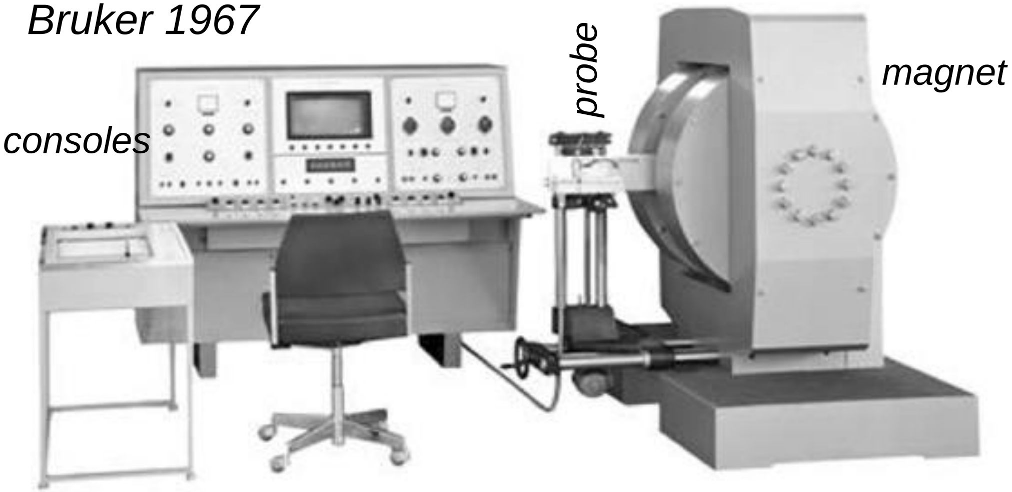
NMR hardware

Radiofrequency pulses

Signal processing

NMR spectrometer

Bruker 1967



<u>Components</u>

- Magnet

  electromagnet × superconducting

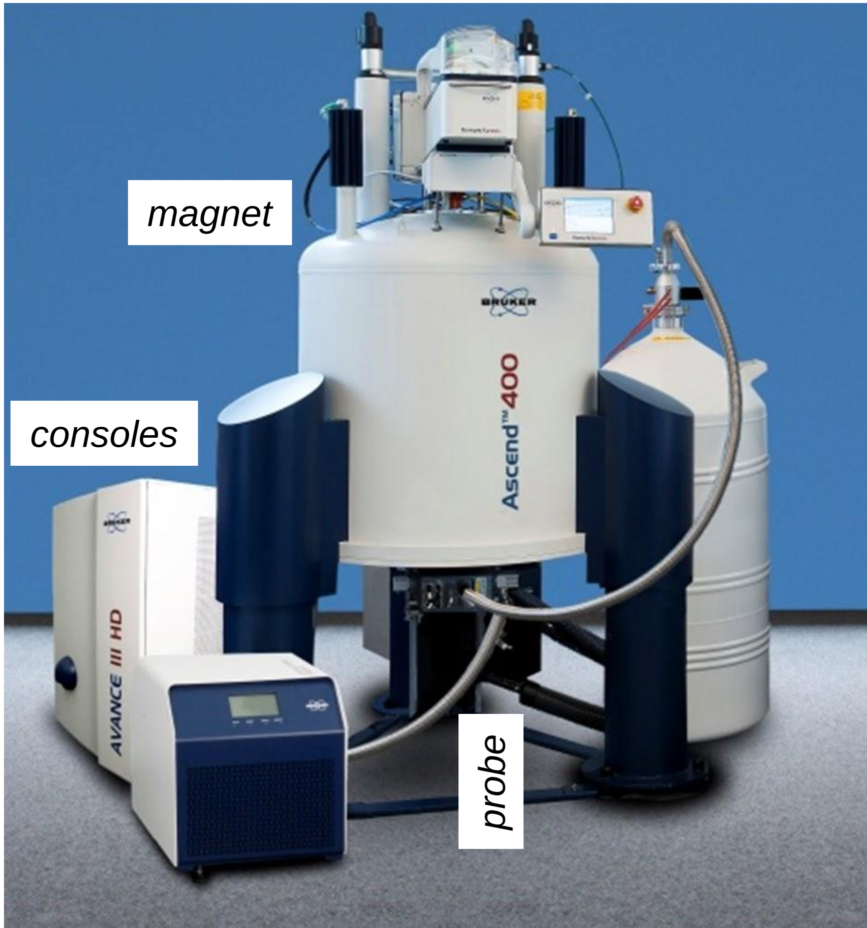
- Console with electronics

  Analog × fully digitized

- NMR probe

  Classic × chilled

- Control computer

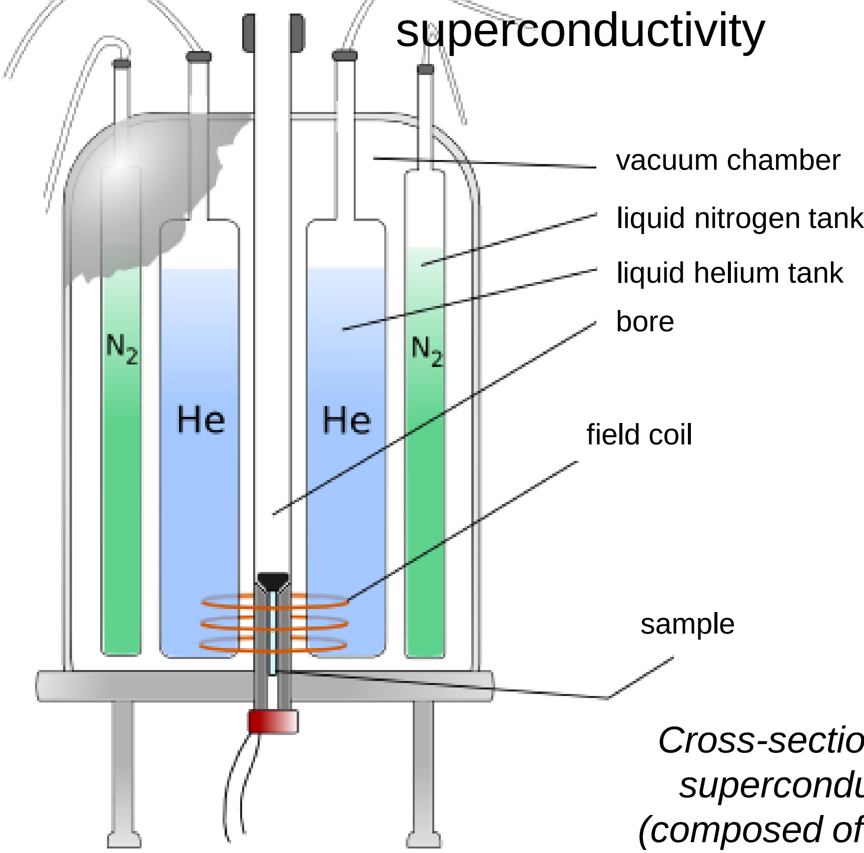


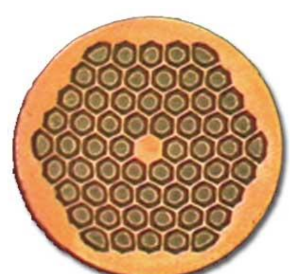
Bruker ~2015

NMR spectrometer– magnet

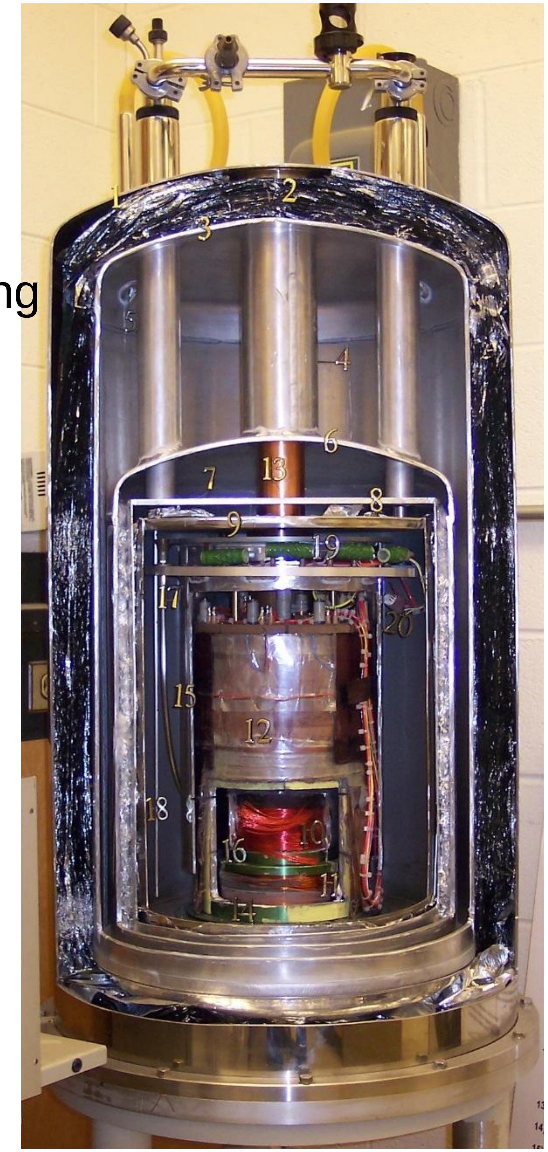
Superconducting coil in double Dewar vessel

- Electric current is high, it can exceed 150 A (depending on the magnetic field)
- Does not need a power source after charging
- Need to refill cryoliquids to maintain superconductivity





Cross-section of a superconductor (composed of fibers)



