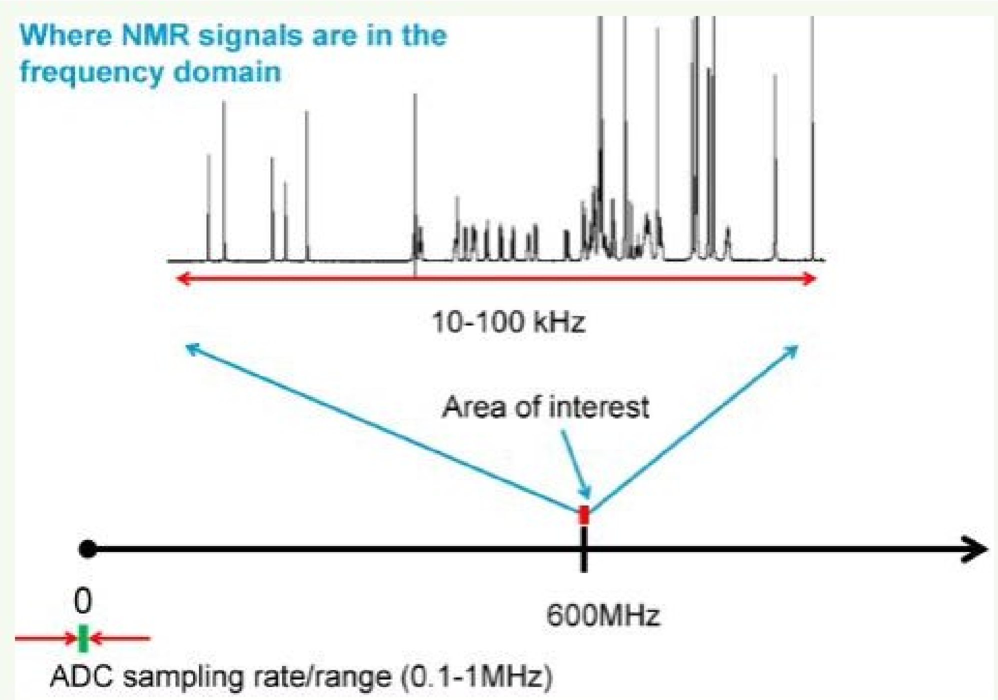
FT-NMR
frequency domain signal
vs.
time domain signal

