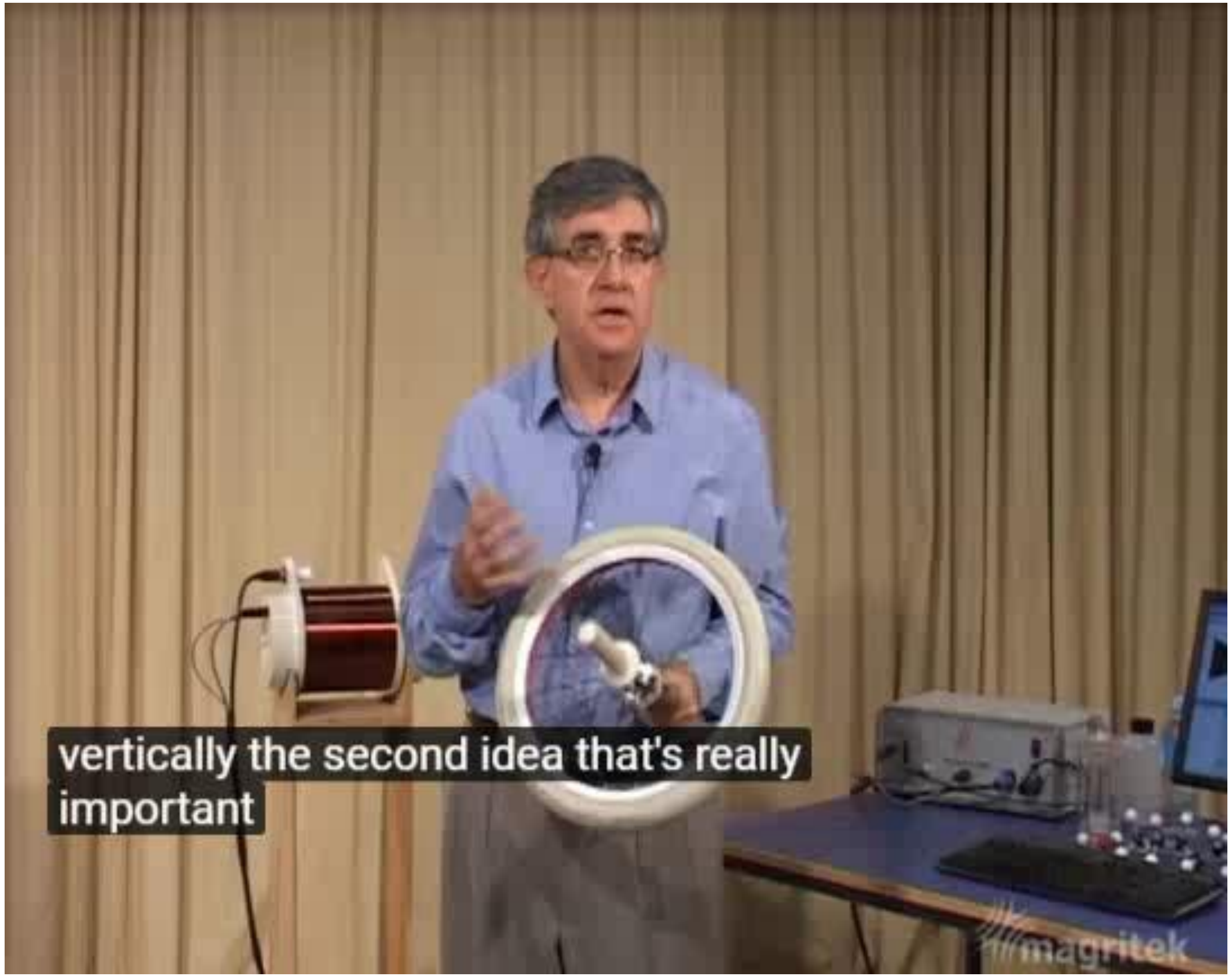
Instrumentation

Nuclei under the effect of magnets

https://www.youtube.com/watch?v=7aRKAXD4dAg

by Sir Paul Callaghan

Spin angular momentum



https://www.youtube.com/watch?v=7aRKAXD4dAg