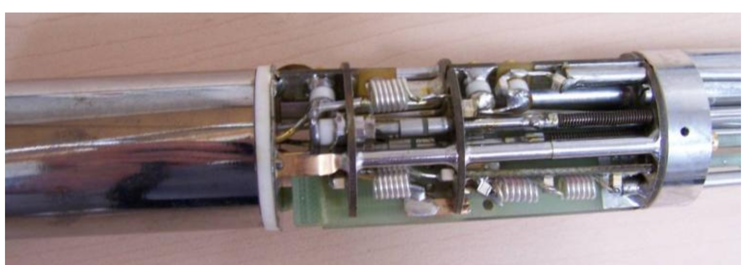
NMR spectrometer – probe

Probe head with coils

Different coils for different frequencies

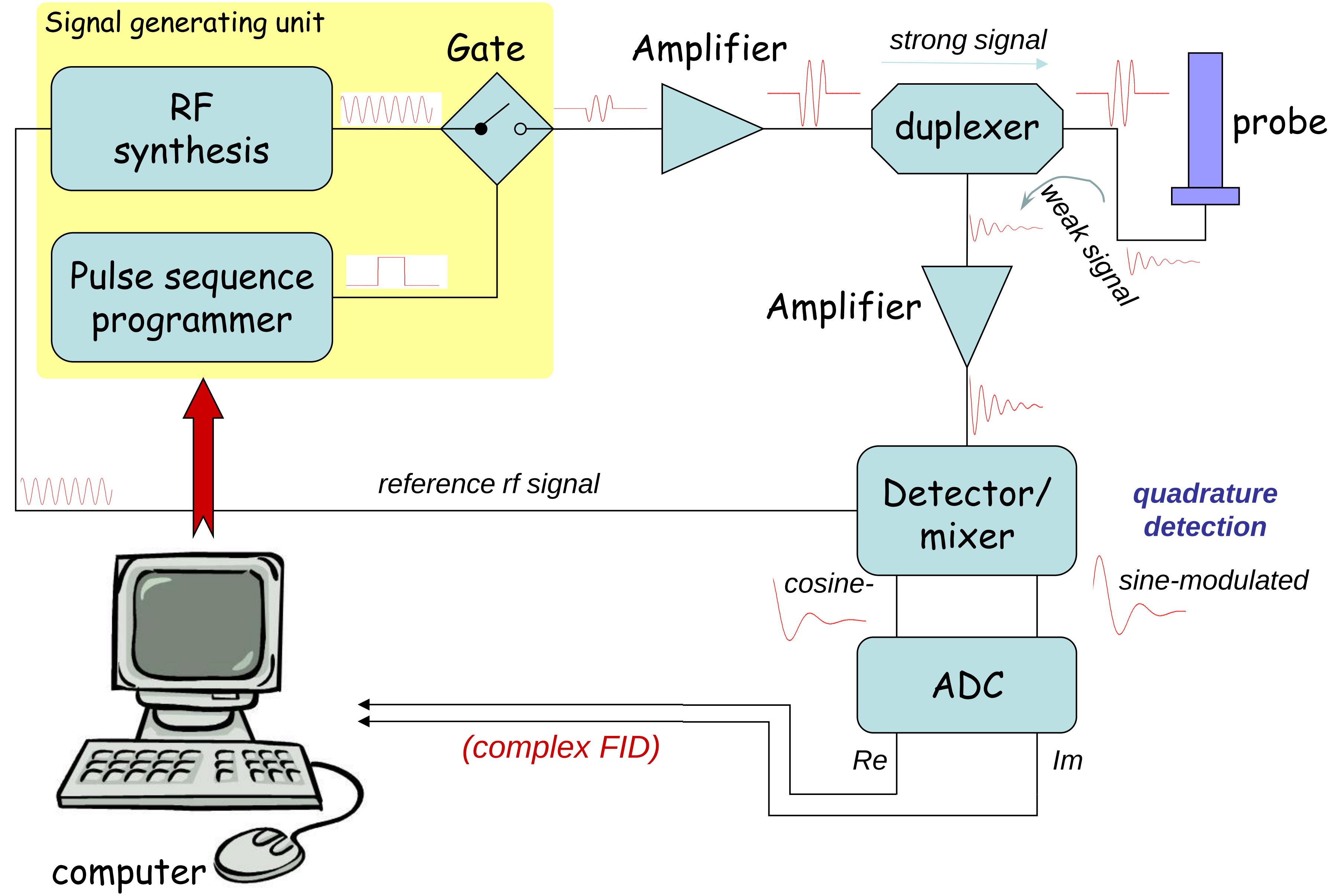
Sample in rotor

Probe tuning elements



for precise frequency adjustment

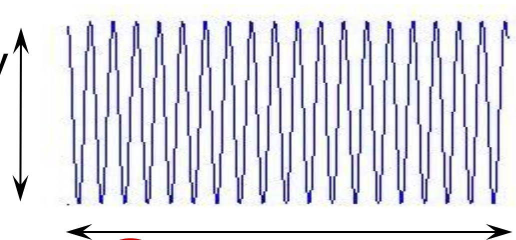
NMR spectrometer – schema



Radiofrequency pulses

<u>Pulse characteristics</u>

1. nutation frequency amplitude ω_1



2. frequency ω_{rf}

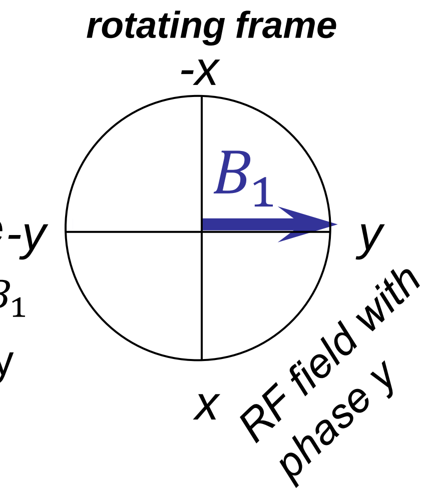
3. phase *x, y, -x, -y*

4. pulse length τ_p

5. Flip angle $\varphi = \omega_1 \tau_p$

We already know:

- The RF field is perpendicular to the static magnetic field
- frequency ω_{RF} should be the same as the Larmor frequency
- We decompose the linearly oscillating RF field into two circularly polarized components with constant magnitude
- Only the component in resonance with Larmor's precession is effective
- In rotating coordinate system, this component is constant, magnitude B_1
- Magnetization rotates around the direction of B_1 with angular frequency $\omega_1 = \gamma B_1$
- During the pulse of length τ_p, magnetization rotates by angle $\varphi = \omega_1 \tau_p$

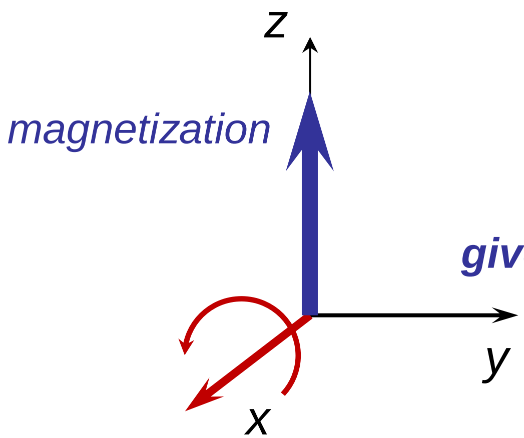


New:

Direction of B_1 in rotating frame is determined by the initial phase of the RF pulse, it can therefore be changed at our will

Radiofrequency pulses

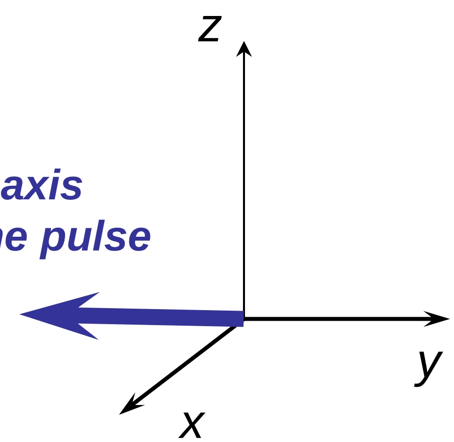
Efect of a pulse

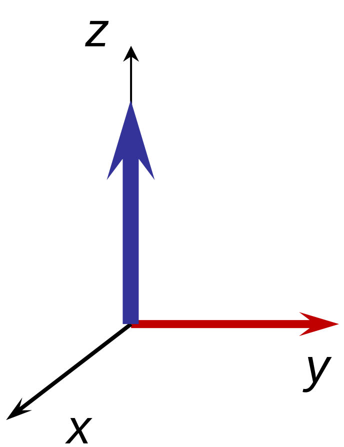


pulse with 90° tilt angle and X-phase

90_x

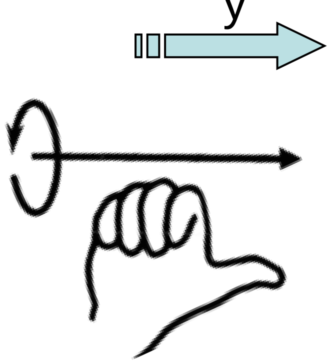
Rotation around the axis given by the phase of the pulse

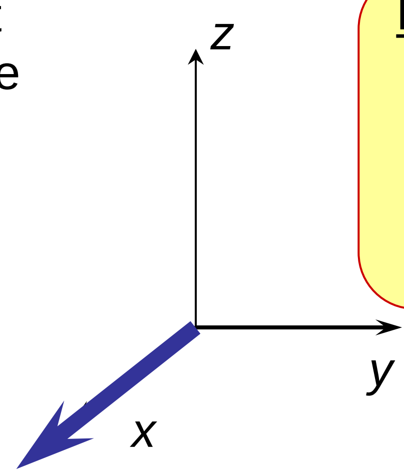




pulse with 90° tilt angle and Y-phase

90_y





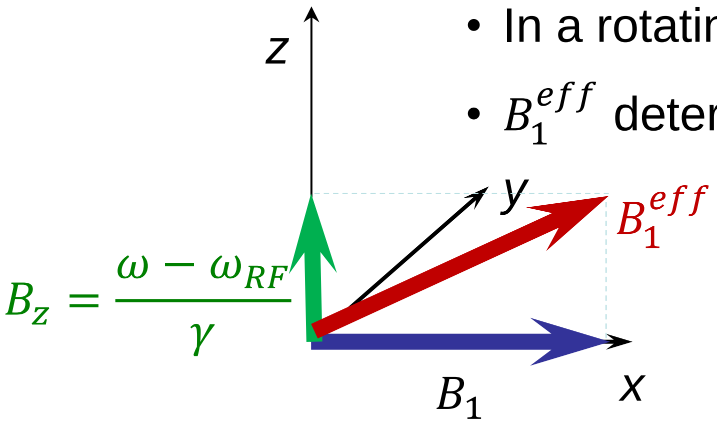
Right-hand rule

- Thumb in the direction of the axis of rotation
- Fingers determine the direction of rotation

Off-resonance effects

Frequency of pulse ω_{RF} is fixed

- nuclei have different chemical shifts, different frequencies
- Strictly speaking, they're out of resonance
- In a rotating frame, they are affected by an effective field B_1^{eff}
- B_1^{eff} determines the axis and frequency of magnetization rotation



$$B_1^{eff} = \left(B_1, 0, \frac{\omega - \omega_{RF}}{\gamma}\right)$$

Assuming fictional force due to non-inertial frame (Coriolis force)

- RF pulse has different effects depending on the signal offset
- for homogeneous excitation, off-resonance effects must be suppressed