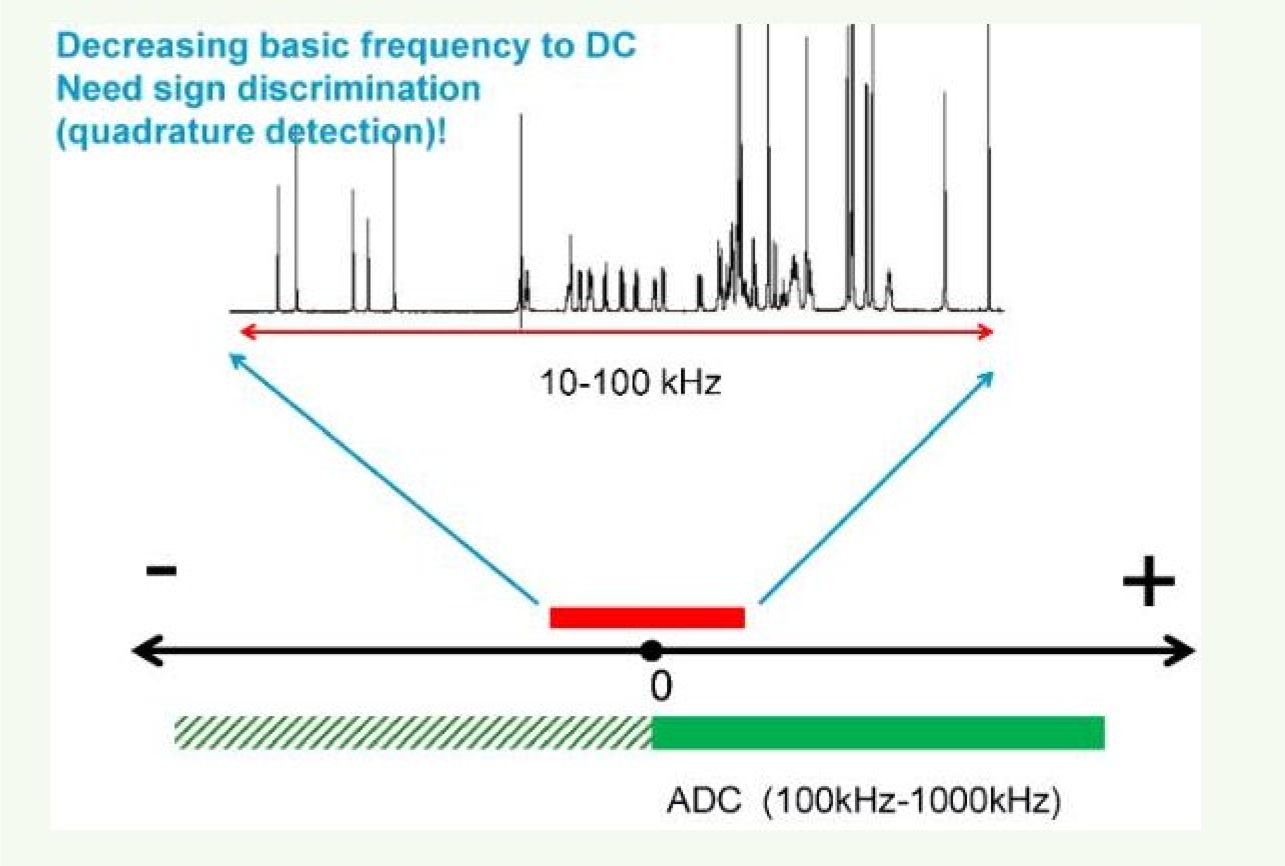


Luckily, NMR signals reside in a relatively tiny 10-100kHz spectral window around NMR base frequency of 600MHz.

One can correctly digitize 100kHz signal with a 500kHz ADC. The trick is to move that 100kHz spectral window from 600MHz base to near zero so it fits into ADC sampling area.

On older systems like INOVA and UNITY it was done in two steps: shifting base frequency from 600MHz to intermediate frequency (IF) and then shifting base frequency to zero.

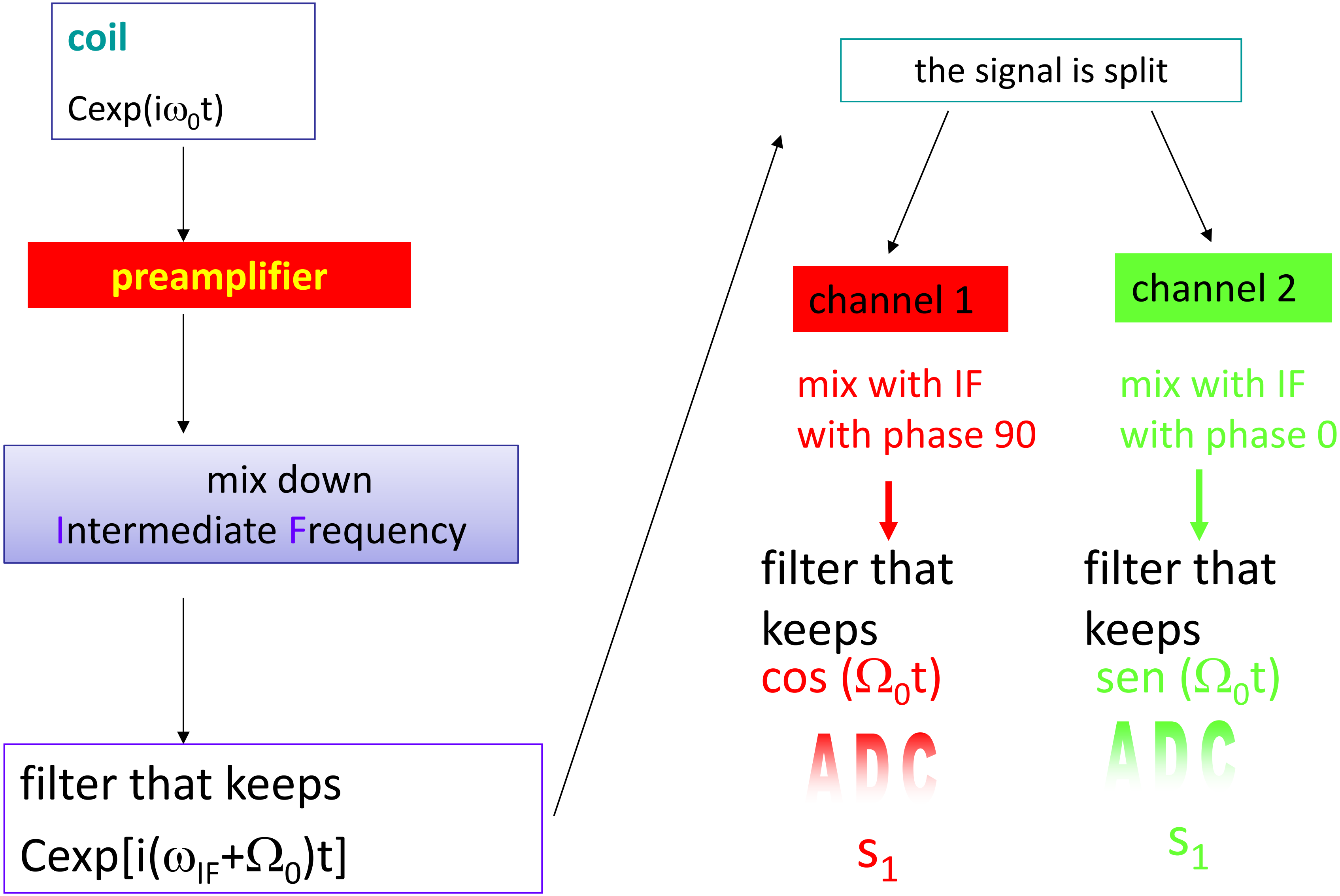
https://spinsights.chem.agilent.com/community/resources/spinsights-blog/blog/2016/02/19/basics-of-nmr-signal-acquisition-draft-internal#comment-4283