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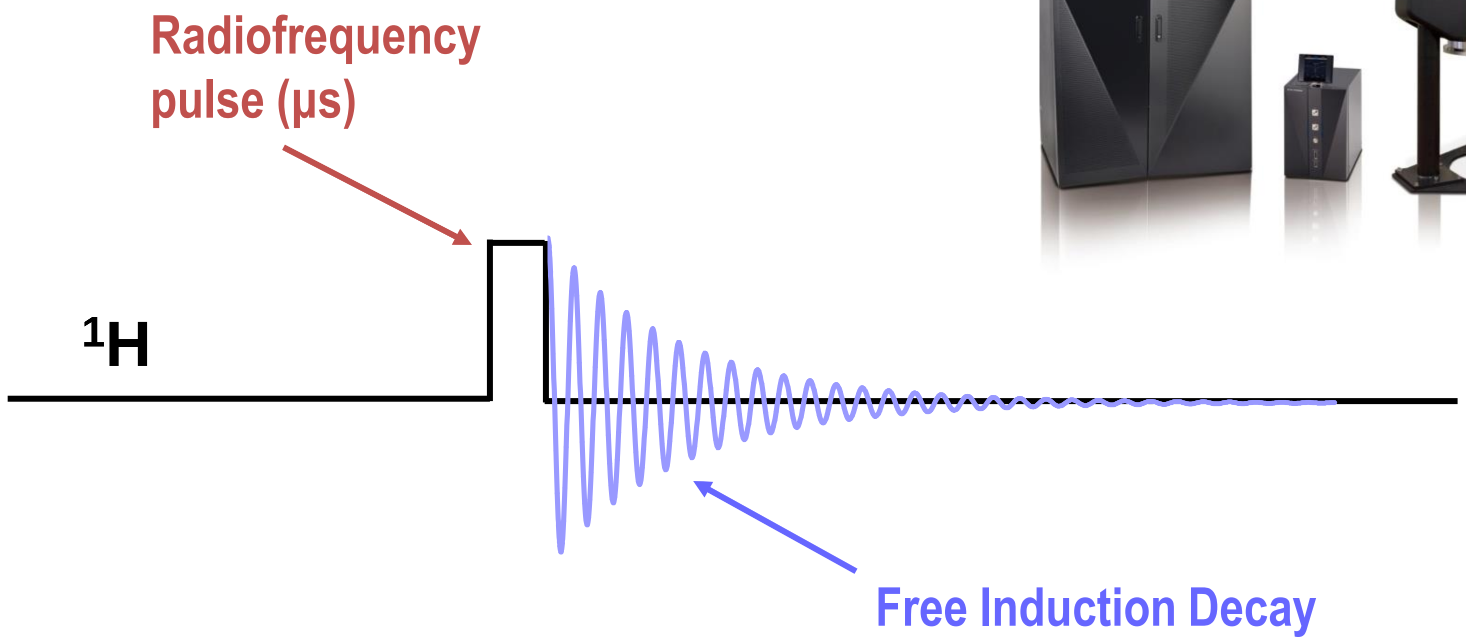
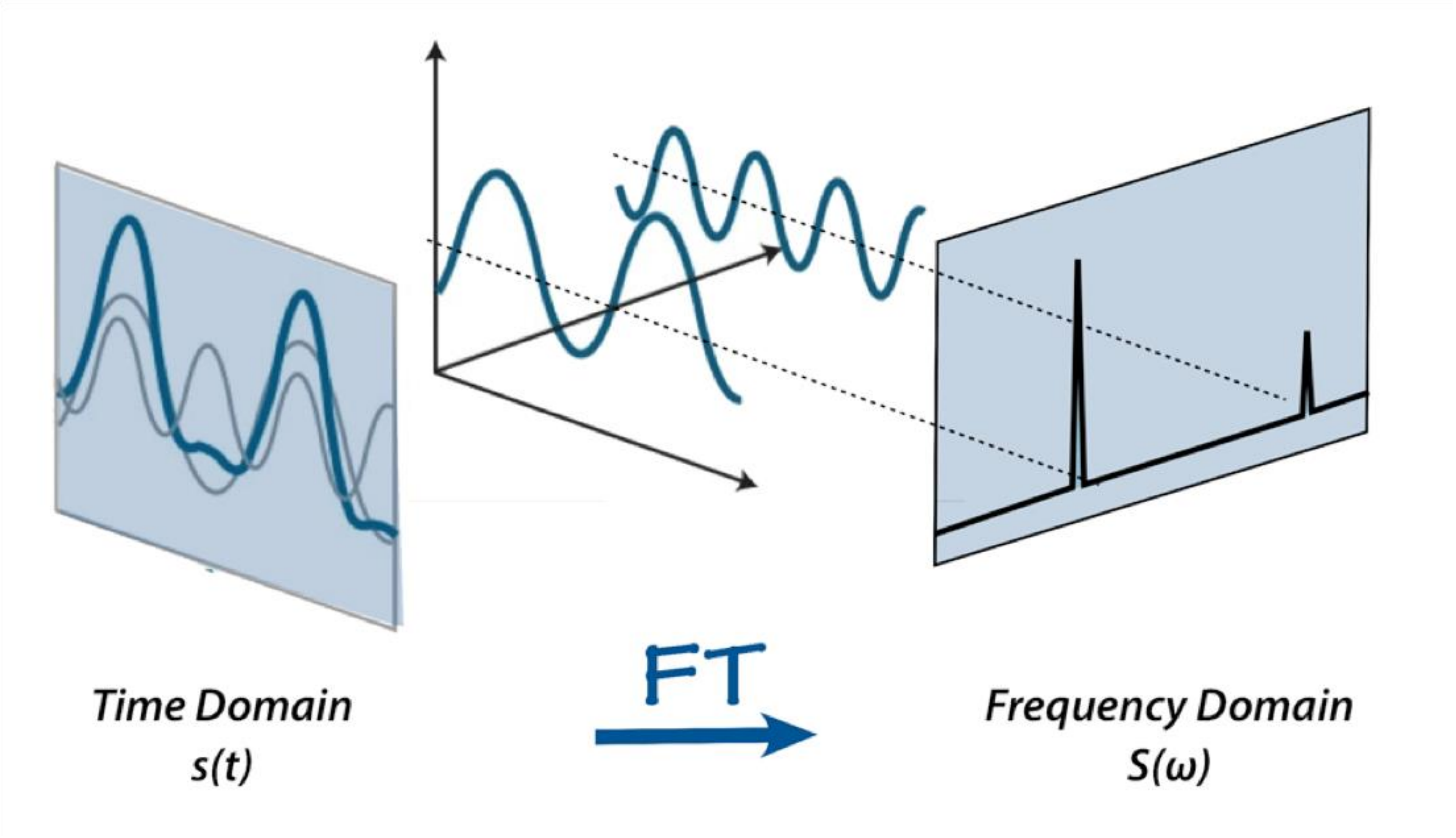
How to observe NMR (pulsed FT NMR)



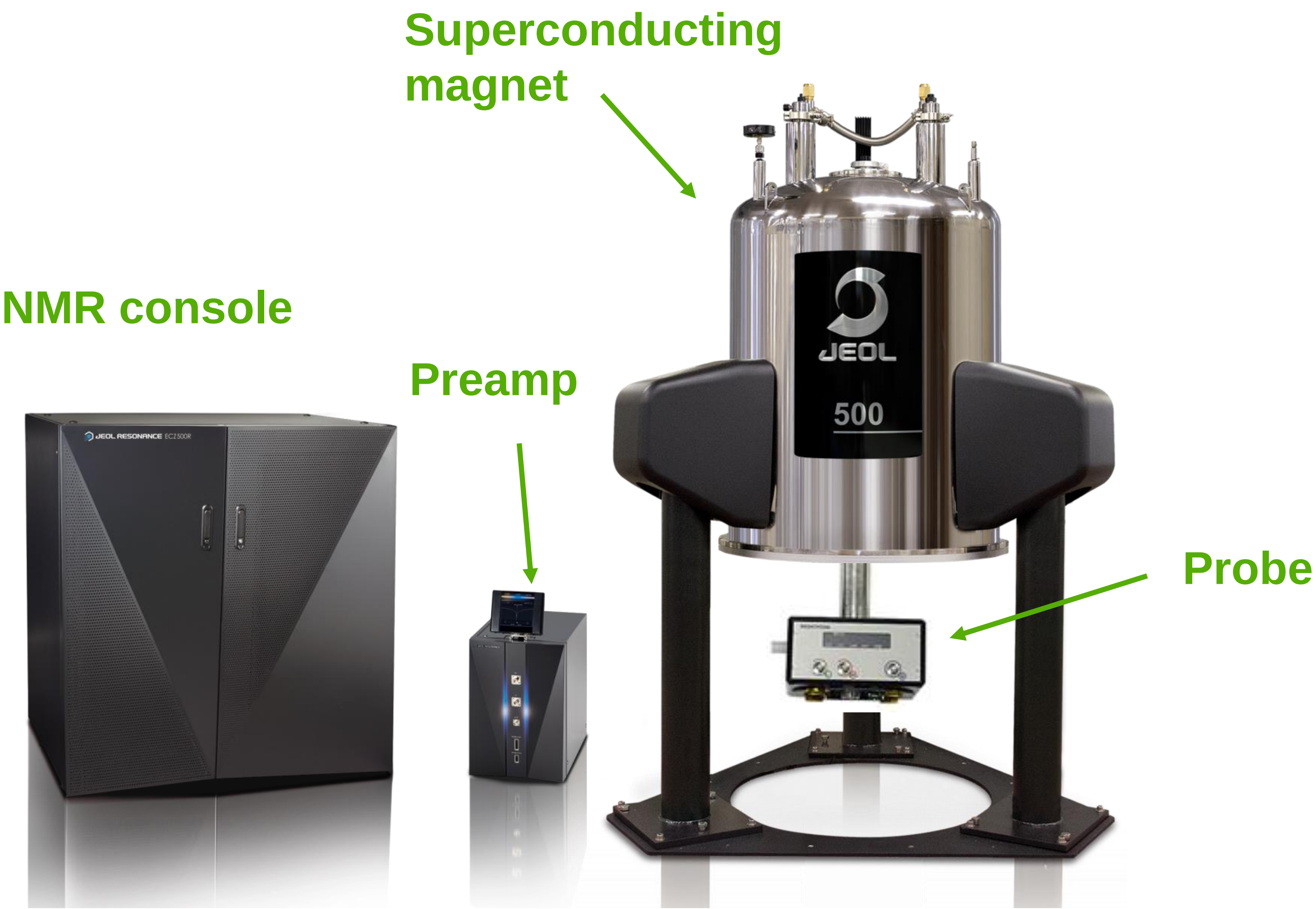
- Apply a very short radio frequency pulse
- NMR signals are detected after the pulse

