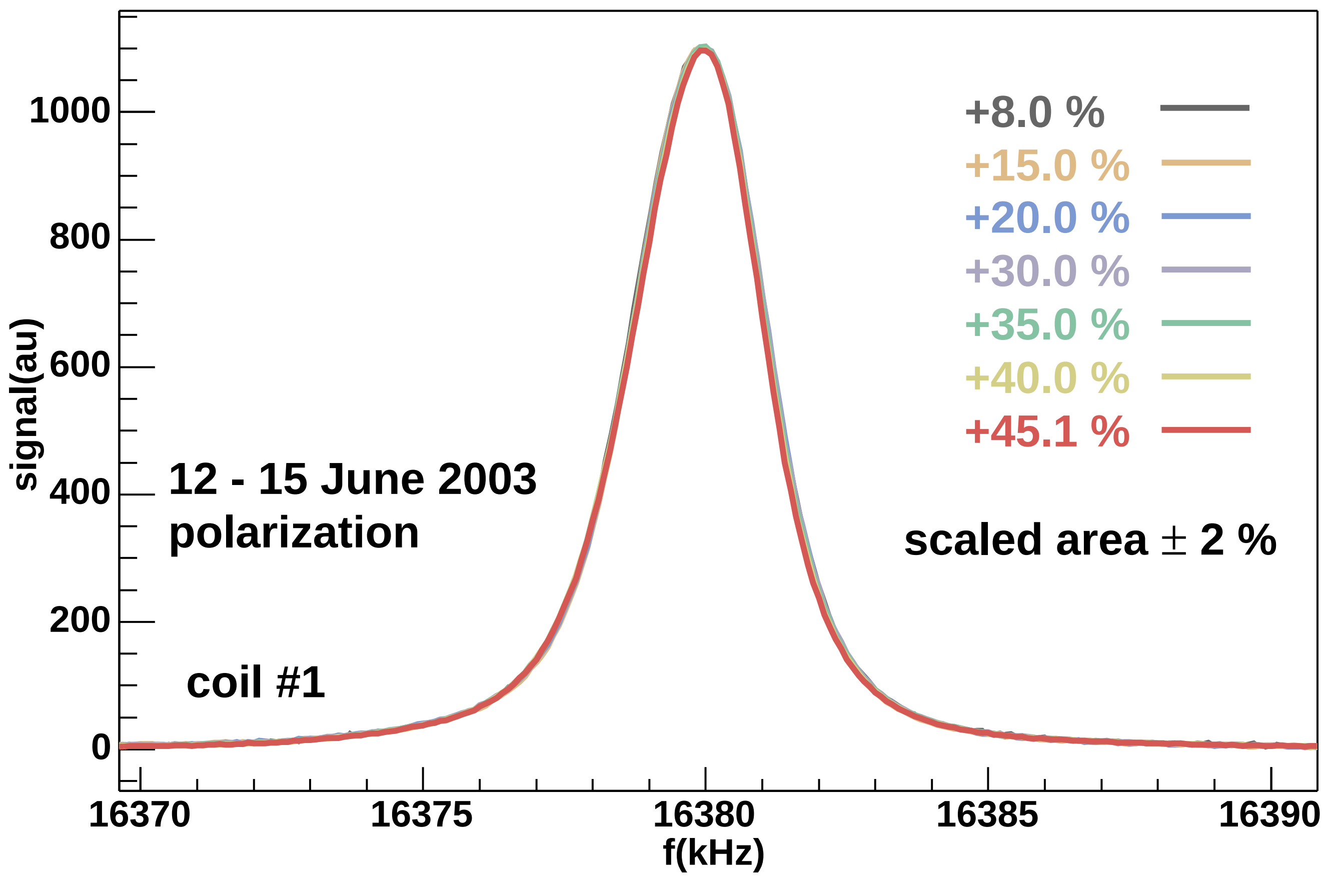


Baseline



20
15
10
5
0
signal(au)
16340
16360
16380
16400
16420
f(kHz)
$1.3 \cdot 10^{20}$ V/m^2
-12.8 kHz
$3.3 \cdot 10^{20}$ V/m^2
-33.3 kHz
$\partial_{xy}V(x,y) \approx \frac{e}{4\pi \epsilon_0 r^3}$
$\approx 1.8 \cdot 10^{20}$ V/m^2