there is a way to correctly distinguish signals from both halves of that spectral region by doing the following trick:

split signal in two, shift one part in phase by a 90 degrees, digitize both parts by two *separate* ADCs ; use those two digitized datasets to make a "complEx" FID later.

Quadrature Detection



coil

$Cexp(i\omega_0 t)$

preamplifier

mix down
Intermediate Frequency

filter that keeps
$Cexp[i(\omega_{IF}+\Omega_0)t]$

the signal is split

channel 1

mix with IF
with phase 90

filter that keeps
$\cos(\Omega_0 t)$

ADC

s_1

channel 2

mix with IF
with phase 0

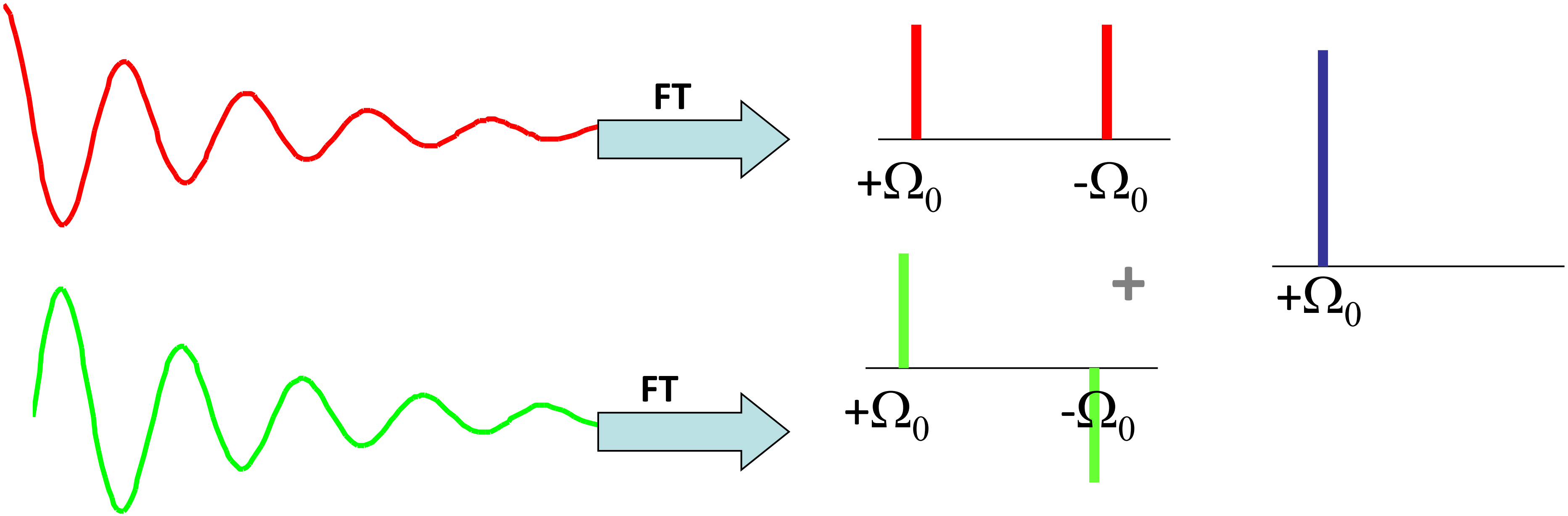
filter that keeps
$\text{sen}(\Omega_0 t)$