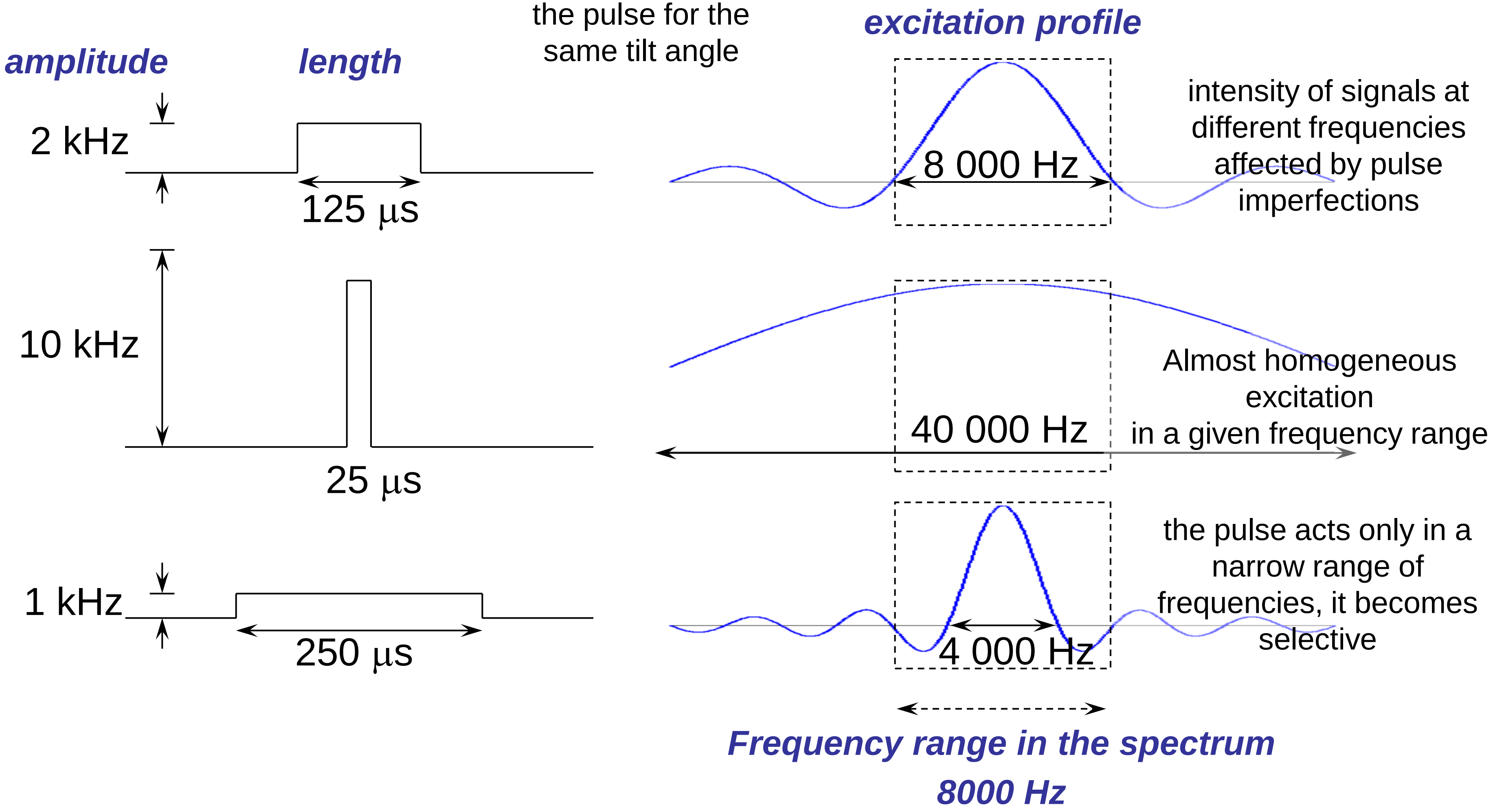
good RF pulse for broadband excitation has a high amplitude (large B_1)

$\frac{\omega - \omega_{RF}}{\gamma}$ negligible to B_1

Pulse length and excitation profile

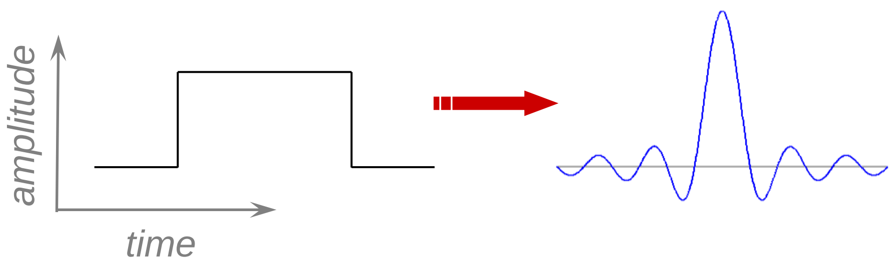
$$\varphi = \omega_1 \tau_p$$

The higher the amplitude, the shorter the pulse for the same tilt angle



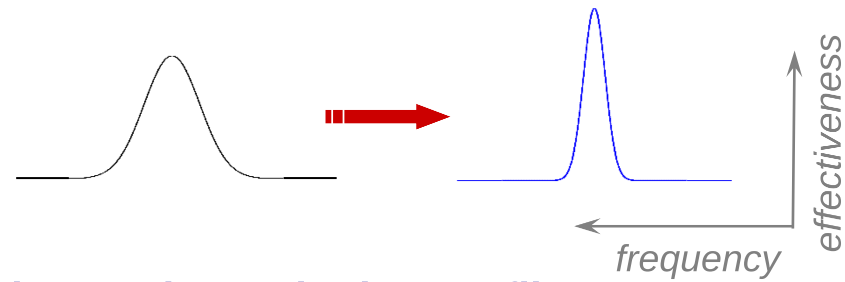
Selective and shaped pulses

Rectangular pulse *excitation profile*

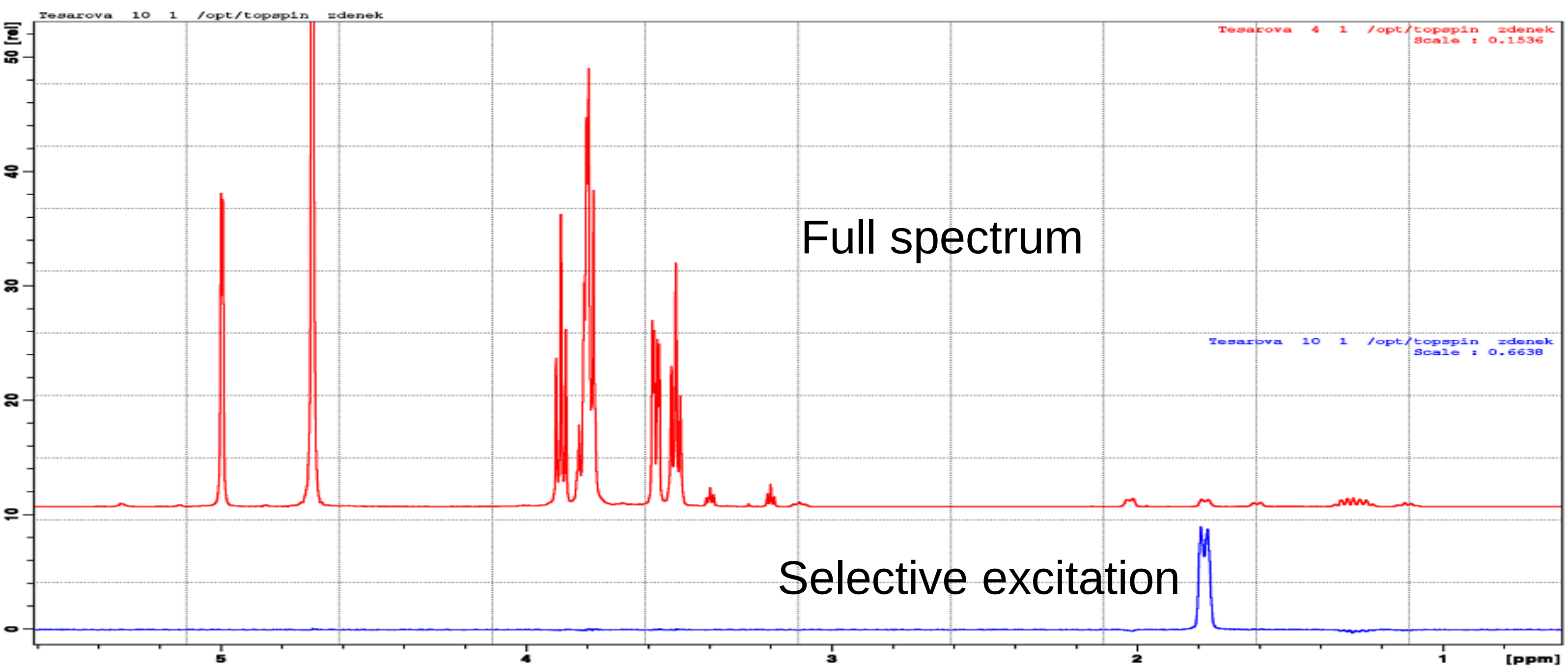


Shaped pulse
Gaussian curve

excitation profile

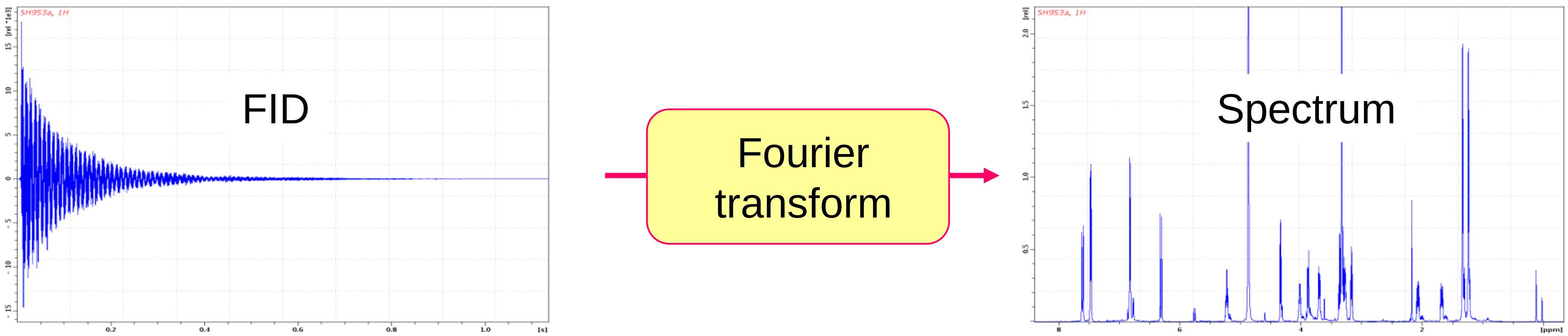


shaped pulses allow us to change the excitation profile

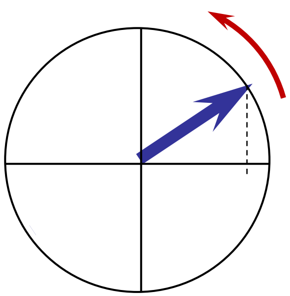


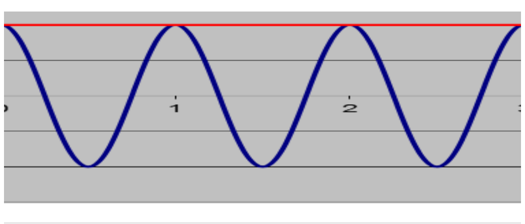
Fourier transform

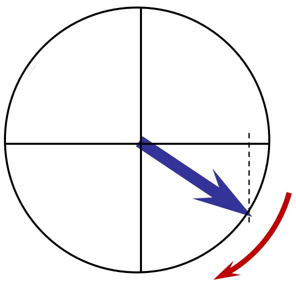
- analyses periodicities in time signal
- converts the time domain to frequency
- is a linear transformation, i.e. it preserves intensity of individual signal components