NMR line-shape

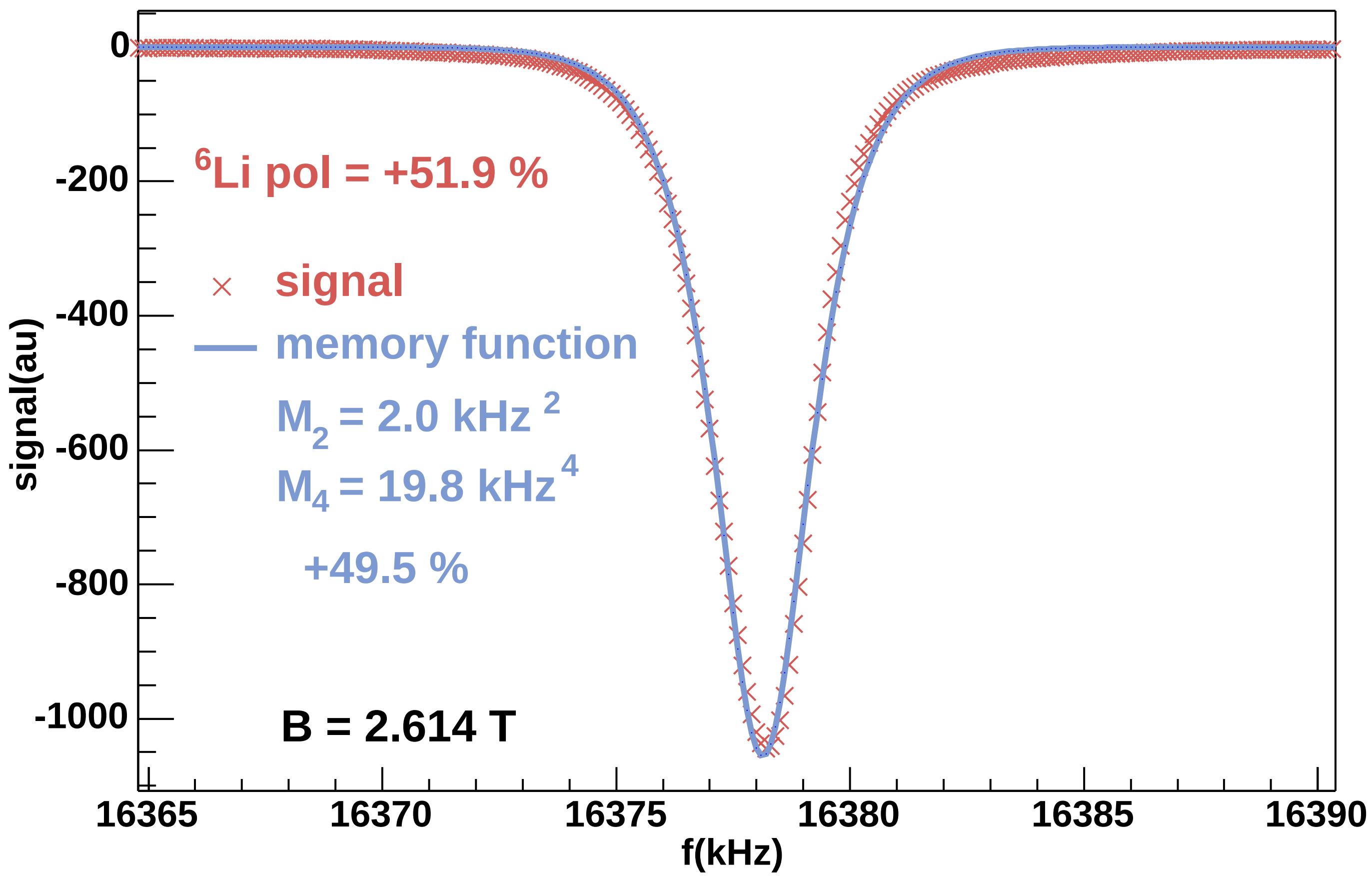


COMPASS

NMR line-shape

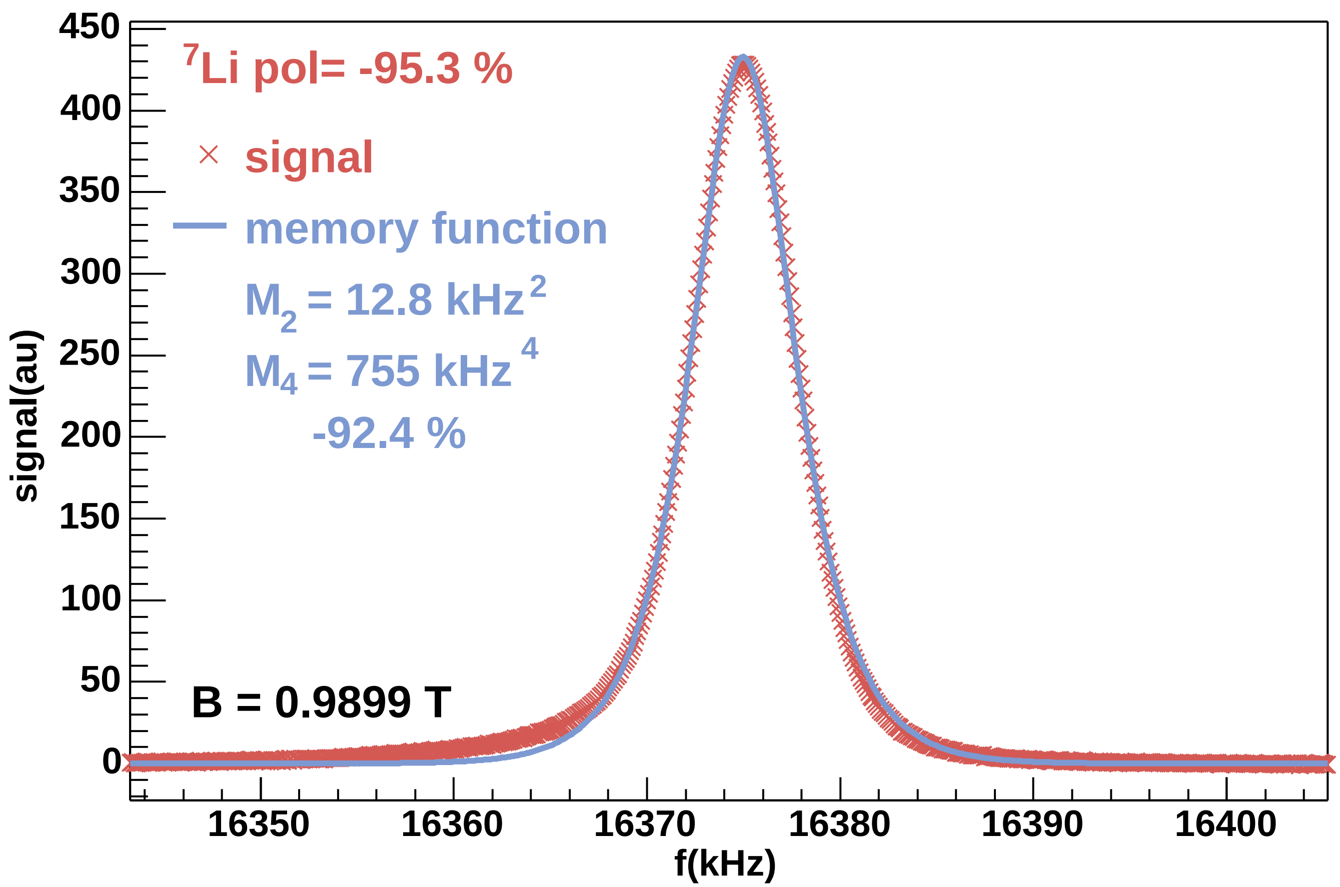
pol[%]	f_0 [kHz]	M_2 [kHz^2]	M_4 [kHz^4]	M_4/M_2^2
8.0	16379.9	2.55	29.8	4.6
15.0	16380.1	2.45	27.9	4.6
20.0	16380.1	2.54	30.4	4.7
30.0	16380.3	2.60	32.4	4.8
35.0	16380.2	2.60	32.7	4.8
40.0	16380	2.62	33.5	4.9
45.1	16380.3	2.63	34.2	4.9