FOURIER TRANSFORM OF FID

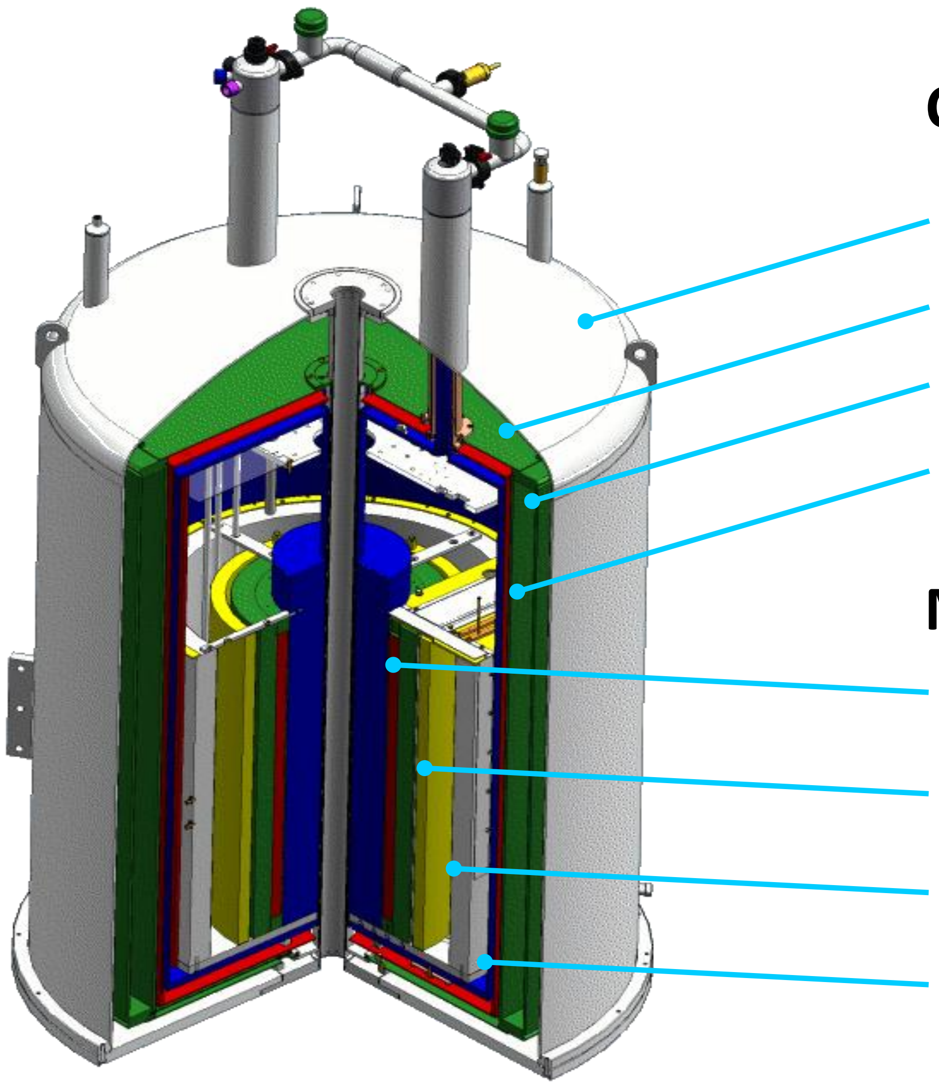


https://sapienlabs.org/brain-waves-sine-waves/

NMR system overview



Inside a super-con magnet



Cryostat

Outer vacuum can (300 K)

Nitrogen can (77 K)

Gas cooled shield (40 K)

He Can (4.2 K)

Magnet

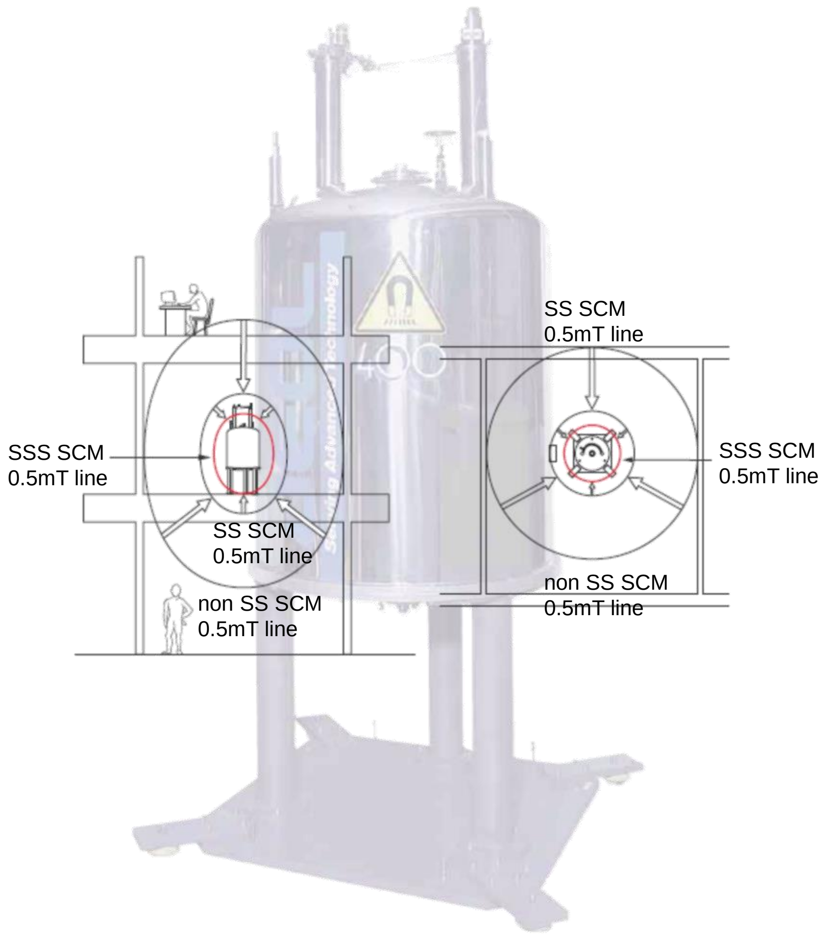
Inner solenoid (Nb_3Sn) >10 Tesla

Cryoshims (NbTi)