Problem of determining the sign of the precession frequency







$\cos(\omega t)$ in both cases, the same signal $\cos(-\omega t)$

The Fourier transform reflects this uncertainty in the spectrum

$-\omega$ $+\omega$

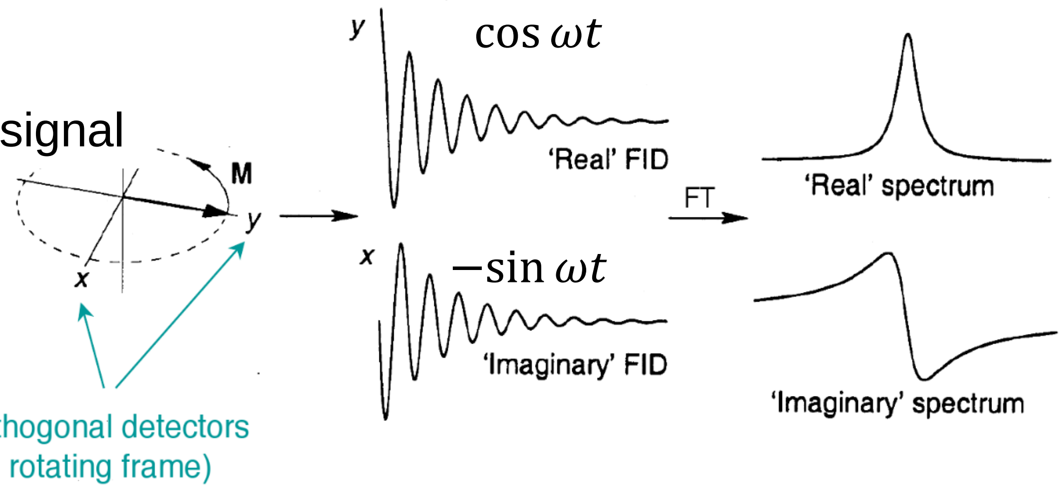
Quadrature detection

Allows

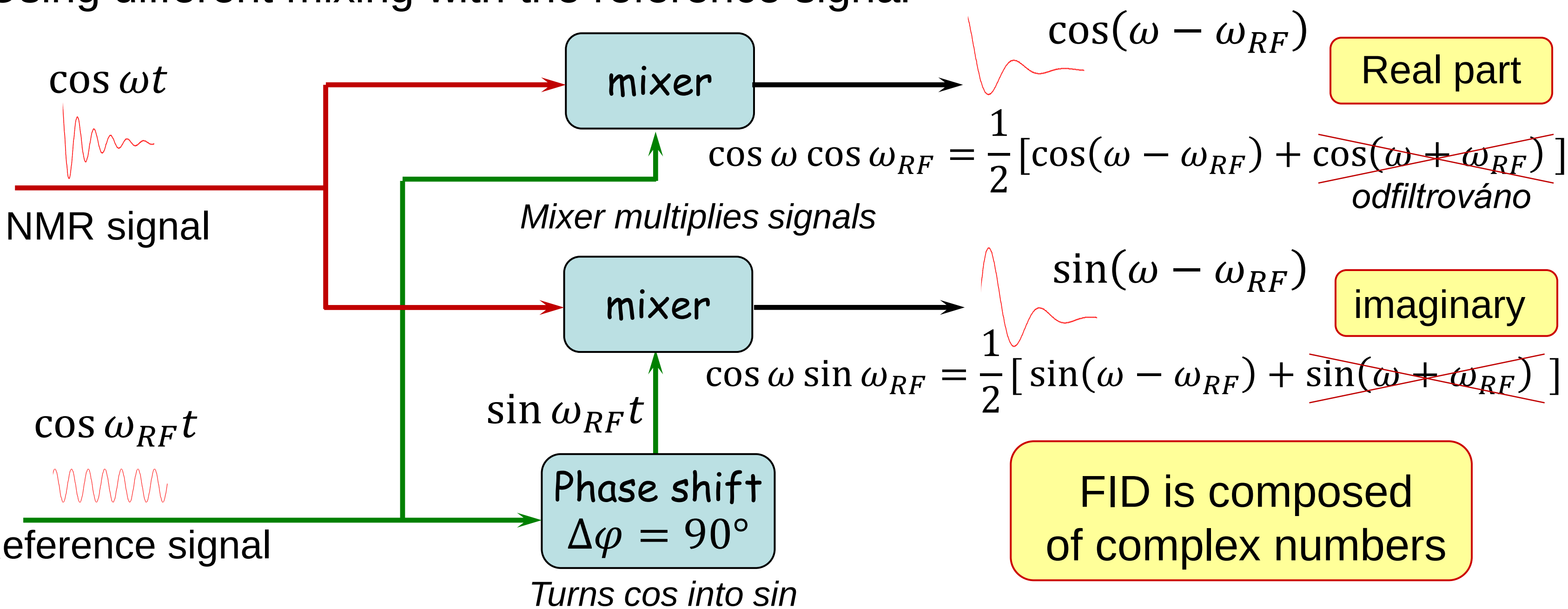
- determine the sign of precession
- correct an unknown phase of the signal

How it works

- Precession of magnetization is detected by two detectors, in X and Y directions



- or
- Using different mixing with the reference signal



FID, Spectrum, and Phase Correction

An NMR signal, FID, is a series of complex numbers

$$s(t) = \exp[i(\Omega t + \varphi)] \exp\left(-\frac{t}{T_2}\right)$$

Precession frequency in a rotating frame

$$\Omega = \omega - \omega_{RF}$$

deviation from offset (RF pulse frequency)

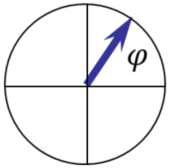
Initial phase

Unknown angle, depends on hardware parameters (dead time, amplifiers,...)

Transverse relaxation

$$e^{ix} = \cos x + i \sin x$$

exponential form of a complex number



receiver dead time

Receiver dead time

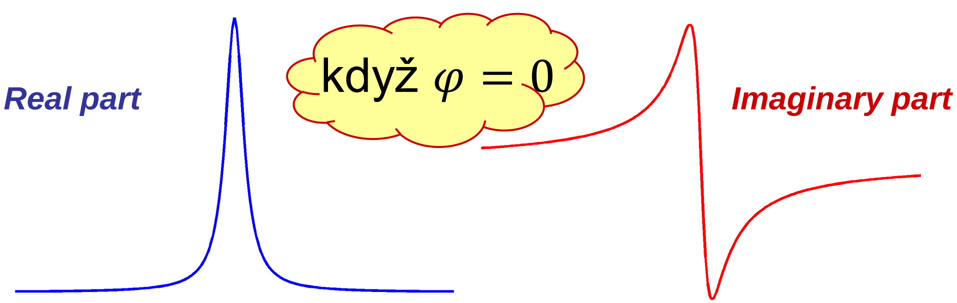
- Measurement cannot start right after the pulse as it rings down in the electronics
- During this time, magnetization deviates from the x-axis due to precession

Spectrum is also complex

$$S(\omega) = \frac{\frac{1}{T_2} - i(\omega - \Omega)}{\left(\frac{1}{T_2}\right)^2 + (\omega - \Omega)^2} \exp(i\varphi)$$

- We show the real part only
- phase correction – to remove the influence of the phase so that the real part has a purely absorption character

Lorentz curve



absorption shape ***Dispersion shape***

Spectrum and phase correction

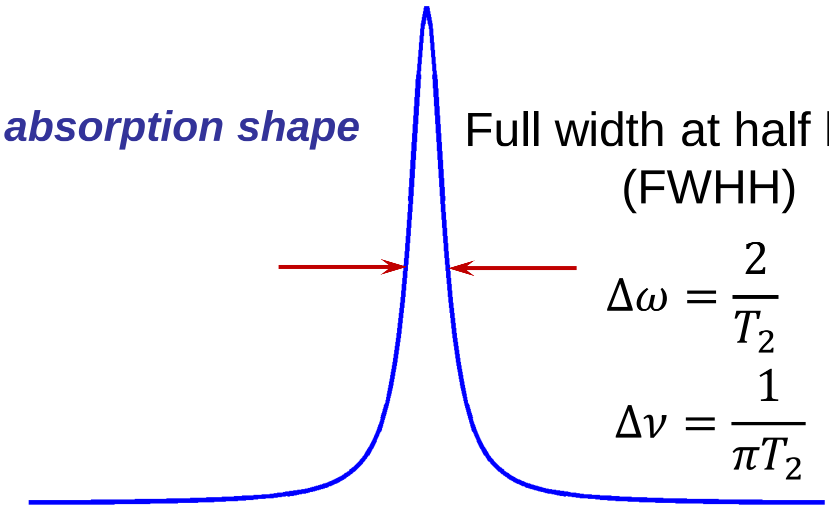
Real part of the spectrum

$$(\varphi = 0)$$

$$\mathbf{Re}\{S(\omega)\} = \frac{\frac{1}{T_2}}{\left(\frac{1}{T_2}\right)^2 + (\omega - \Omega)^2}$$