^{6}Li



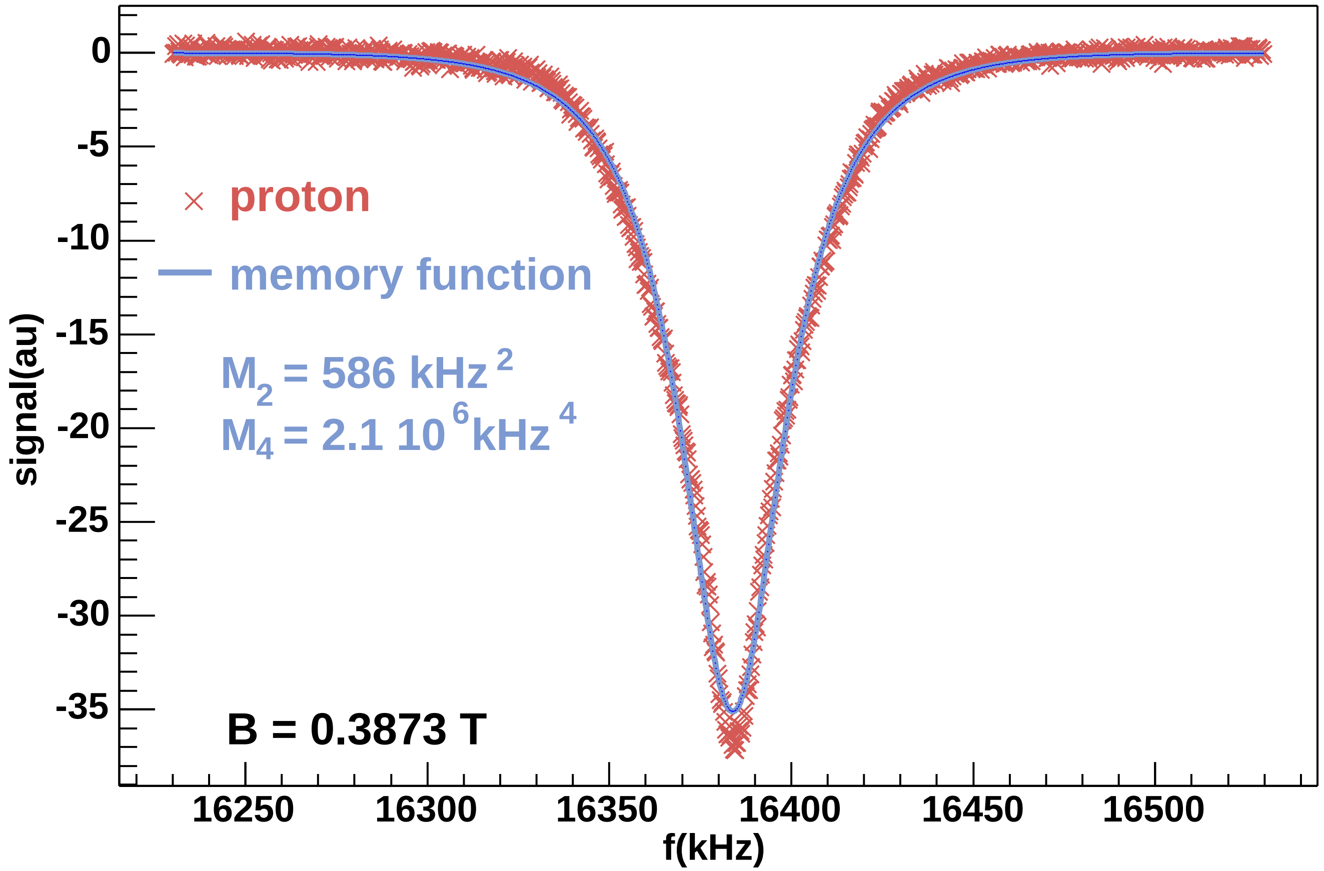
^{6}Li pol = +51.9 %
signal
memory function
M_2 = 2.0 kHz ^{2}
M_4 = 19.8 kHz ^{4}
+49.5 %
B = 2.614 T
0
-200
-400
-600
-800
-1000
signal(au)
16365
16370
16375
16380
16385
16390
f(kHz)