Shield (NbTi)

Separate shim stack with room temperature shim coils

Super conducting magnets



Modern magnets have self shielding to reduce the stray magnetic field outside. 5 gauss line (Earth's field 0.5 gauss) is 0.6m-1.0m from the center.

However, it is NOT zero and extremely strong inside the magnet bore.

Do not get following items close to the magnet:

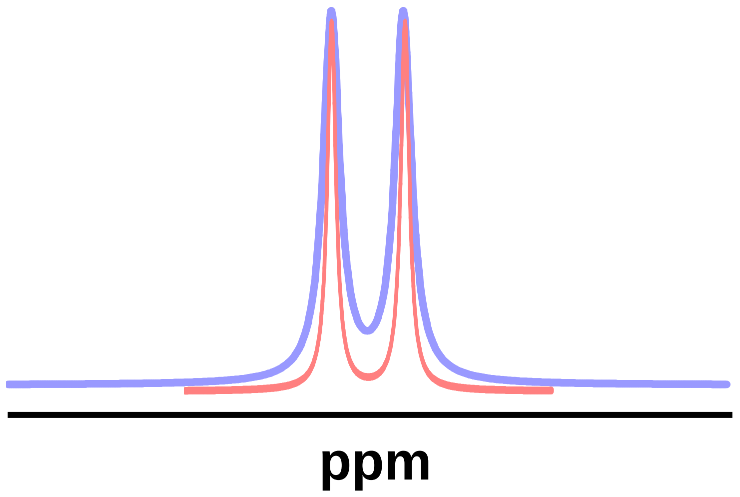
- Mechanical (expensive) watch
- Bank cards
- Cameras
- Pacemaker
- Any magnetic metal

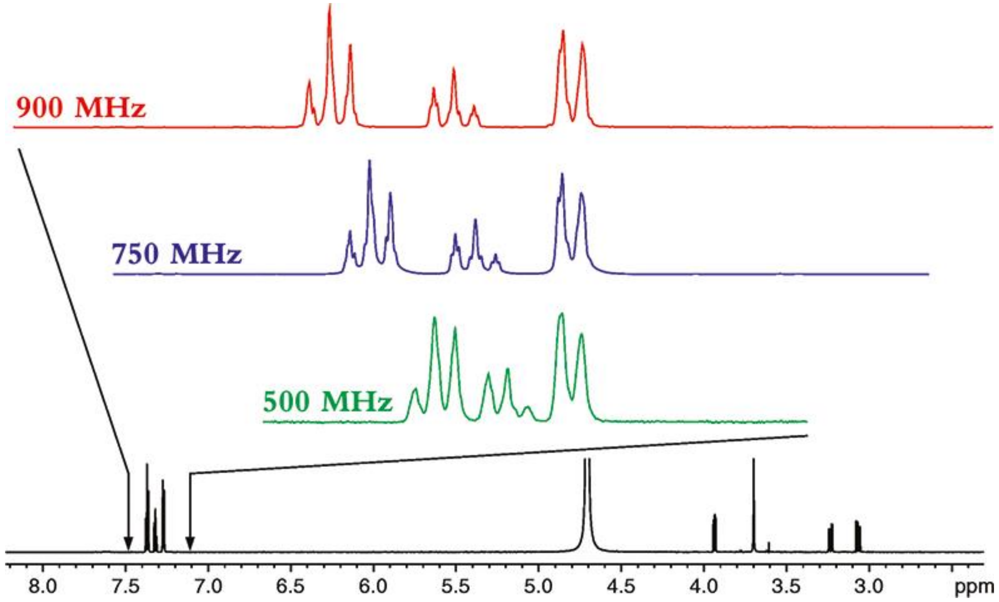
Magnets, why bigger is better…

- Chemical shift (ppm) and J splittings (Hz) are <u>independent</u> of $\mathbf{B_0}$:
- Peak separation is <u>better</u> at higher field

30 Hz @ 300 MHz = 60 Hz @ 600 MHz

Two separate peaks
@ 300 MHz and @ 600 MHz :



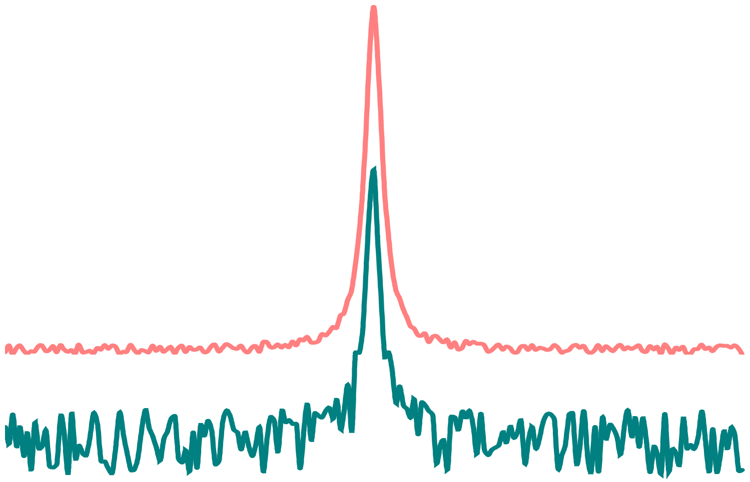


https://www.spectroscopyeurope.com/article/900%C2%A0mhz-nuclear-magnetic-resonance-shows-great-promise