Lorentz curve

absorption shape

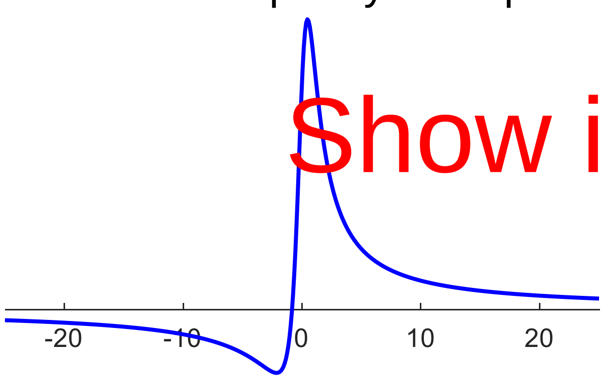


Full width at half height (FWHH)

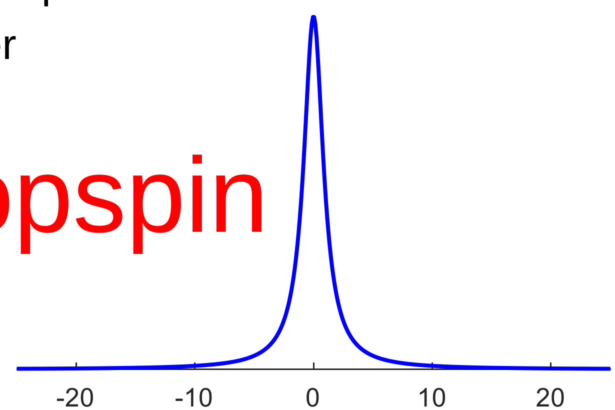
$$\Delta\omega = \frac{2}{T_2} \quad \text{rad/s}$$

$$\Delta\nu = \frac{1}{\pi T_2} \quad \text{Hz}$$

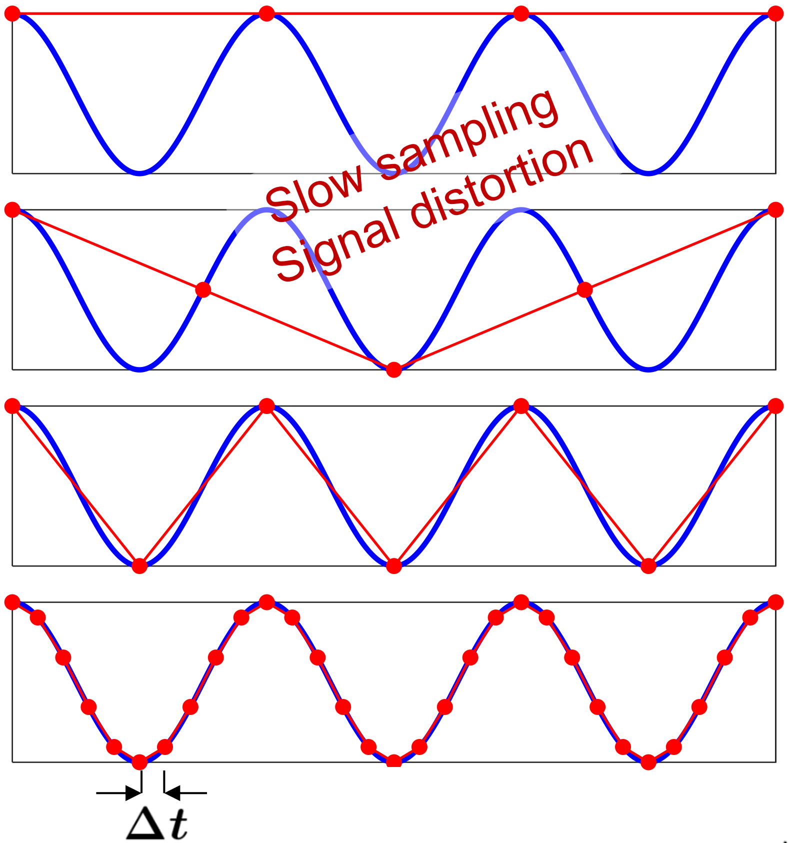
phase correction – to remove the influence of the phase so that the real part has a purely absorption character



Show in topspin



Signal Digitization



$$\Delta t = \frac{1}{\nu}$$

$$\Delta t = \frac{3}{4\nu}$$

$$\Delta t = \frac{1}{2\nu}$$

$$\Delta t = \frac{1}{10\nu}$$

The time signal needs to be correctly sampled

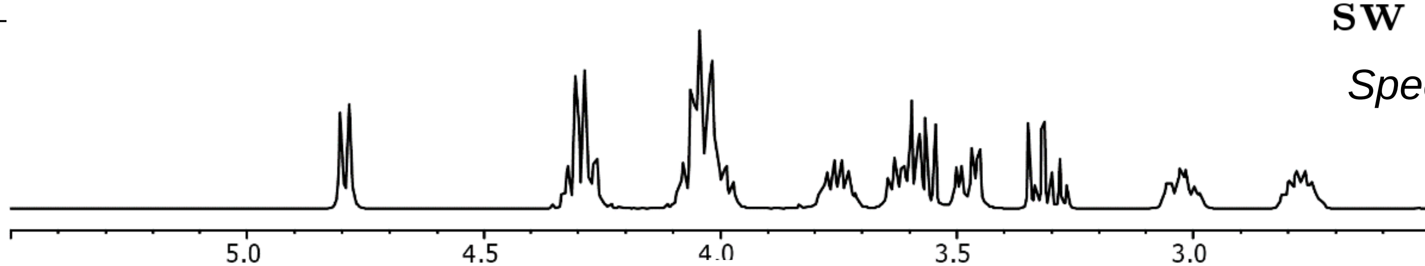
Nyquist's theorem

To faithfully capture the ν signal, we need to sample at 2ν

Spectrometer settings

$$\Delta t = \frac{1}{\mathbf{sw}}$$

Spectral Width

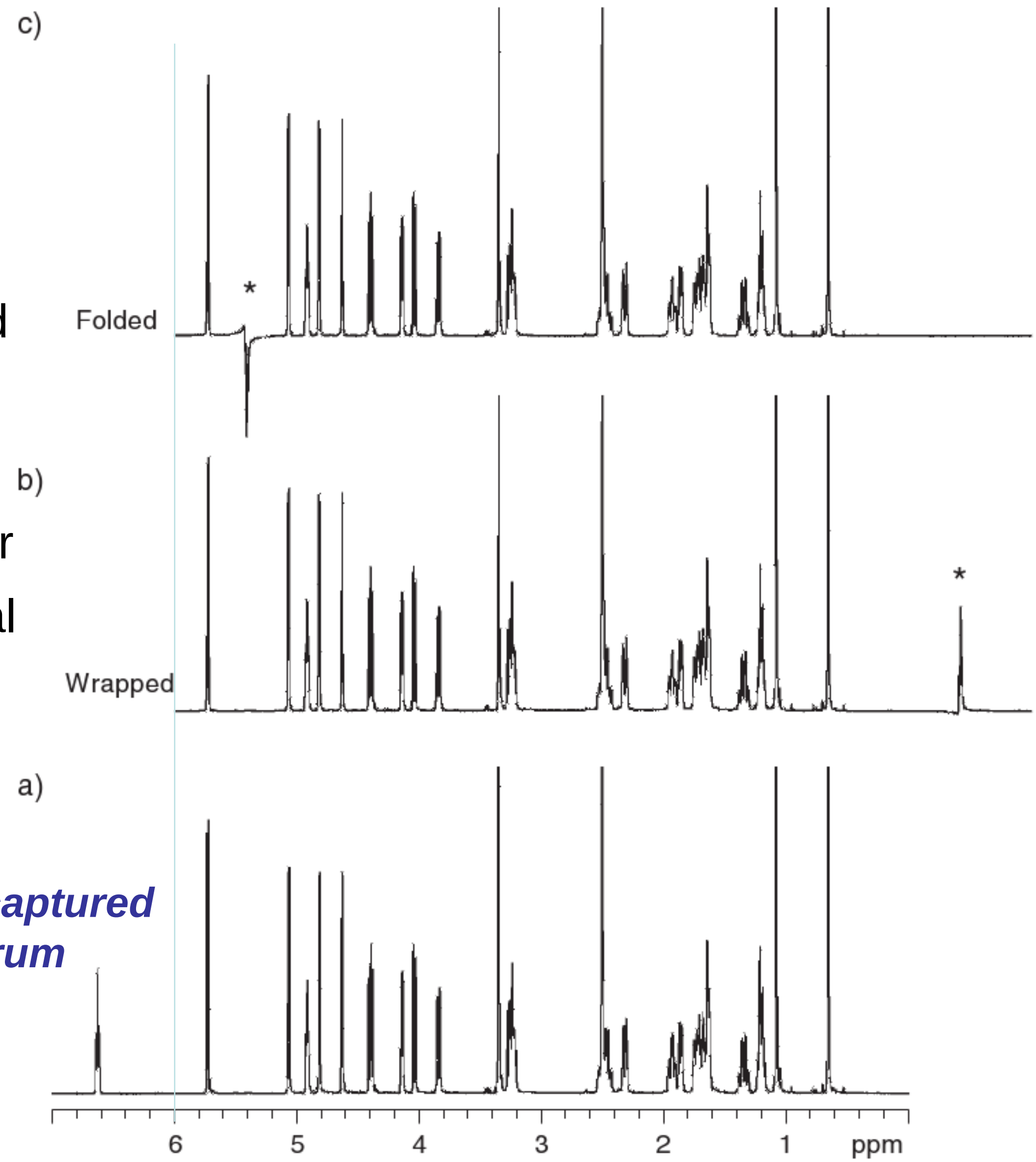


spectral width

+sw/2 — *offset* ω_{RF} — **-sw/2**

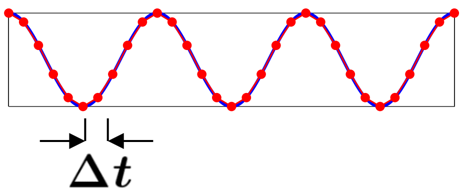
Spectral window

- It is determined by the choice of offset and spectral width
- It should include all signals in the spectrum
- A poorly chosen window can lead to false signals
- The form of the artefact depends on the design of the spectrometer
- Modern spectrometers with digital filters eliminate this problem



correctly captured spectrum

Spectral resolution



Acquisition time (length of FID)

