Pulse calibration

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Principle of reciprocity

> The sensitivity of a magnetic resonance assembly, ***used as a receiver***, to nuclides present at a point X is proportional to that assembly's efficiency, ***when used as a transmitter***, to generate at that same location X a radiofrequency field B_1.

$\Rightarrow$ Sensitivity $\propto \frac{1}{\text{pulse length}}$

Hard to get pulses <u>into</u> sample

$\Leftrightarrow$ hard to get signal <u>out</u> !

Filling factors / Biot-Savart law

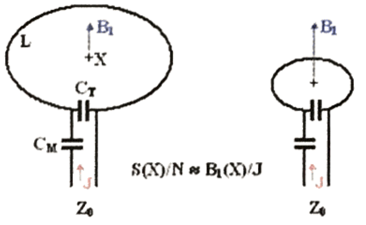

Figure 1. Illustration of the *NMR Antenna Reciprocity Law*.

$$\mathbf{B}(\mathbf{r}) = \frac{\mu_0}{4\pi}\int_C \frac{I d\mathbf{l} \times \hat{\mathbf{r}}}{|\mathbf{r}|^2}$$

Smaller coil

$\Rightarrow$ stronger B_1 field in sample

$\Rightarrow$ higher sensitivity (principle of reciprocity)

Probe design:

TXI = inverse, ^1H on inner coil, best sensitivity

vs TXO, ^1H on outer coil

— good for ^{13}C detection

http://www.ebyte.it/library/educards/nmr/Nmr_AntennaTheorem.html

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Bruker nomenclature

Different default units !!

- Pulse lengths: pX in µs
- Pulse power: plX in dB
  - ATTENUATION NOT POWER!
- Shape power: spX in dB
- Delays: dX in s
- Channels (usually): f1=H, f2=C, f3=N
- Offsets: oX in Hz, oXp in ppm

dB are logarithmic!

eg. $\Delta dB = -10 dB$

$\Rightarrow$ 10x more power

N.B. Varian is other way round!

TopSpin3 — forces distinction between pldBx and plWx

attenuation as before

power in W

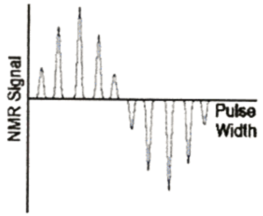
Bruker nomenclature – common pulses

- ^{1}H hard 90° – p1 @ pl1
- ^{1}H hard 180° – p2 @ pl1
- Water selective ^{1}H 90° – shaped pulse @ sp1
  - Applied on-resonance at offset o1
- ^{13}C 90° – p3 @ pl2 (on channel f2)
- ^{15}N 90° – p21 @ pl3 (on channel f3)

labels for pulse lengths and powers do not need to be the same (and usually are not!)

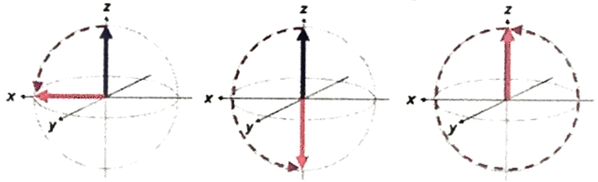
N.B. these are only conventions! check your individual pulse programs!

Hard proton 90° calibration

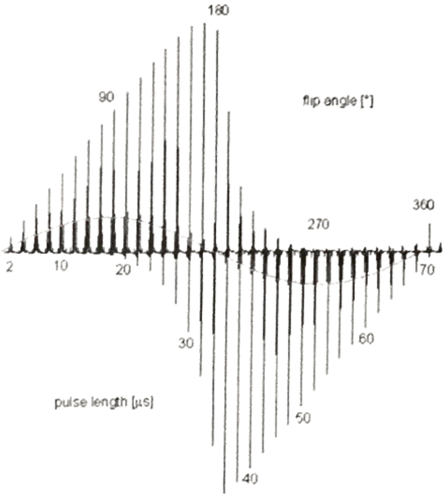


- Maximum pulse power
- 0.1 μs pulse length – small flip angle for phase correction
- Find 360° pulse

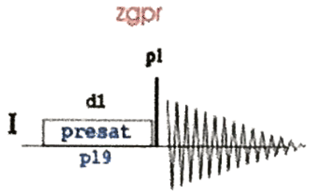
- avoid radiation damping effects
- avoid large relaxation delays