Why bigger is better…

- Sensitivity (S/N) increases as $\mathbf{B_0}^{3/2}$

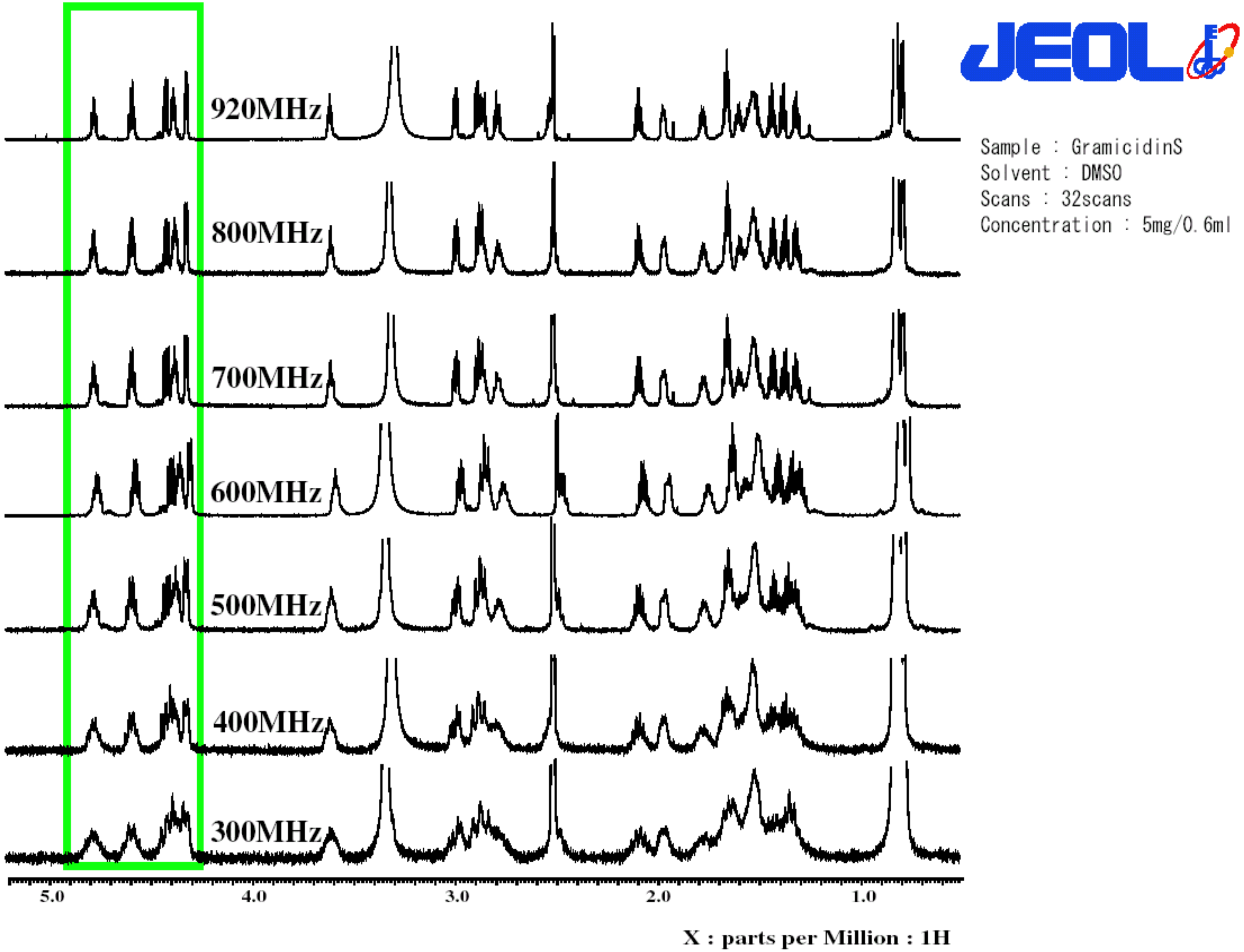
Signal/Noise @ 600MHz ≈ 2.8 x Signal @ 300MHz



Thus, as SNR increases with the square root of the number of scans, measurement time decreases as per $1/(\mathbf{B_0}^{6/2})$

Time @ 600MHz = 1/8 Time @ 300MHz

B_0 effects


920MHz
800MHz
700MHz
600MHz
500MHz
400MHz
300MHz
5.0
4.0
3.0
2.0
1.0
X : parts per Million : 1H
JEOL
Sample : GramicidinS
Solvent : DMSO
Scans : 32scans
Concentration : 5mg/0.6ml

1st order effects of spin coupling

First-order rules ($\Delta\nu / J >> 1$)

- For nuclei with I=1/2 the multiplicity of the splitting equals $n+1$, where n is the number of nuclei in the neighbouring group (for $I > 1/2 \Rightarrow 2\,n\,I+1$)

Pascal triangle:

n=0						1					
n=1					1		1				
n=2				1		2		1			
n=3			1		3		3		1		
n=4		1		4		6		4		1	
n=5	1		5		10		10		5		1

2^{nd} order effects

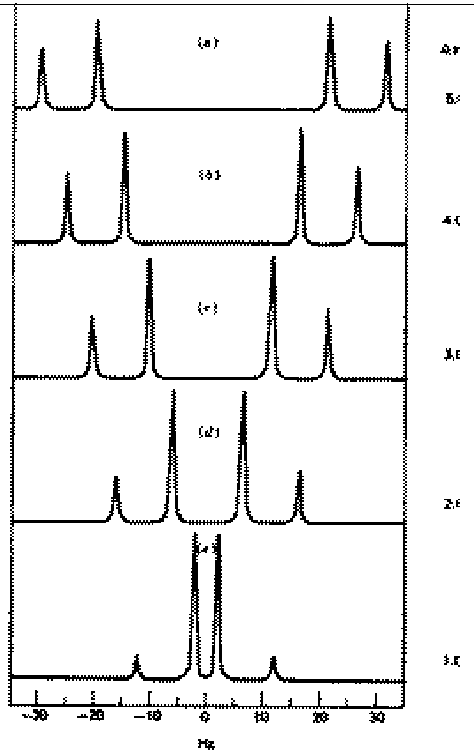
Strong coupling

When the chemical shift values are very close and the difference in chemical shifts are comparable to J values one finds second order effects in the NMR spectra

Typically when $(\Delta\delta)/J$ is less than 10, second order effects are seen in the spectra

Unusual intensities of multiplets
More than expected number of lines in multiplets
Number of lines (frequency and intensities) can be theoretically calculated

These are characteristic features of a second order spectrum



https://www.ucl.ac.uk/nmr/NMR_lecture_notes/L3_3_97_web.pdf
http://nptel.ac.in/courses/104106075/Week2/MODULE%206.pdf
https://www.chem.wisc.edu/areas/reich/nmr/05-hmr-09-2ndorder.htm