ADC

s_1

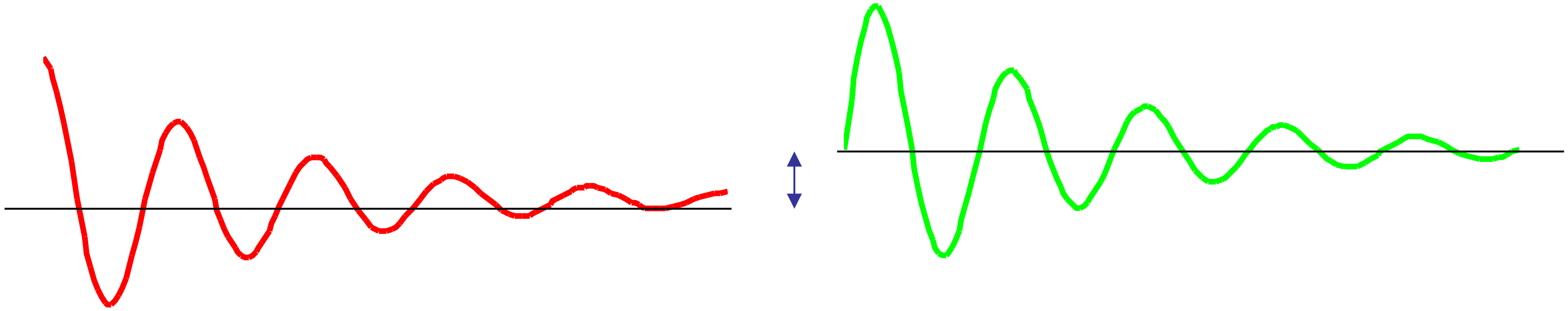
Quadrature detection

- The time domain signal: $S(t)=C\exp(i\Omega_0 t)\exp(-t/T_2)= C[\cos(\Omega_0 t)+i\,\mathrm{sen}(\Omega_0 t)]\exp(-t/T_2)$
- Both components (cos e sen) of the time domain signal are required for a non ambiguos frequency spectrum

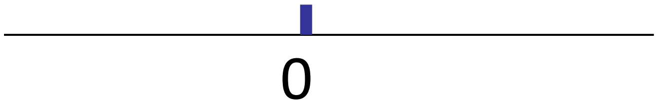


Problems of Quadrature Detection

- Offset of the baseline of the two channels



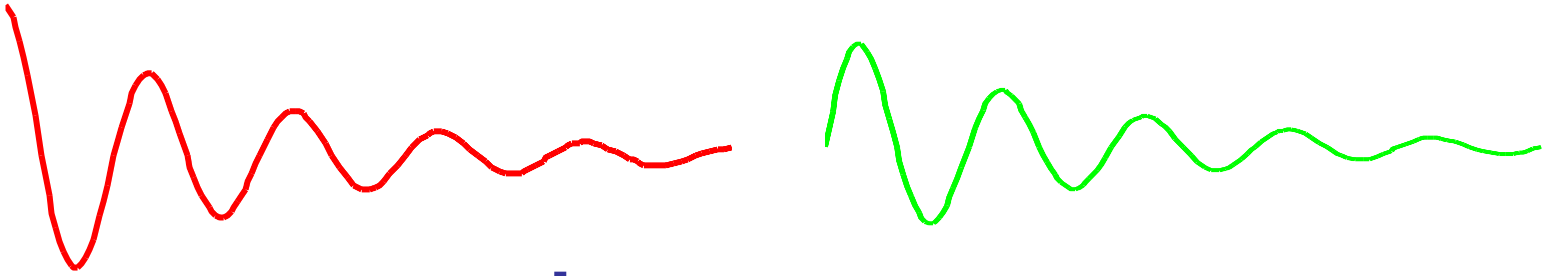
It is like a zero frequency signal and produces a glitch at the center of the spectrum

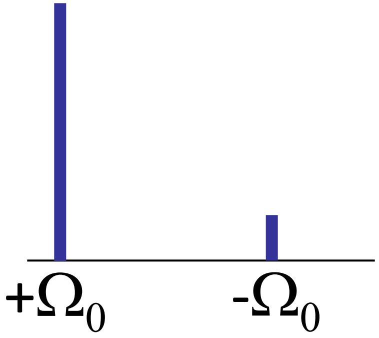


it appears more evident in spectra acquired with a single scan (phase cycle averaging does not apply)