Hard proton 90° calibration: effect of radiation damping

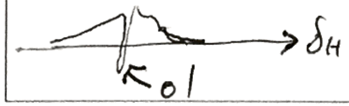


Offset calibration

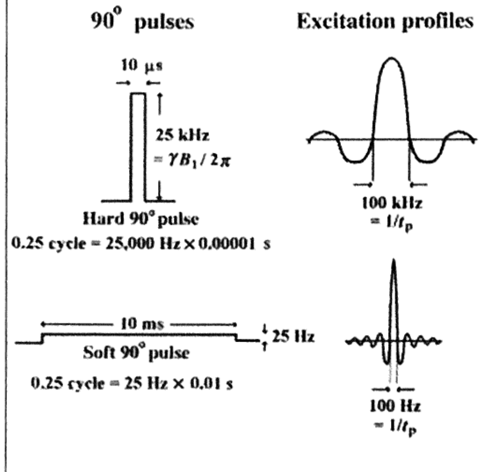


- 1D with presaturation – water suppression based on irradiation of H2O resonance (at offset o1) before acquisition
- H2O must be exactly on-resonance for good suppression
- Adjust o1 to minimise H2O signal (use 'gs' mode)

Approximate method:
'notch' in H_2O signal after 360° pulse

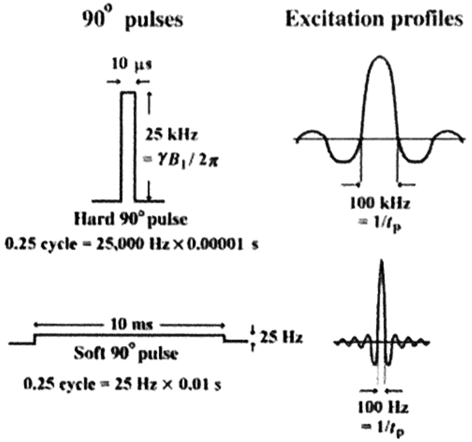


Soft pulses: selective excitation



- Excitation profile = FT of pulse shape:
  - Square pulse = sinc profile
  - Short (hard) pulse = broad excitation profile
  - Long (soft) pulse = narrow (selective) excitation profile

Soft pulses: selective excitation



- Apply hard pulses at maximum power:
  - Calibrate pulse length
- Pulse length is very important for soft pulses (= frequency selectivity):
  - Calibrate pulse power
  - Specify pulse length as time or frequency

Changing pulse powers and pulse lengths

Keep pulse area constant:
e.g. double the length, half the amplitude

Power = (amplitude)^2 — Ohm's Law $P = I^2 R$

B_1 field prop. to current, I

Attenuation in decibels = $-10 \log_{10} (P / P_0)$

$$\Delta dB\ (P_{soft} - P_{hard}) = -10 \log_{10} (P_{soft} / P_{hard})$$
$$= -10 \log_{10} (A_{soft}^2 / A_{hard}^2)$$
$$= -20 \log_{10} (A_{soft} / A_{hard})$$
$$= -20 \log_{10} (L_{hard} / L_{soft})$$

N.B. need to apply as a change to the hard pulse power!

Changing pulse powers and pulse lengths

Example: hard 90°: 9.8 μs @ 3 dB

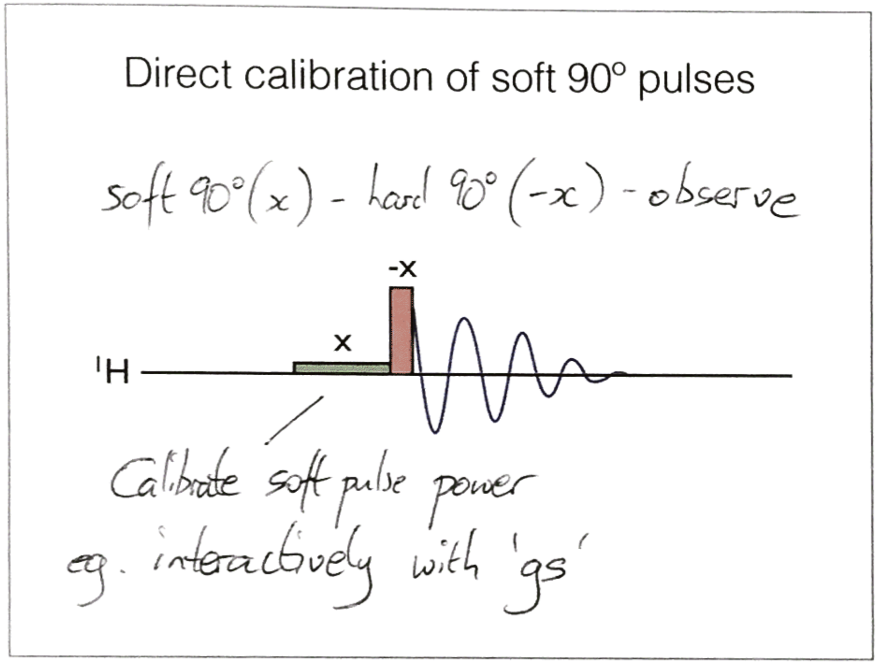
power for 1.2 ms pulse?