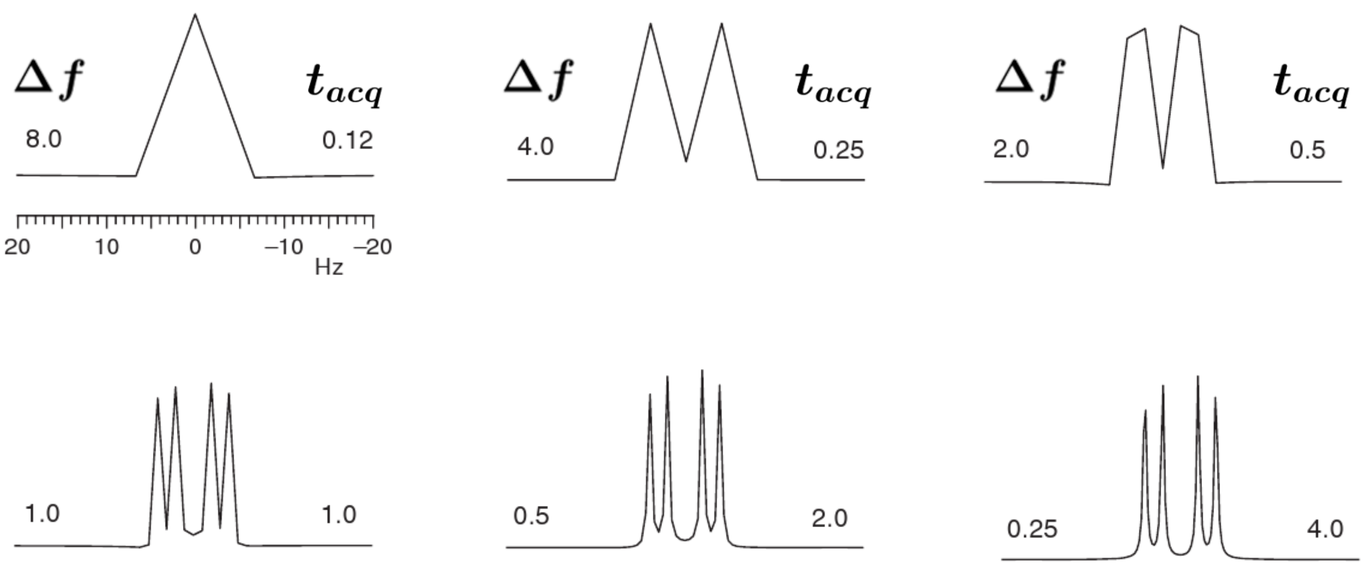
$$t_{acq} = N_p \Delta t$$

Number of points in FID

After the Fourier transform, the resulting spectrum has the same number of points(N_p)

Resolution in spectrum depends on length of acquisition time

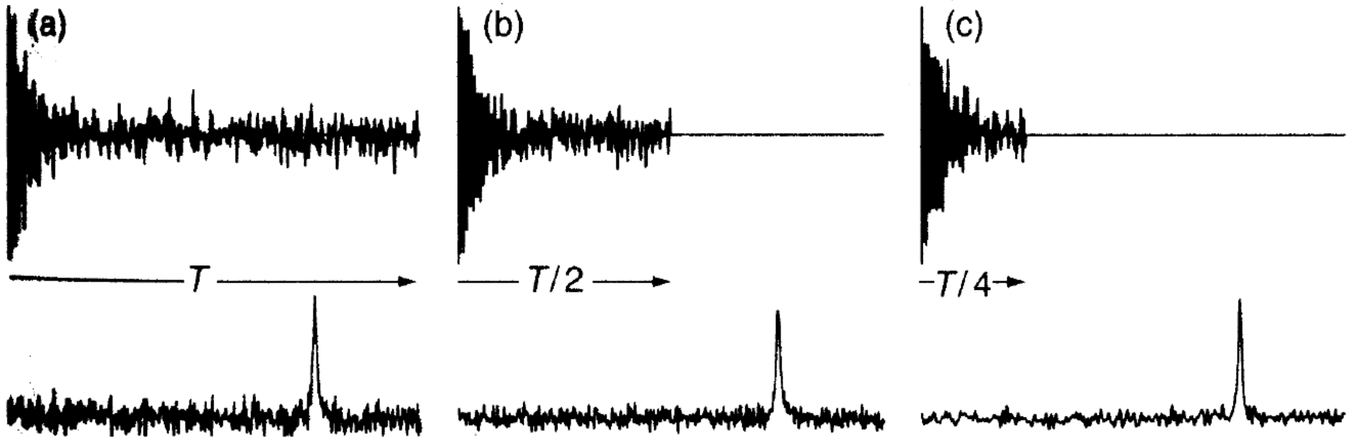
$$\Delta f = \frac{\mathrm{sw}}{N_p} = \frac{1}{\Delta t \; N_p} = \frac{1}{t_{acq}}$$



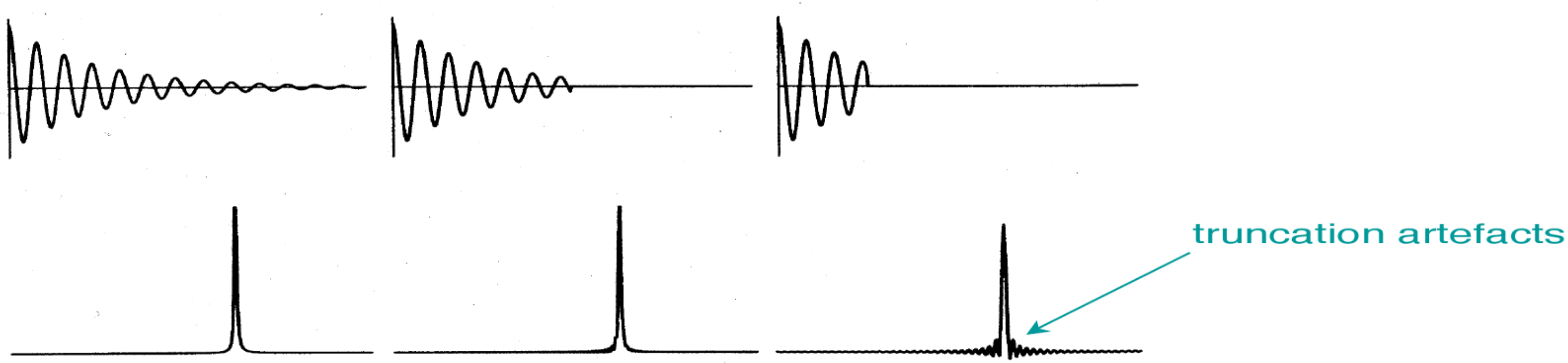
Short acquisition time
bad resolution

Long acquisition time
Excellent resolution

Choice of acquisition time



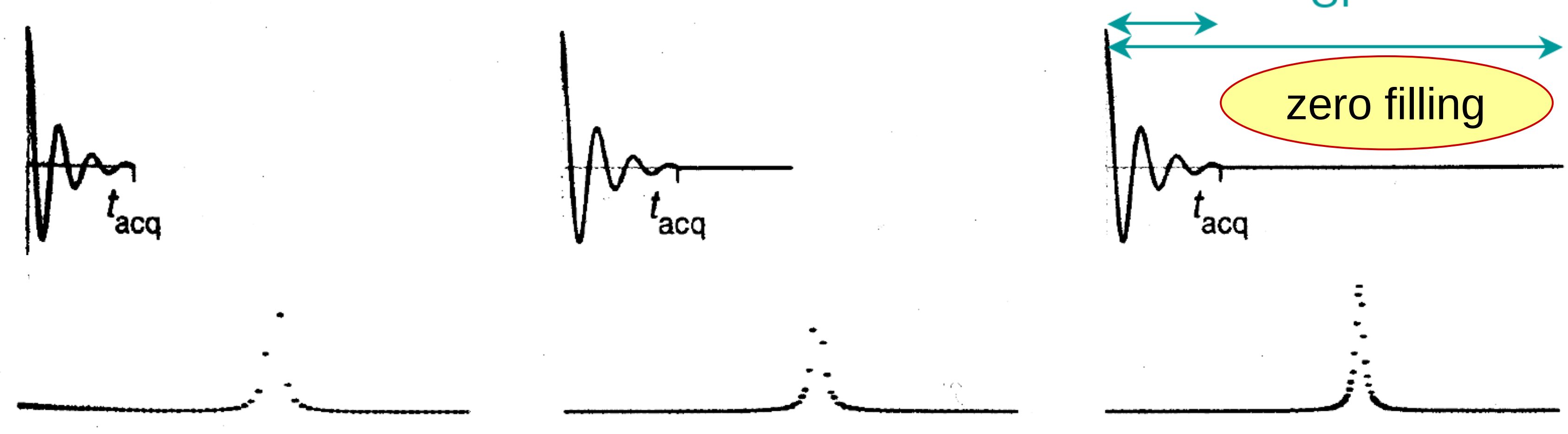
Too long acquisition time → ***measuring noise*** *Compromise with resolution is needed*



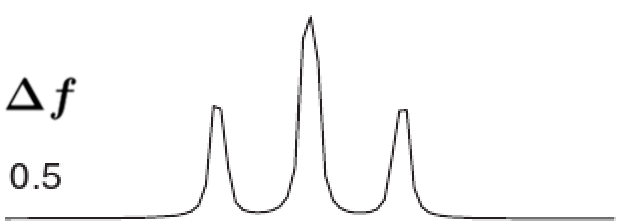
Too short acquisition time, up to cutting FID → ***truncation artefacts***

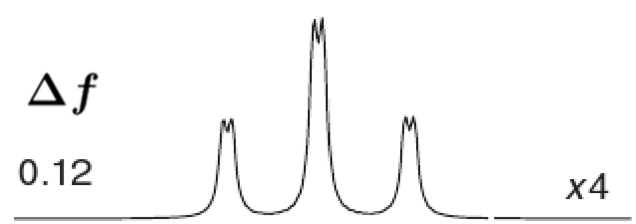
Adding zeros to FID

- Artificially extending the acquisition time
- Instead of picking up noisy data, the part of the FID without a signal is digitally replaced by zeros