software correction: dc balance

When the two channels have different gains the subtraction is not complete

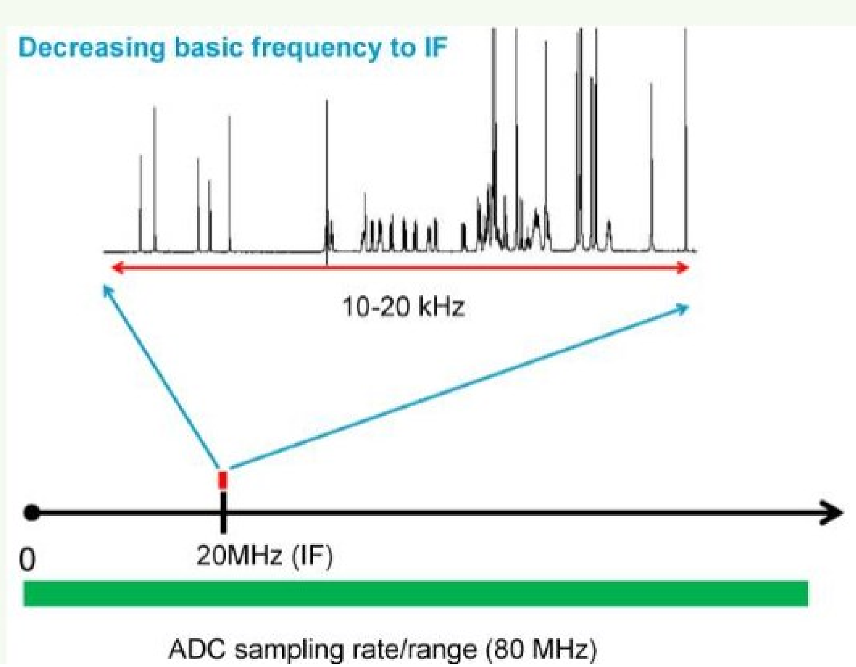


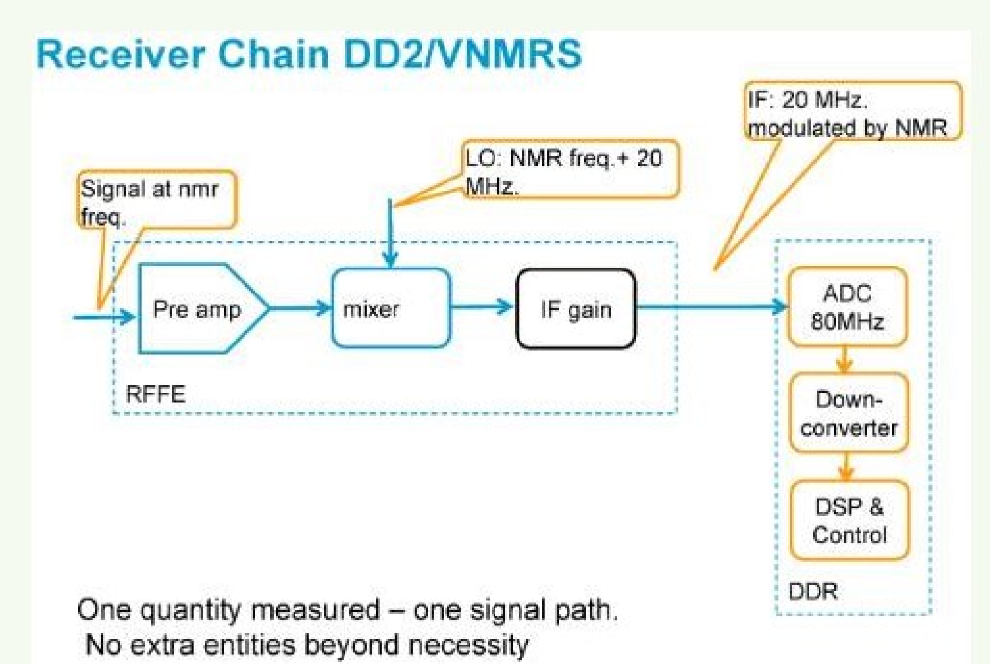


The problems appears because the Ω_0 are not all either positive or negative. The transmitter frequency is placed at the centre of the spectral window to minimize off-resonance effects

These problems are coped with by phase cycles

Digitization at Intermediate Frequency: direct drive receiver of the Agilent spectrometers at DSCF