Relative amplitude = 9.8 / 1200 = 0.008167

ΔdB = $-20 \log_{10} 0.008167 = 41.76$ dB

Required power = 3 + 41.76 = 44.76 dB

hard pulse ΔdB

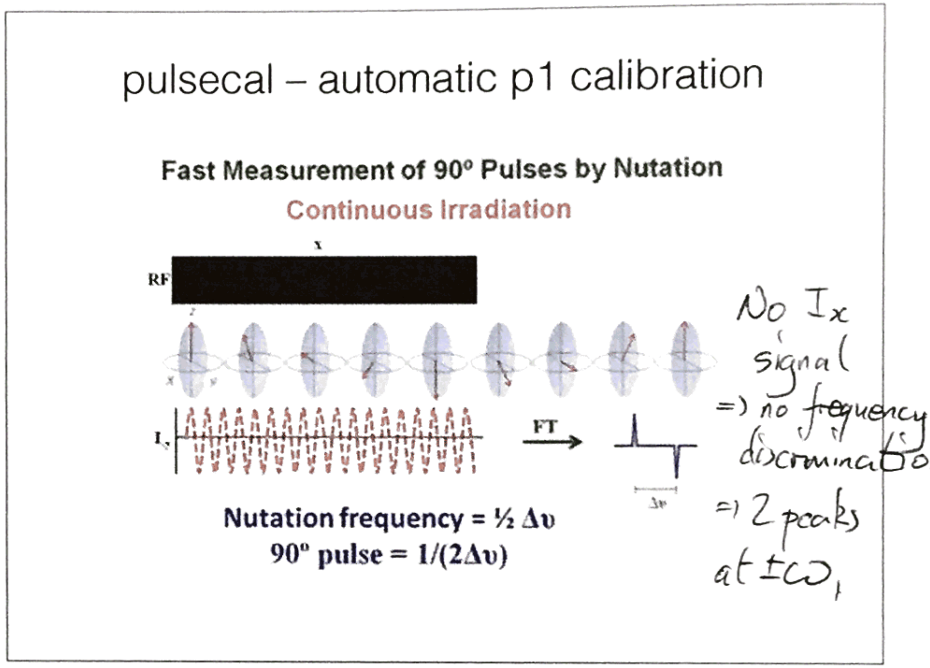


Direct calibration of soft 90° pulses

soft 90°(x) - hard 90° (-x) - observe

Calibrate soft pulse power

eg. interactively with 'gs'