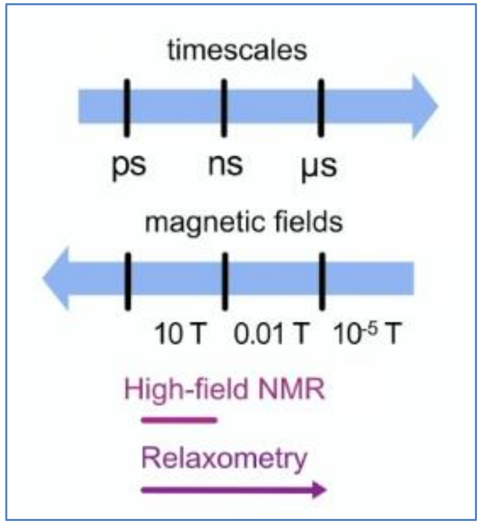
Simulate:

- http://www.nmrdb.org/simulator/index.shtml
- https://www.chem.wisc.edu/areas/reich/plt/windnmr.htm

Why bigger is worse…

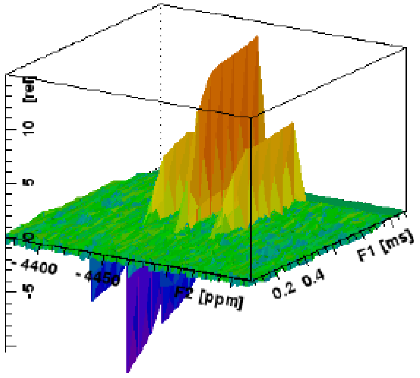
- the major relaxation mechanism for many transition metals is CSA (chemical shift anisotropy)

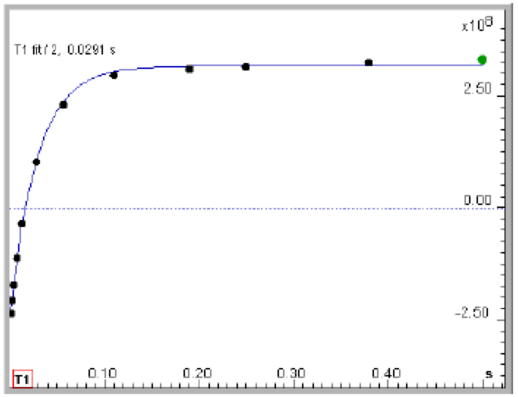
$$1/T_1 = 1/T_{1DD} + 1/T_{1SC} + 1/T_{1QF} + 1/T_{1SR} + 1/T_{1CSA}$$

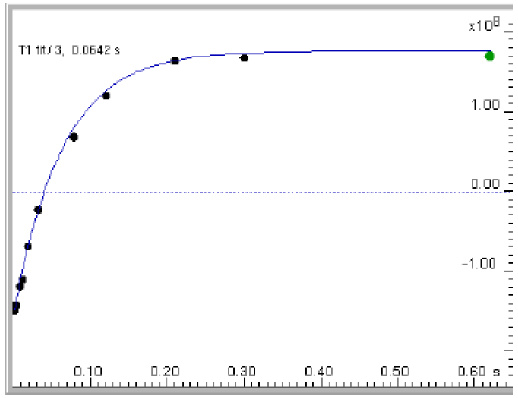


Chemical shift anisotropy term

$$\frac{1}{T_{1CSA}} = \frac{2}{15}\gamma^2 B_0^2 \Delta\sigma^2 \tau_c$$







$$\left(\frac{600}{400}\right)^2 = 2.25$$

$$15.6 \times 2.25 = 35$$

relaxation = 100% CSA

^{195}Pt inversion recovery

600 MHz
T_1 = 29 msec
R_1 = 34.5 sec^{-1}

400 MHz
T_1 = 64 msec
R_1 = 15.6 sec^{-1}

Why bigger is worse…

Excitation profile:

Larger dispersion increases the difficulty of uniform excitation: harder decoupling / quantitation / spin-lock etc.

Dielectric losses:

Organic solvents<water<<water with charged species dissolved

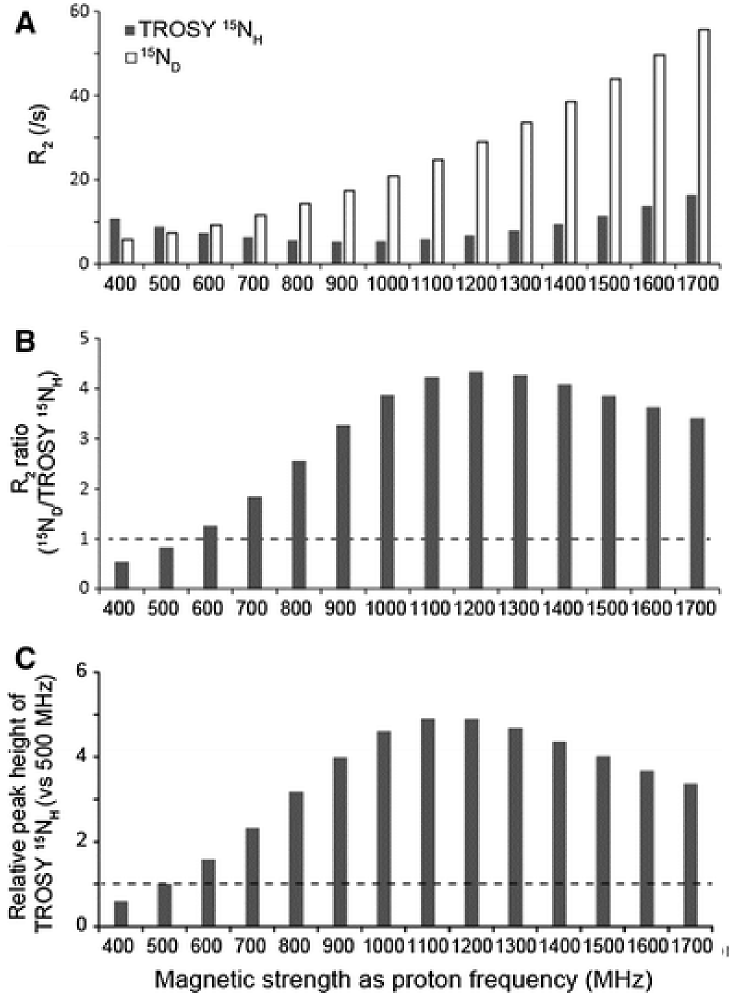
The higher the probe Q (efficiency), the higher the losses