^{7}Li



^{7}Li pol= -95.3 %
signal
memory function
M_2 = 12.8 kHz^2
M_4 = 755 kHz^4
-92.4 %
B = 0.9899 T
signal(au)
f(kHz)
0
50
100
150
200
250
300
350
400
450
16350
16360
16370
16380
16390
16400

proton



0
-5
-10
-15
-20
-25
-30
-35
signal(au)
proton
memory function
M2 = 586 kHz 2
M4 = 2.1 10 6 kHz 4
B = 0.3873 T
16250
16300
16350
16400
16450
16500
f(kHz)

Moments

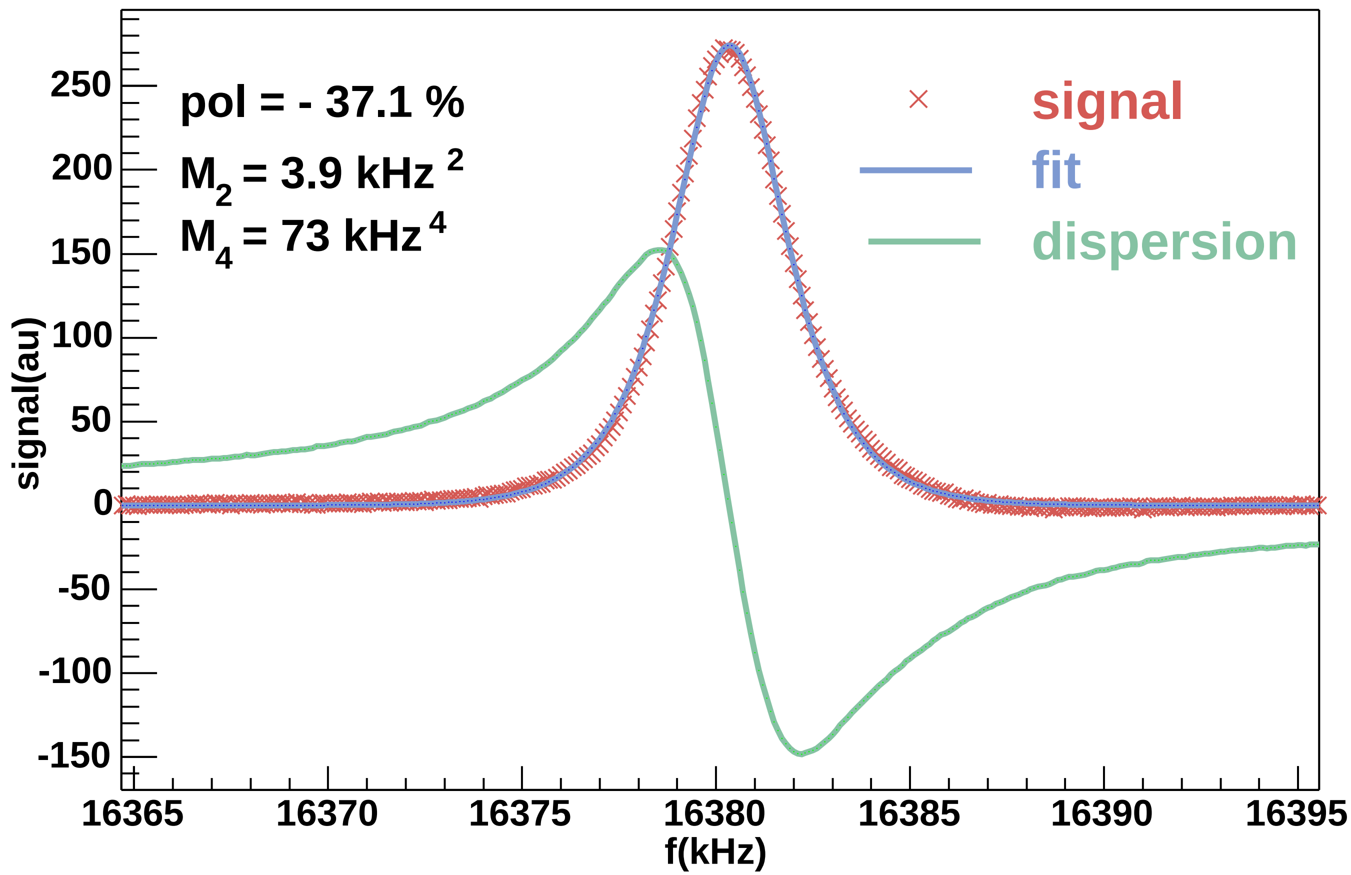
coil	pol[%]	f_0 [kHz]	M_2 [kHz^2]	M_4 [kHz^4]	M_4/M_2^2
D coils 1 - 4	-49.9	16379.6	2.47	28.4	4.7
D coils 7 - 10	+51.2	16381.0	2.59	33.8	5.0
D coil 6	+50.2	16381.2	3.99	84.6	5.3
^{6}Li coils 1 - 4	-48.5	16376.0	2.11	21.2	4.7
^{6}Li coils 7 - 10	+50.6	16377.4	2.34	31.0	5.7
^{6}Li coil 6	+51.7	16378.7	3.50	66.7	5.4
^{7}Li coils 1 - 4	-94.0	16375.5	13.6	867	4.7
^{7}Li coils 7 - 10	+96.6	16377.9	14.1	951	4.8
^{7}Li coil 6	-	16377.8	20.9	2191	5.0
p coils 7 - 10	-	16383.2	512	$1.9 \cdot 10^6$	7.3
p coil 6	-	16383.3	414	$1.3 \cdot 10^6$	7.6