pulsecal – automatic p1 calibration

Fast Measurement of 90° Pulses by Nutation

Continuous Irradiation

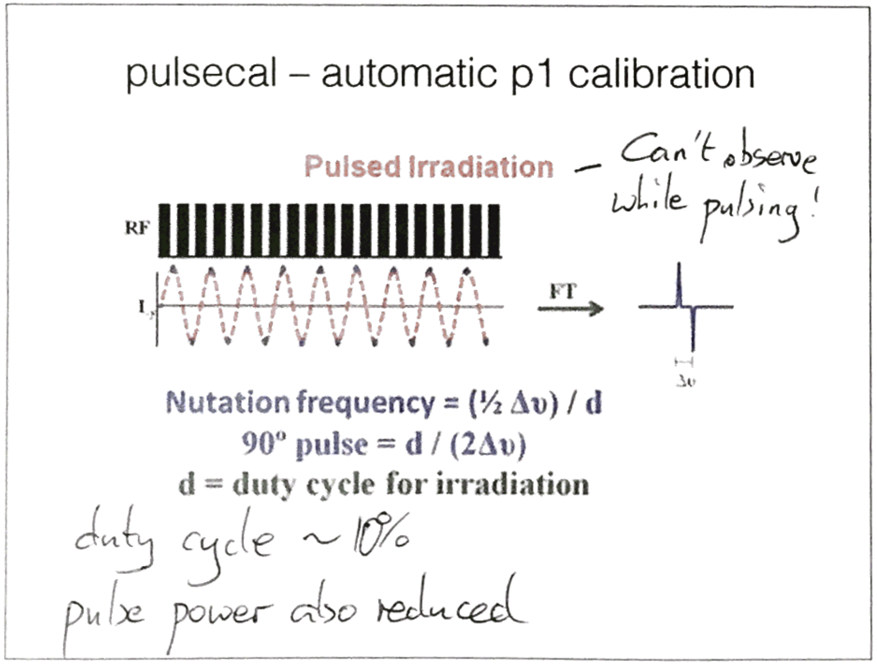
Nutation frequency = ½ Δν

90° pulse = 1/(2Δν)

No I_x signal

⇒ no frequency discrimination

⇒ 2 peaks at $\pm\omega_1$



pulsecal – automatic p1 calibration

Pulsed Irradiation – Can't observe while pulsing!

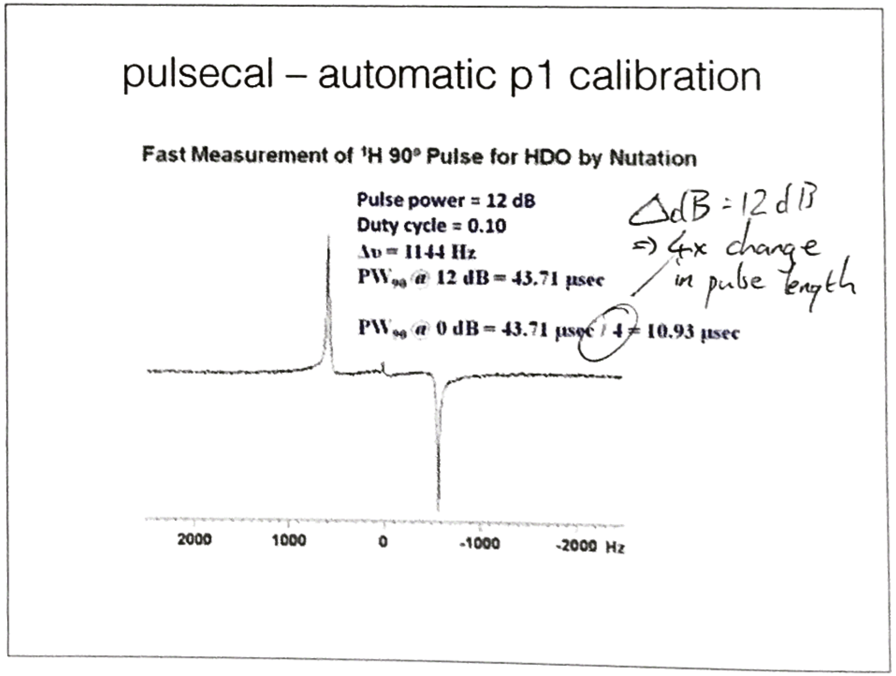
Nutation frequency = (½ Δν) / d

90° pulse = d / (2Δν)

d = duty cycle for irradiation

duty cycle ~ 10%

pulse power also reduced



pulsecal – automatic p1 calibration

Fast Measurement of ^{1}H 90° Pulse for HDO by Nutation

Pulse power = 12 dB
Duty cycle = 0.10
Δν = 1144 Hz
PW_{90} @ 12 dB = 43.71 μsec

PW_{90} @ 0 dB = 43.71 μsec / 4 = 10.93 μsec

ΔdB = 12 dB
⇒ 4x change in pulse length

Shaped pulses

- Excitation profile = FT of pulse shape
  - e.g. sinc pulse => square profile
  - Many pulses available! Sinc, Gauss, EBURB, REBURB, RSNOB…
- Estimation based on hard pulse
- Direct calibration
- Calibration using gs

Pulses can be optimised for excitation (90°, $z \to x$), inversion (180°, $z \to -z$) refocussing (180°, $x \to -x$)