The larger the sample the larger the losses

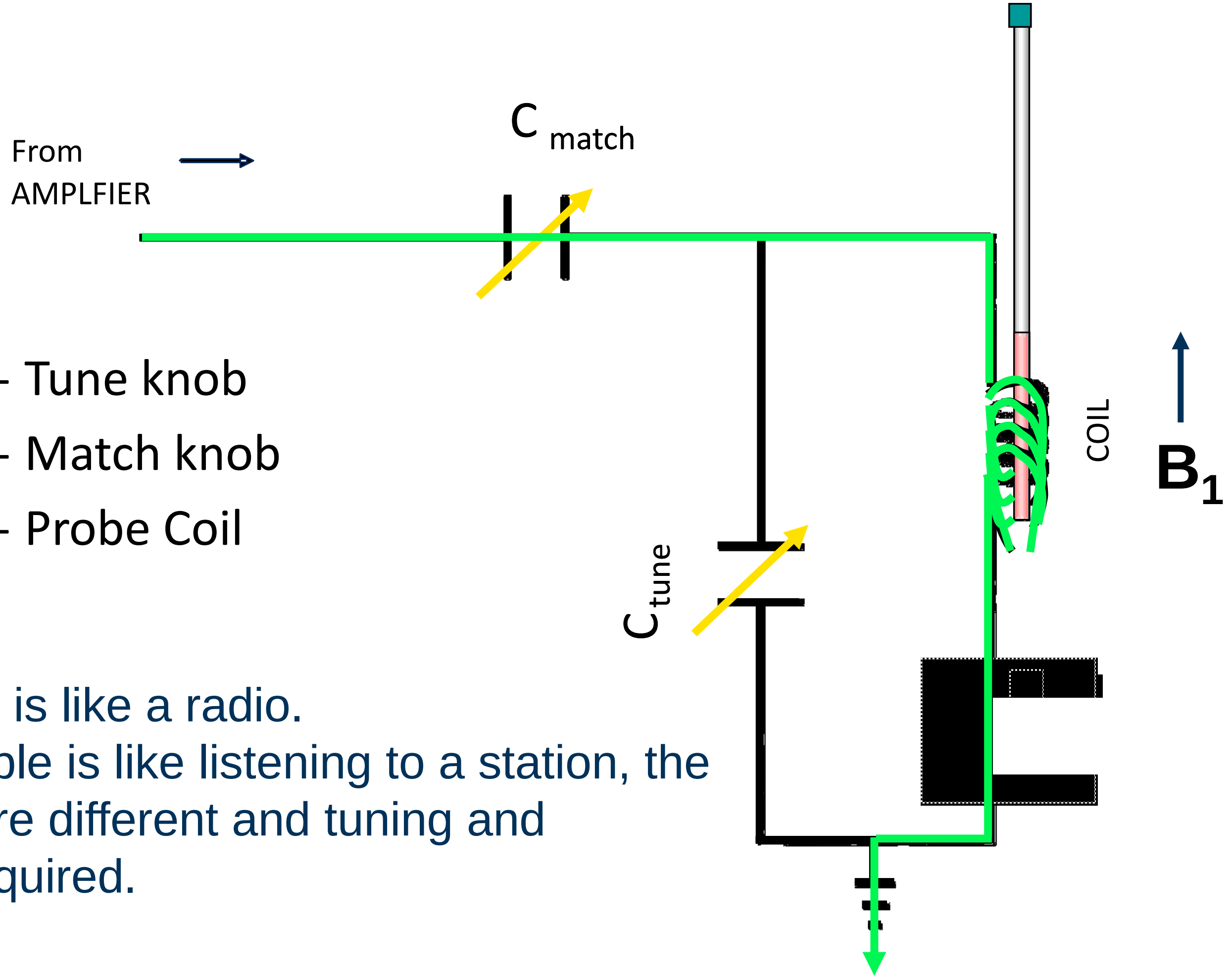
https://doi.org/10.1016/j.jmr.2005.01.004

TROSY effect:

https://doi.org/10.1007/s10858-015-9991-y



Simplified probe



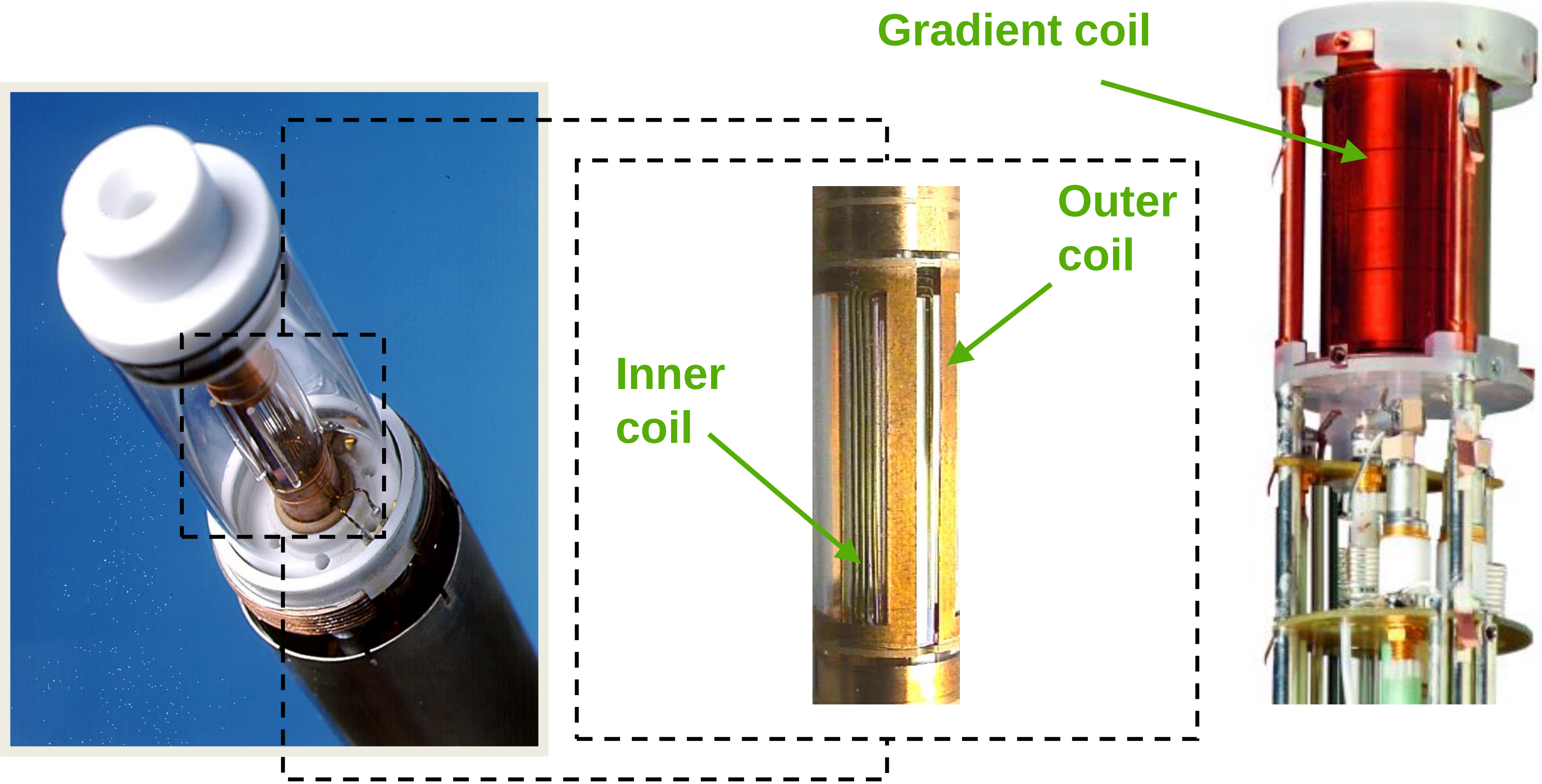
C_{tune} - Tune knob

C_{match} - Match knob

L_{coil} - Probe Coil

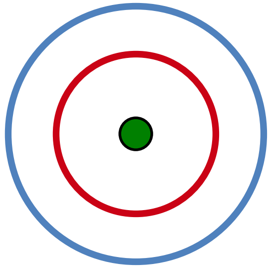
The NMR probe is like a radio.
Studying a sample is like listening to a station, the RF conditions are different and tuning and matching are required.