One quantity measured – one signal path.
No extra entities beyond necessity

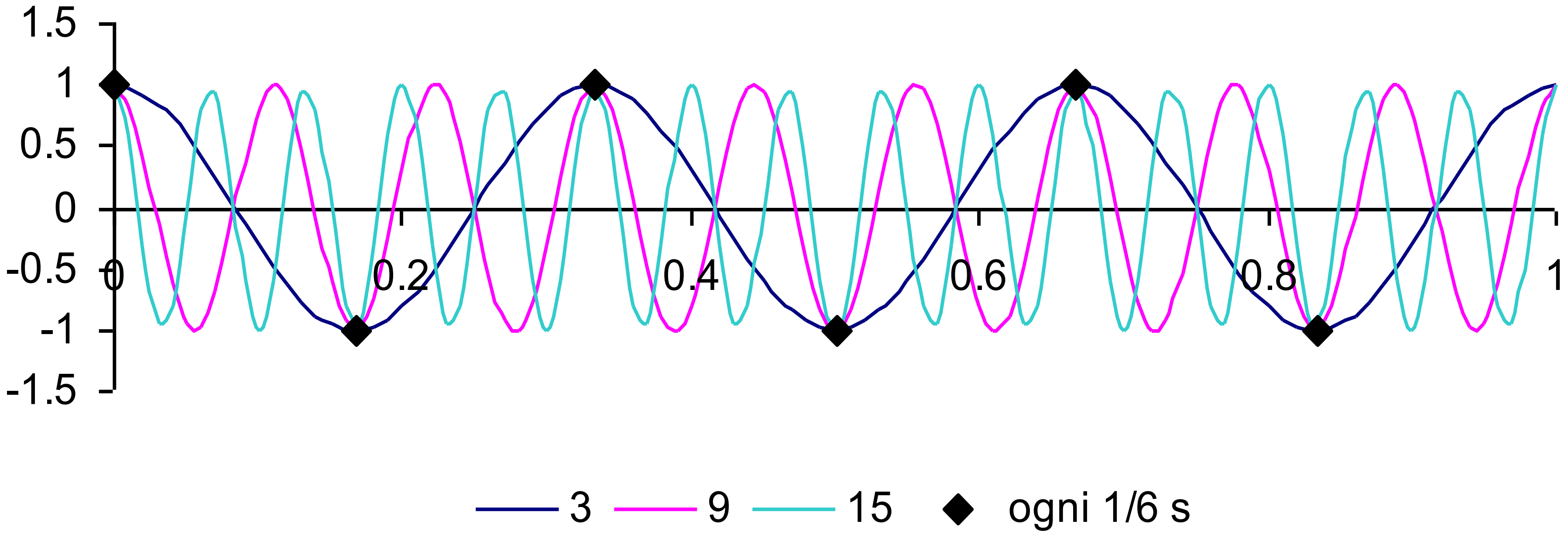
Current ADCs are fast enough to sample at the level of intermediate frequency, which is higher than all frequencies in the spectral window and thus no ambiguity is left

The problems arising from quadrature images are avoided

Digitization

- Working with descrete data: the signal is know only at the measurement instant
- The discrete FT affords the correct freqeuncy provideed there are enough sampling per unit time
- Nyquist Criterium: a sinus curve must be sampled at least two times per cycle to get the right frequency

$$\nu_{Nyquist} = \frac{\nu_{sampling}}{2}$$



Nyquist criterium establishes the minimun sampling rate for getting correct frequency values in the spectrum

- The Max number of acuired datapoints is limited by computer RAM
- The dwell time (time interval between two consecutive sampling points, inverse of ν_{sampling}) times the number of points is equal to the acquisitio time
- It is not wise to acquire for longer than a few T_2 because the signal has disappeared so that one acquires only noise
- N.B. The old spectrometers reuired a number of datapoints equal to a power of two because of the FFT algorithm
- 2^n: 2 4 8 16 32 64 128 256 512 1024 2048 4096 ....
- 1 K = 1024 punti

- When quadrature is used the actual number of datapoints is twofold
- The number of points in the frequency domain after the FT is equal to the number of points in the time domain before the FT
- It gives the digital resolution: Hz/pt
- An important property of the FT is the possibility of the Zero Filling, which artificially increases the digital reolution without the need to acquire the spectrum again

- The FT establishes an univoque correspondence between the two functions: time domain s(t) and frequency domain S(ω)
- t and ω: conjugate variables