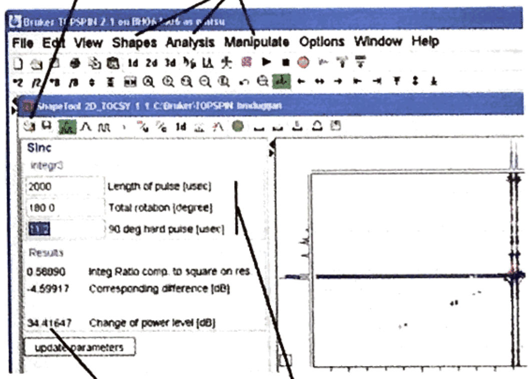
Pulse lengths depend on field strength & frequency range

→ fix and calibrate the pulse power

Shaped pulse calibration

Click here to select shape

New options on TopSpin menubar



2000 Length of pulse [usec]

180 0 Total rotation [degree]

[illegible] 90 deg hard pulse [usec]

Results

0.58890 Integ Ratio comp. to square on res

-4.59917 Corresponding difference [dB]

34.41647 Change of power level [dB]

Enter your values here

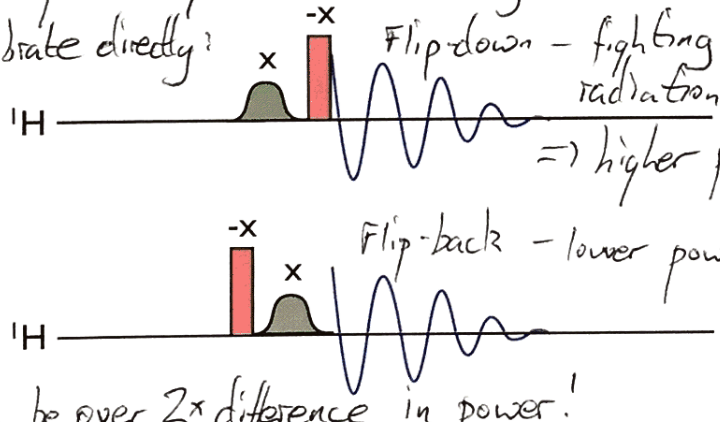
Change in attenuation reported here → NB. relative to hard pulse power

- Estimation based on hard pulse by integration using shape tool ('stdisp')
- Direct calibration as for soft pulses

Flip-down / flip-back pulses

Use pulse sequences that distinguish between these!

Calibrate directly?



Flip-down – fighting against radiation damping ⇒ higher power

Flip-back – lower power

Can be over 2× difference in power!

Due to radiation damping effects – particularly important on cryoprobes (and high fields)

Adiabatic pulses

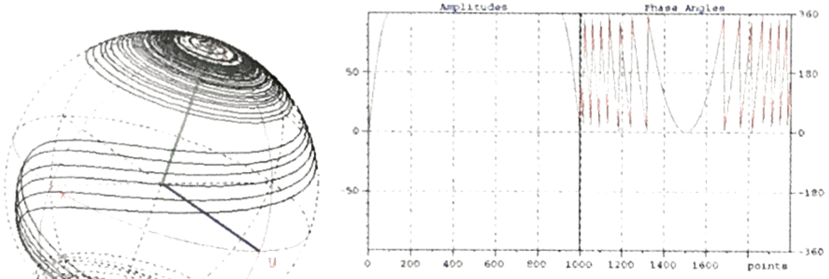
Completely different principle to other pulses!

- Low-power pulses for [selective] excitation or inversion
- Insensitive to miscalibration – just make sure power is strong enough
- Very wide bandwidth
  - important at higher fields
- Operate on different principle to hard pulses or shaped pulses: slowly sweep field so that magnetisation vectors stay locked to B_{eff}
- Must satisfy adiabatic condition (slowly changing Hamiltonian):

$$\left|\frac{d\theta}{dt}\right| \ll \omega_{\text{eff}}$$

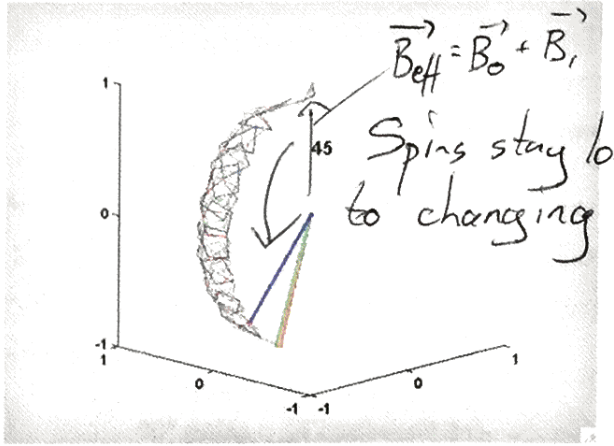
- Disadvantage – long pulses, relaxation losses