Inside the probe



- ⇨ Note that coil is not helical! (in liquid state probes)
- ⇨ Each coil tuned to a single nucleus (or more at a loss)

Direct vs Inverse probes

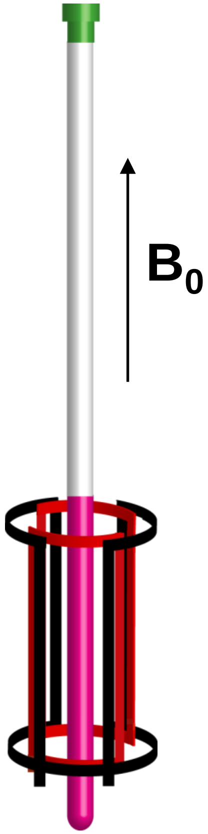


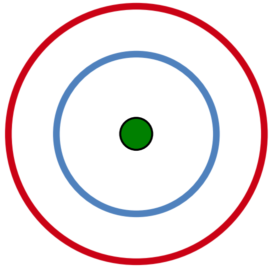
Direct geometry

- observe LF
- decouple HF

LF Coil

HF Coil



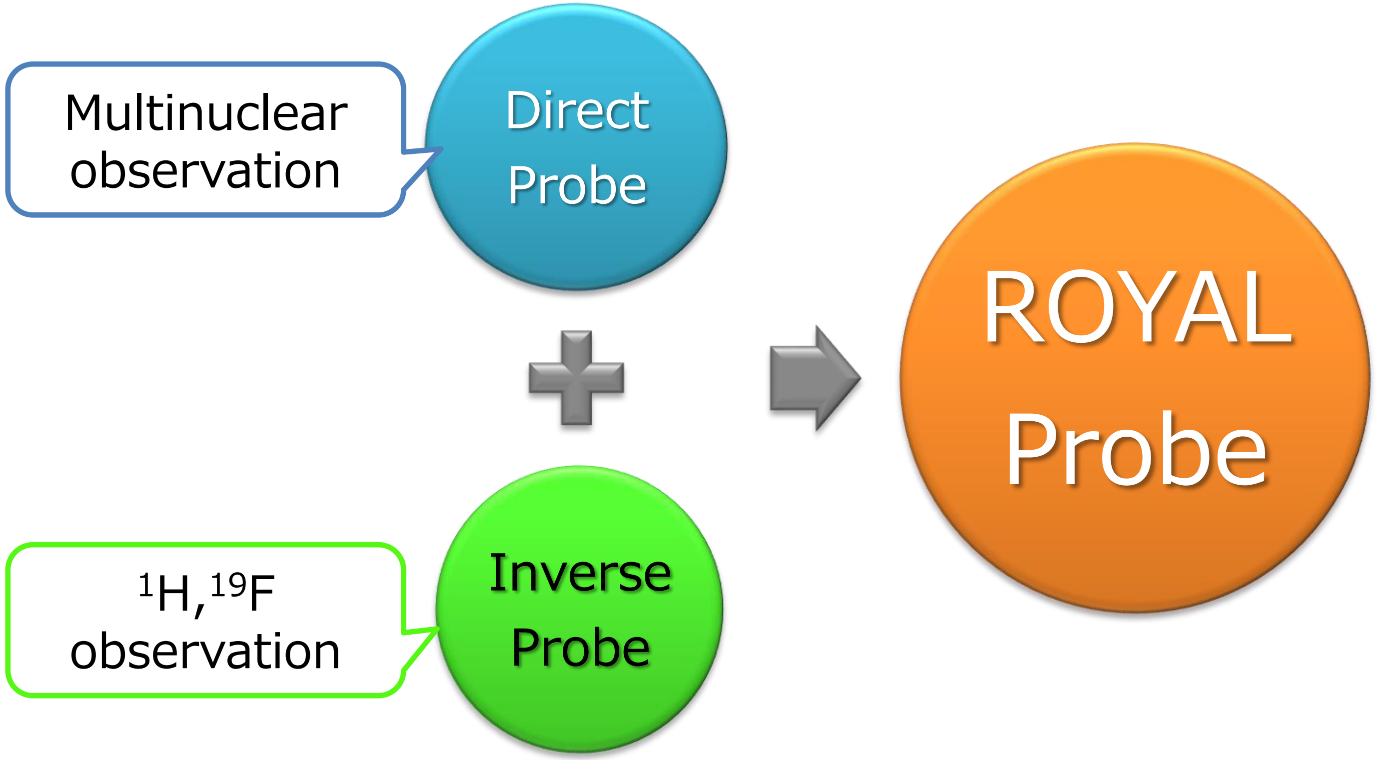


Inverse geometry

- decouple LF
- observe HF

JEOL ROYAL Probe

High Sensitivity both LF and HF channel



Nuclei measurable

400 ROYAL (1 HF nucleus + 1 LF nucleus)
HF channel:
1H, 19F

LF channel:
31P, Lithium7, Tin117, Tin119
11B, Bromine81, Copper63, Copper65, Gallium71, Praseodymium141, Rubidium87, Sodium23, Tellurium125, Vanadium51, Xenon129
13C, Aluminum27, Bromine79, Europium151, Gallium69, Manganese55, Niobium93, Scandium45, Tellurium123, Terbium159
29Si, Antimony121, Cadmium111, Cadmium113, Cobalt59, Holmium165, Indium113, Indium115, Iodine127, Lead207, Platinum195, Rhenium185, Rhenium187, Technetium99
2H, Arsenic75, Bismuth209, Lithium6, Mercury199, Selenium77, Ytterbium171
17O, Antimony123, Beryllium9, Cesium133, Lanthanum138, Lanthanum139, Lutetium175, Tantalum181
15N, Boron10, Barium137, Europium153
39K, Silver109

In **bold**: nuclei calibrated during installation
Nuclei around 2H frequency can only be measured without lock