- More points in the spectrum
- Fourier transform performs data interpolation

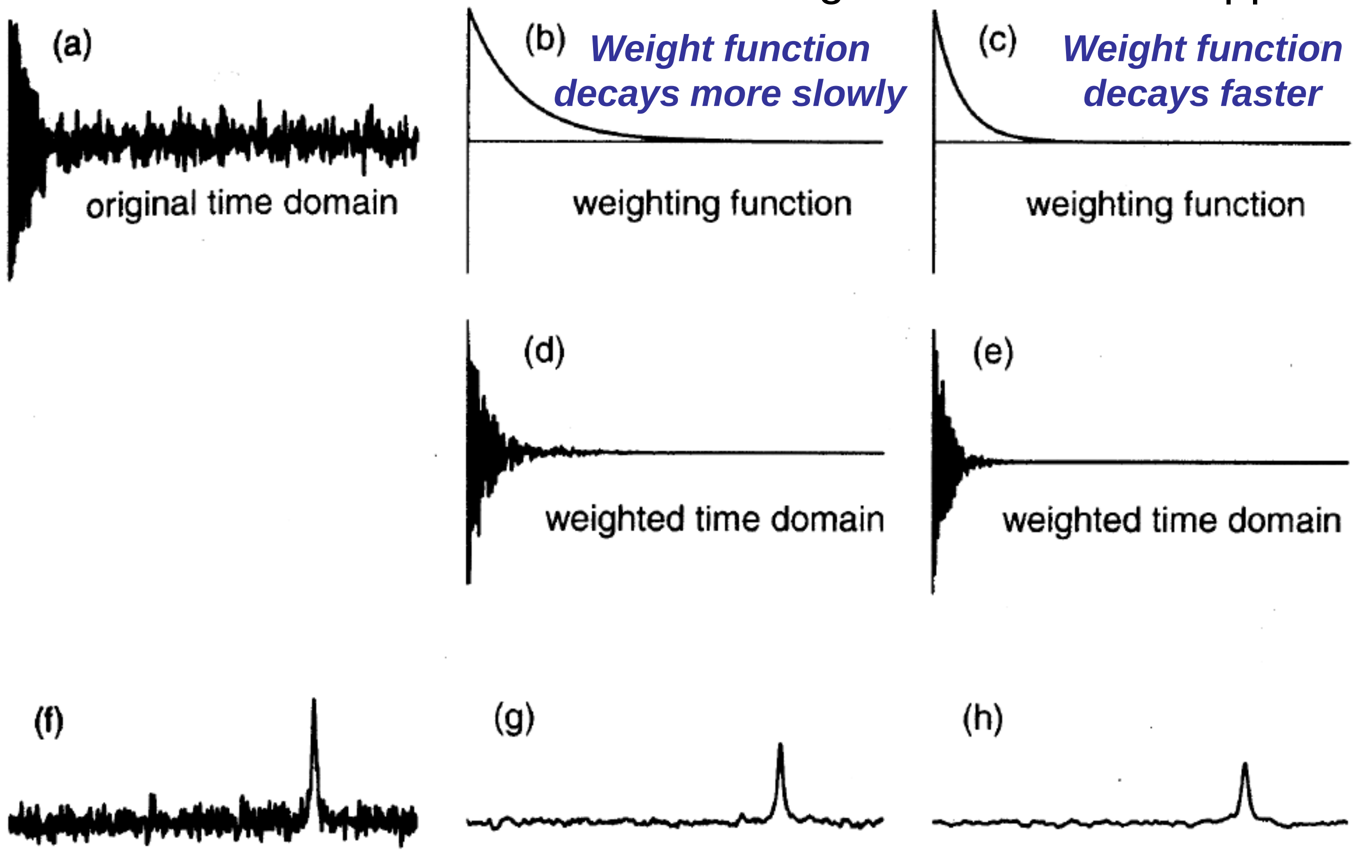




improved resolution

Signal apodization

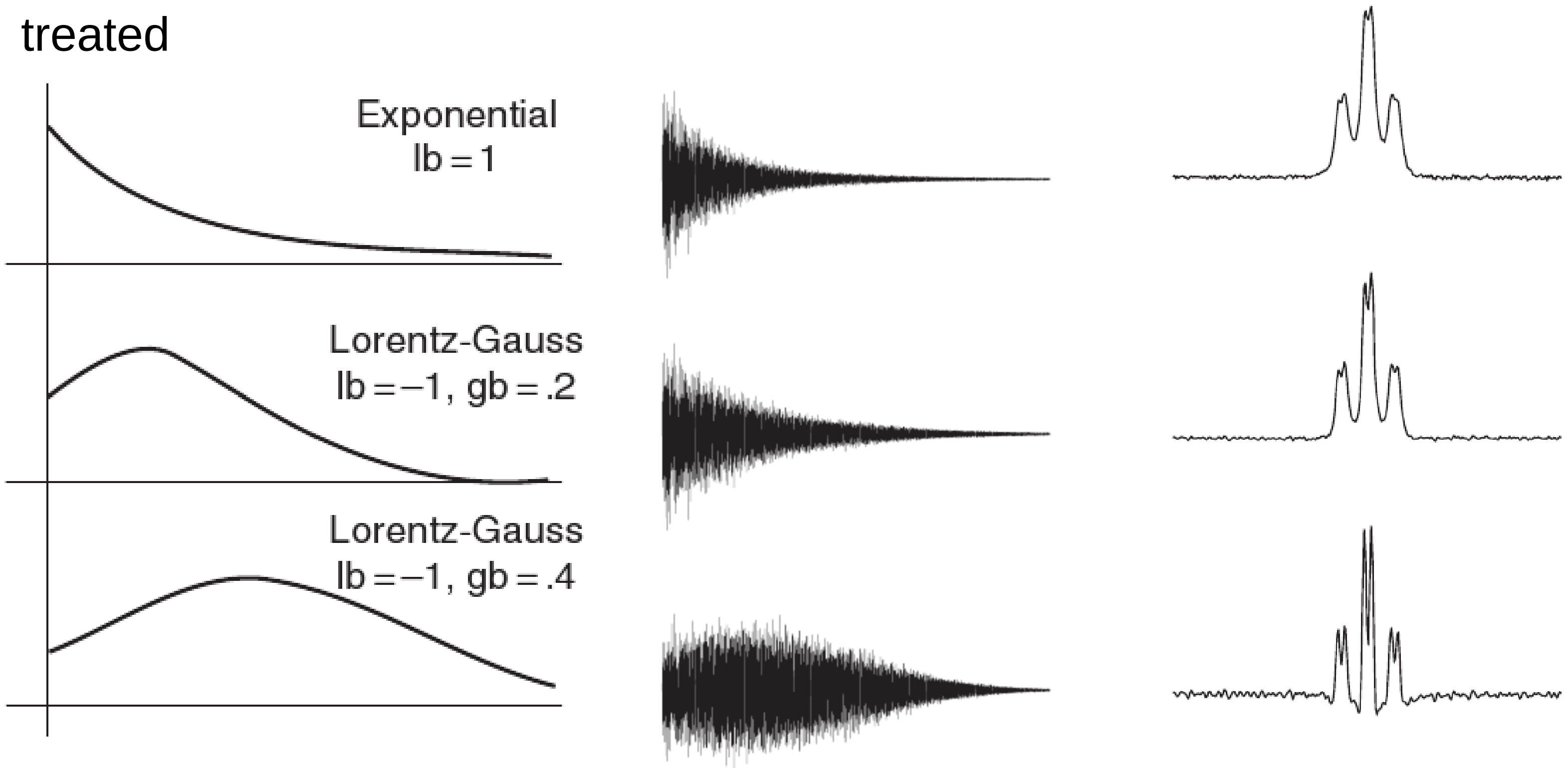
- Data at the beginning of FID, where the NMR signal is highest, are of greater importance
- The data at the end of FID contains a lower signal and can be suppressed



Noise suppression at the cost of widening peak lines in the spectrum

Signal apodization

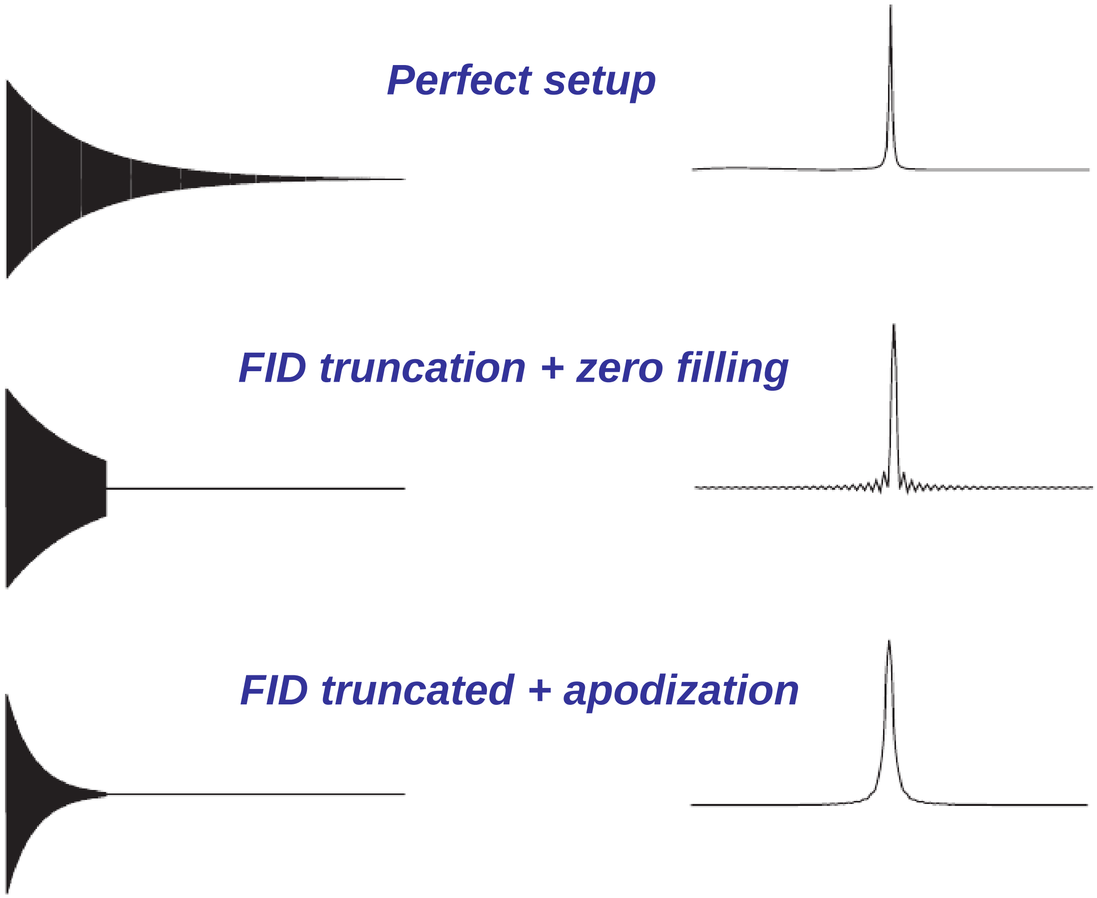
- The weight function is combined with the natural decay of FID (T2 relaxation) and thus affects the signal width
- Decreasing exponential weight function leads to expansion of signals
- Increasing exponential can narrow the signals, but "truncation" needs to be treated



Narrowing of signals in the spectrum at the cost of increased noise level

Signal apodization

- Apodization can be used to suppress clipped FID artifacts
- We artificially suppress FID so that it smoothly transitions into a zero signal (at the cost of expanding peaks)