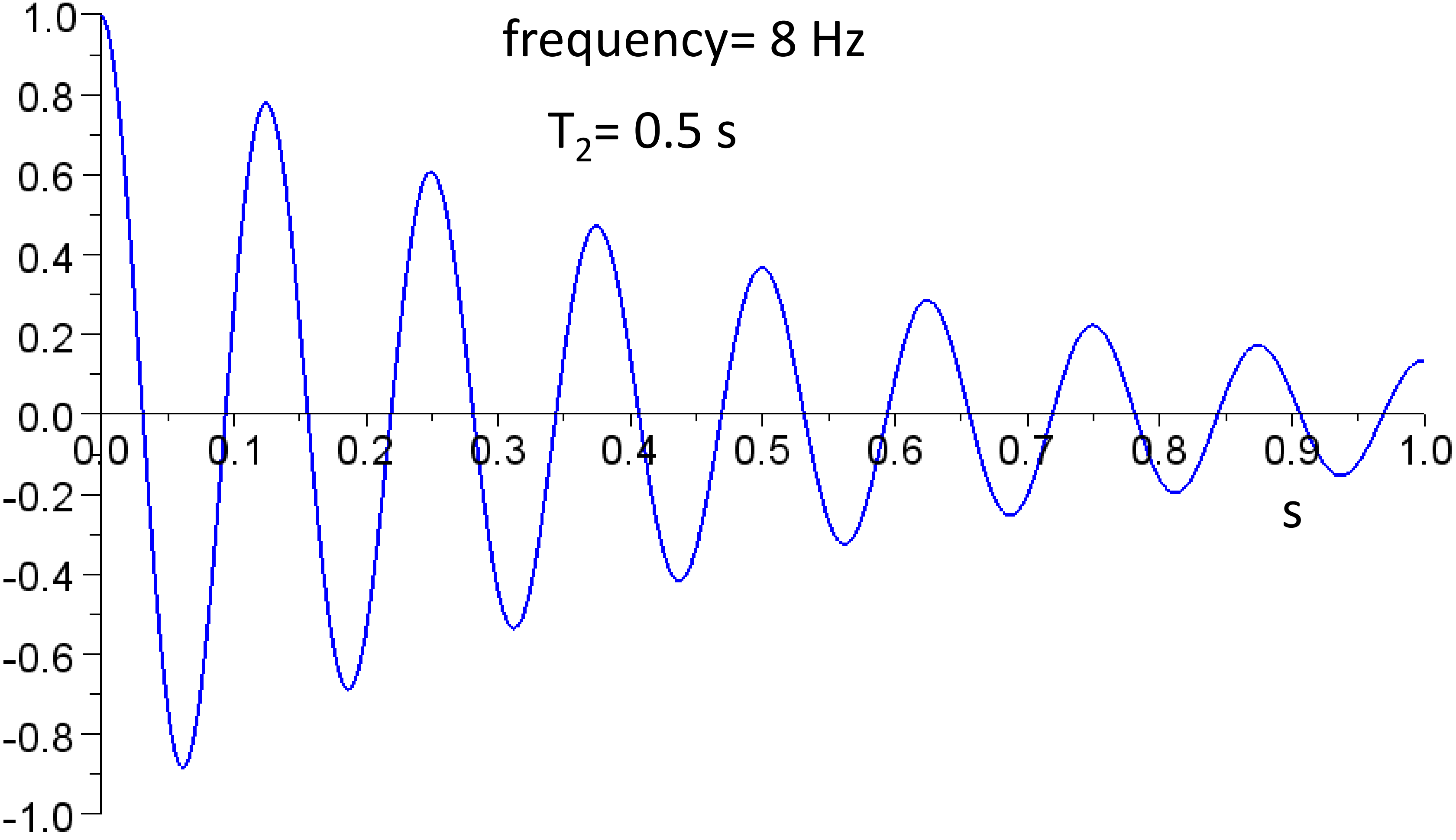
Fourier Transform

Inverse Trasformata

$$S(\omega)=\int_{-\infty}^{+\infty} s(t)e^{-i\omega t}dt$$

$$s(t)=\frac{1}{2\pi}\int_{-\infty}^{+\infty} S(\omega)e^{i\omega t}d\omega$$