microwaves off

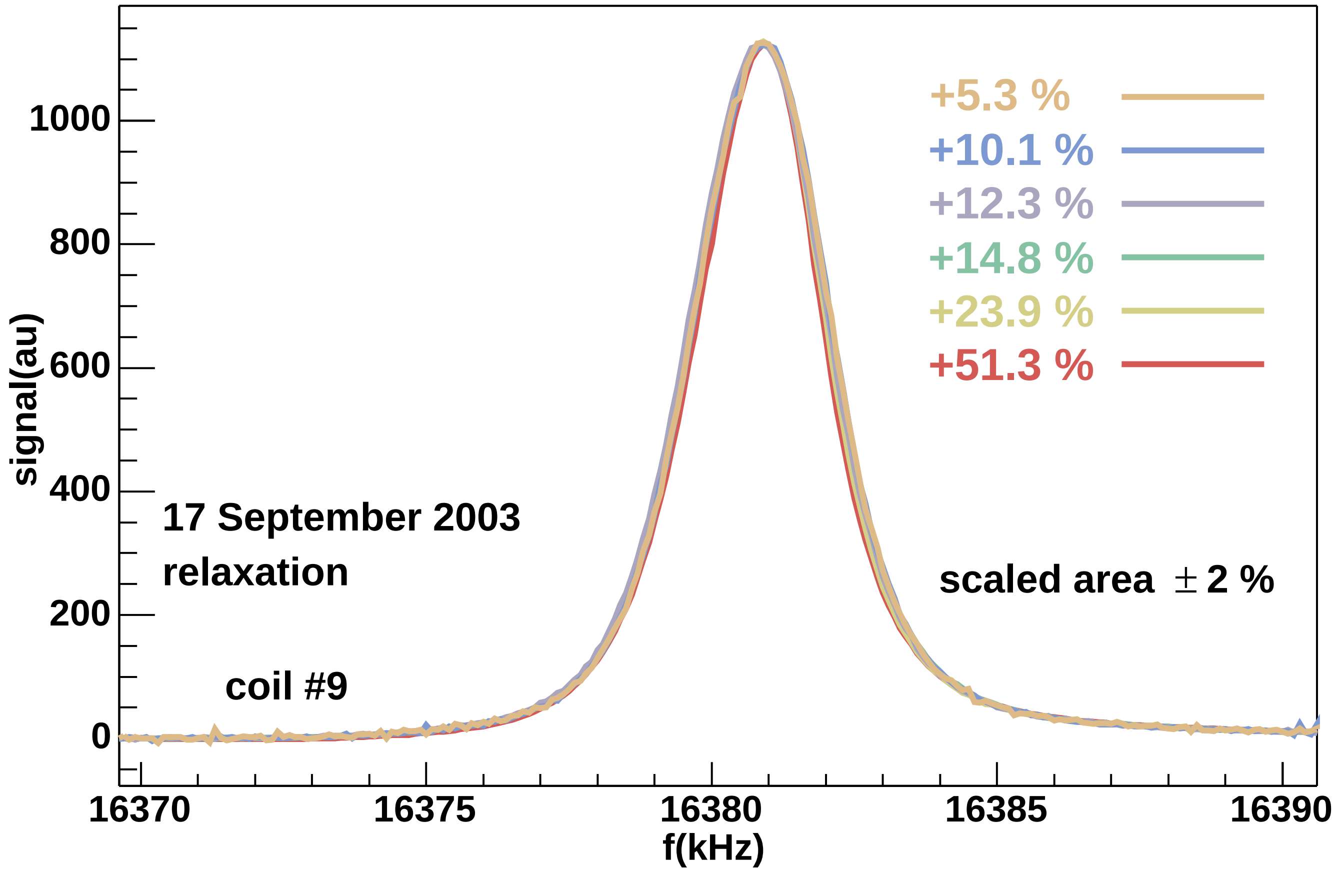
Summary

- ^{6}LiD has single NMR-line $\sim$ 3 kHz wide compared to double peaked 300 kHz of deuterated butanol
- line-shape can be understood from dipole-dipole interaction and is easier to model than for deuterated butanol
- fitting and raw polarization agree within $\sim$ 2 %
- 2nd moment larger than expected from simple dipole model
- small difference in line-shape M_4/M_2^2 for positive and negative polarizations D and ^{6}Li
- small change in line-shape during polarization

Dispersion corrections



NMR line-shape



NMR line-shape

pol[%]	f_0 [kHz]	M_2 [kHz^2]	M_4 [kHz^4]	M_4/M_2^2
51.3	16380.8	2.54	32.3	5.0
23.9	16380.8	2.45	28.2	4.7
14.8	16381.2	2.49	28.3	4.5
12.3	16380.7	2.49	27.9	4.5
10.1	16380.5	2.44	26.8	4.5
5.3	16380.4	2.42	26.1	4.5