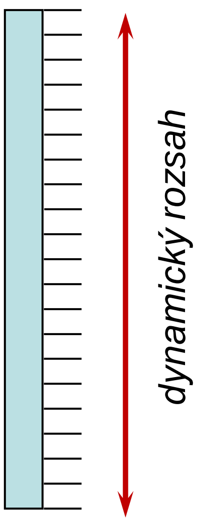


Signal amplification

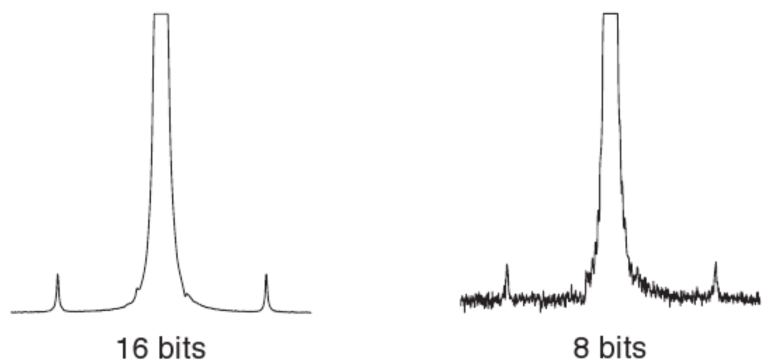
- For optimal use of the dynamic range of the ADC converter
- For detecting both intense and weak signals at the same time, it is advantageous that the strongest signal reaches the maximum level of the converter
- The range of the converter is given in bits (hence the number of converter levels)
- Higher transmitter range leads to lower noise after digitization

ADC receiver

analog-to-digital converter

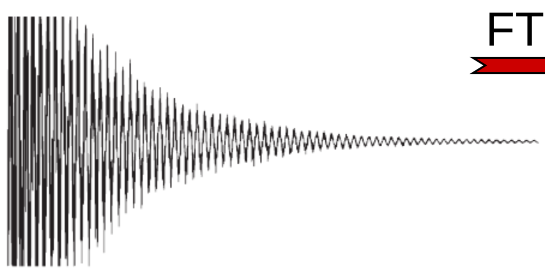


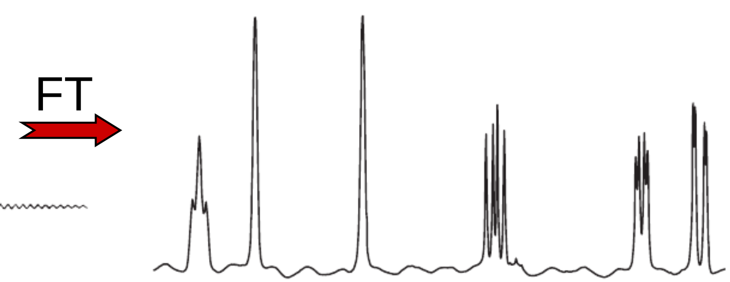
Receiver gain – Signal amplification before detection



Receiver overflow

Too high gain leads to receiver overflow and FID clipping





Artifact in spectrum

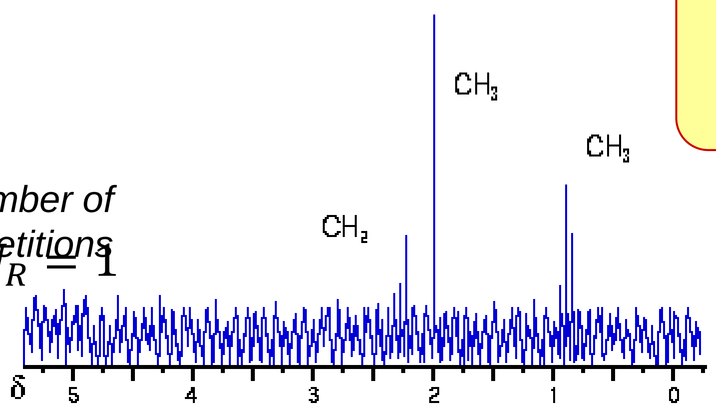
Coherent summation

- To improve the signal-to-noise ratio, the measurement is repeated and summed up
- NMR signal is always the same and thus proportional to the number of repetitions N_R
- The noise is random and partially cancels out, proportional to $\sqrt{N_R}$

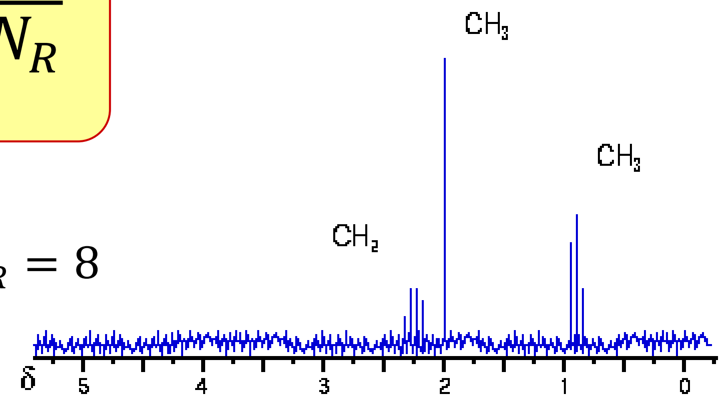
$$\frac{S}{N} = \sqrt{N_R}$$

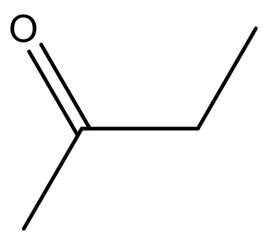
Number of repetitions

$N_R = 1$

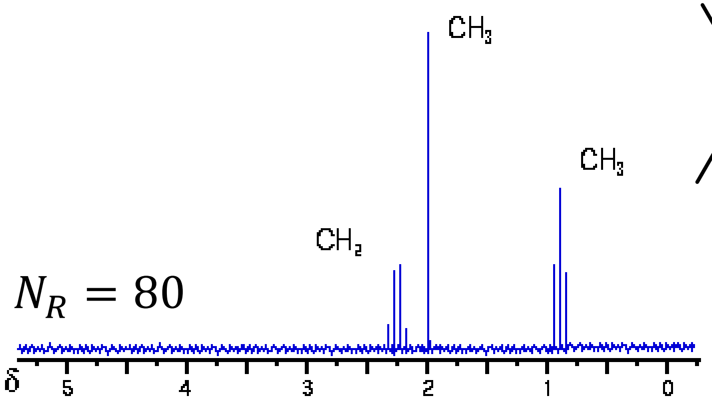


$N_R = 8$

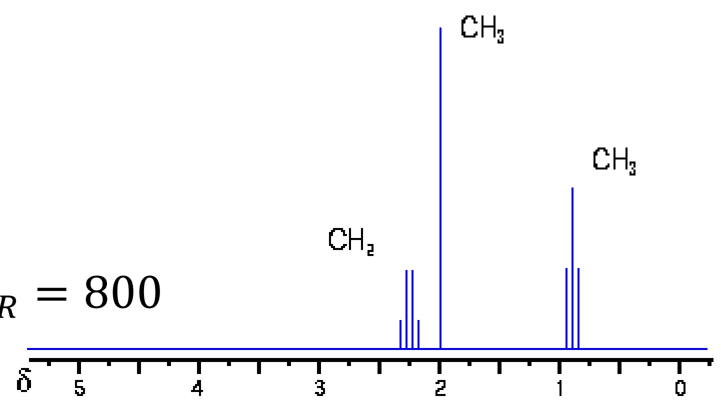




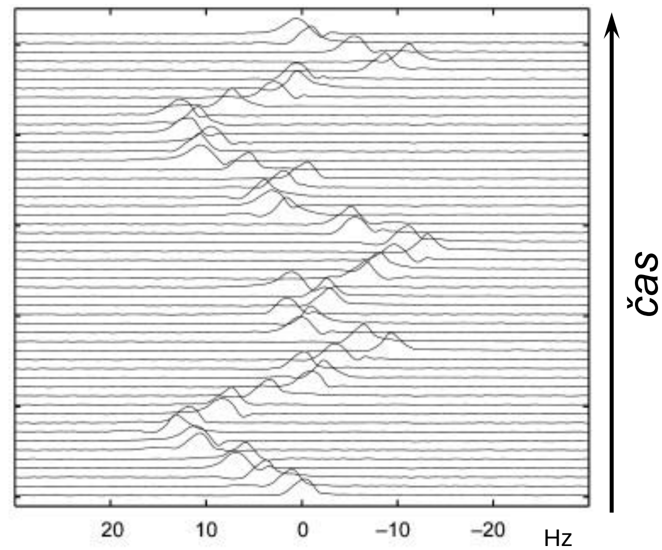
$N_R = 80$



$N_R = 800$



Stability and homogeneity of magnetic field



Stability over time

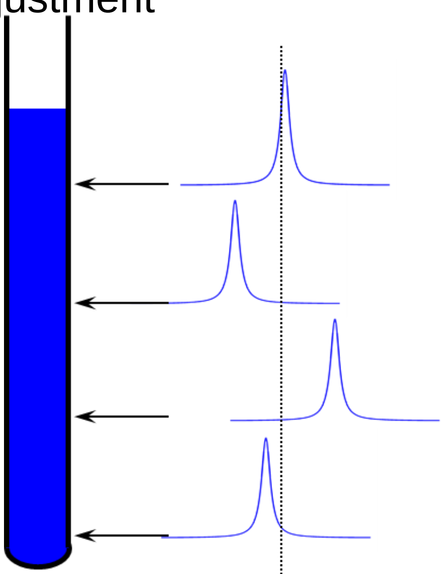
Field-frequency lock

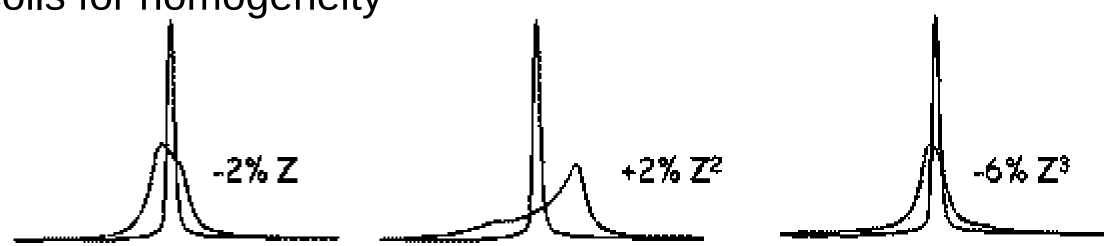
- the position of the signal must be maintained for repeated measurements,
- Lock system – independent spectrum (deuterium) is monitored and changes in the magnetic field are compensated for

Homogeneity over sample volume

Shim

- for narrow peaks, the Larmor frequency needs to be the same throughout the sample volume
- magnet equipped with a system of coils for homogeneity adjustment





systém korekčních cívek, až 36