Adiabatic pulses



CHIRP pulse

Adiabatic pulses

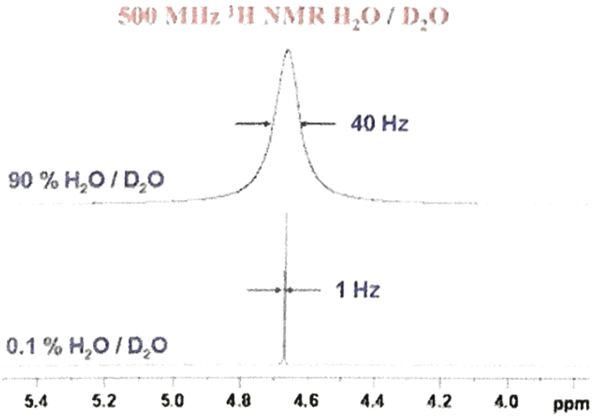


$\vec{B}_{eff} = \vec{B}_0 + \vec{B}_1$

Spins stay locked to changing $\vec{B}_{eff}$

tan/tanh pulse

Radiation damping



http://u-of-o-nmr-facility.blogspot.co.uk/2007/10/width-of-your-water-line-radiation.html

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Radiation damping

- 700 MHz (on resonance) rf pulse in probe induces 90° rotation of spins
- Spins precess at Larmor frequency (700 MHz)
- Changing magnetic field of spins induces 700 MHz rf signal in probe ('the signal')
- BUT! 700 MHz rf signal in probe induces rotation of spins…
- Result: rapid rotation of H2O back to equilibrium (taking other spins along for the journey)

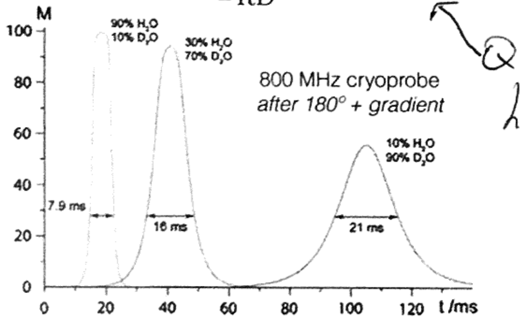
Radiation damping

- Misnomer – 'radiation feedback' would be more appropriate
- Associated with characteristic timescale:

filling factor

$$\frac{1}{T_{\mathrm{RD}}} = 2\pi\gamma M_0 Q\xi = \frac{\xi Q \gamma^3 h^2 N_0 B_0}{8\pi k_{\mathrm{B}} T}$$

Q = quality factor, high for cryoprobes



800 MHz cryoprobe
after 180° + gradient

Temperature

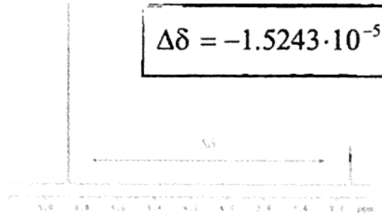
^{1}H H_2O chemical shift (relative to DSS)

$$\boxed{\Delta\delta\ (H_2O) \approx 7.83 - T / 96.9}$$

Rule of thumb:
Shift of 0.01 ppm / K

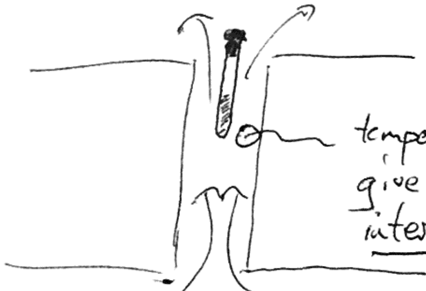
Useful for detecting heating during heavy-duty expts eg. SOFAST, relaxation...

Highly deuterated MeOH



$$\boxed{\Delta\delta = -1.5243\cdot10^{-5}\times T^2 - 5.1576\cdot10^{-4}\times T + 3.0528}$$

Importance of knowing/controlling temperature precisely
- particularly for different relaxation pulse sequences and measurements at multiple field strengths



temperature sensor does not give direct measure of <u>internal</u> sample temperature
- must be calibrated directly during periodic maintenance

temperature-controlled air flow over sample