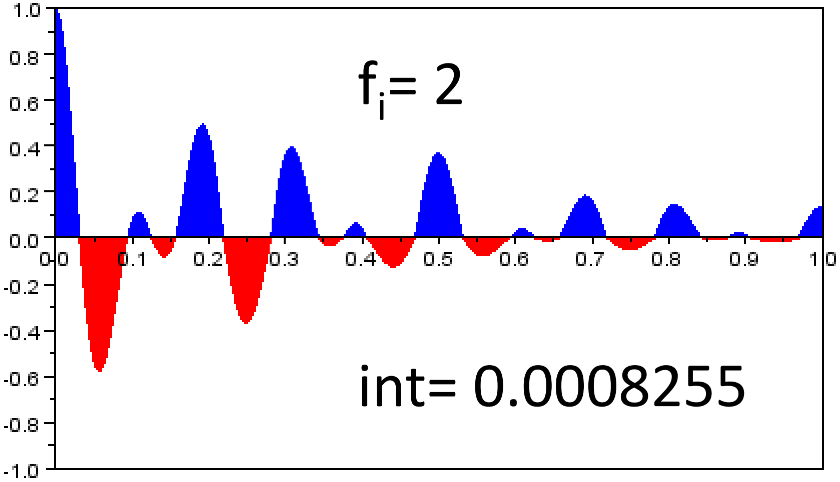
signal, function of time

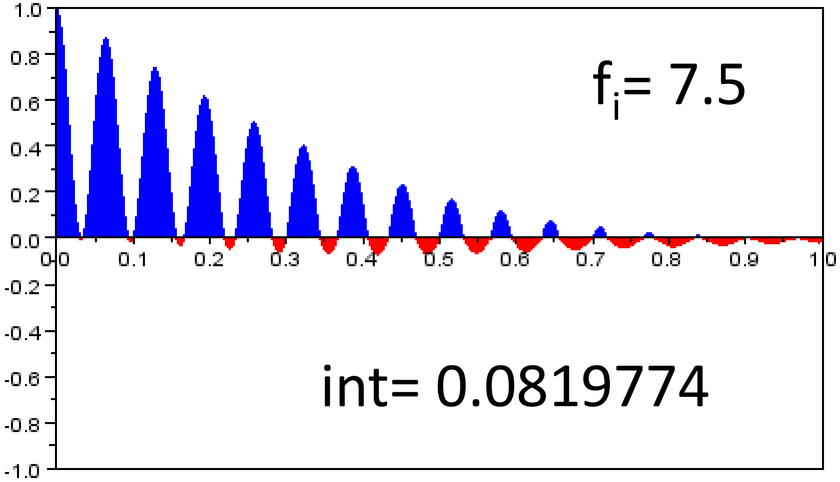


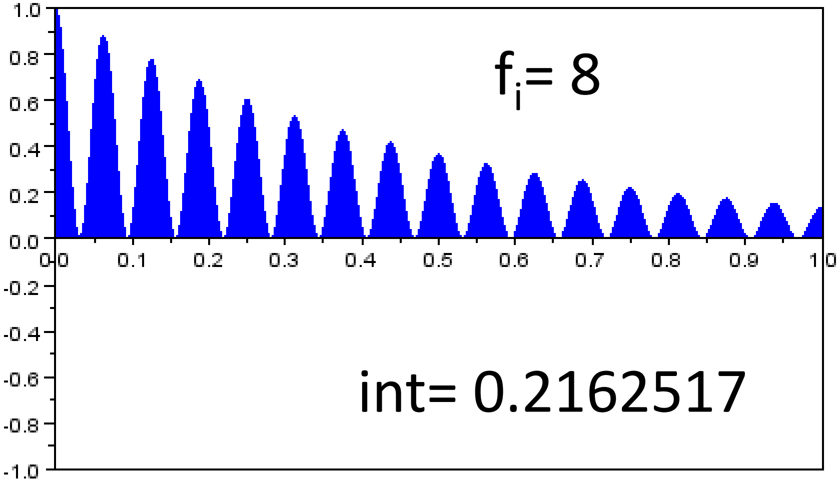
frequency= 8 Hz

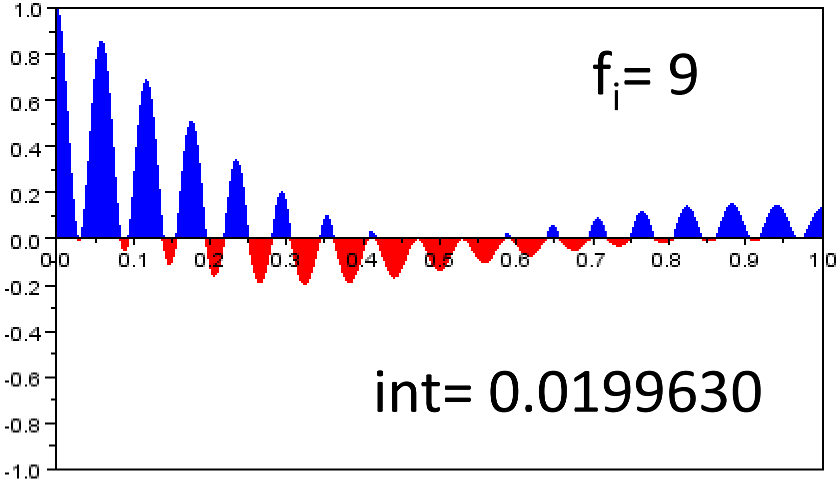
T_2= 0.5 s

$s(t)*\cos(2\pi f_i*t)$







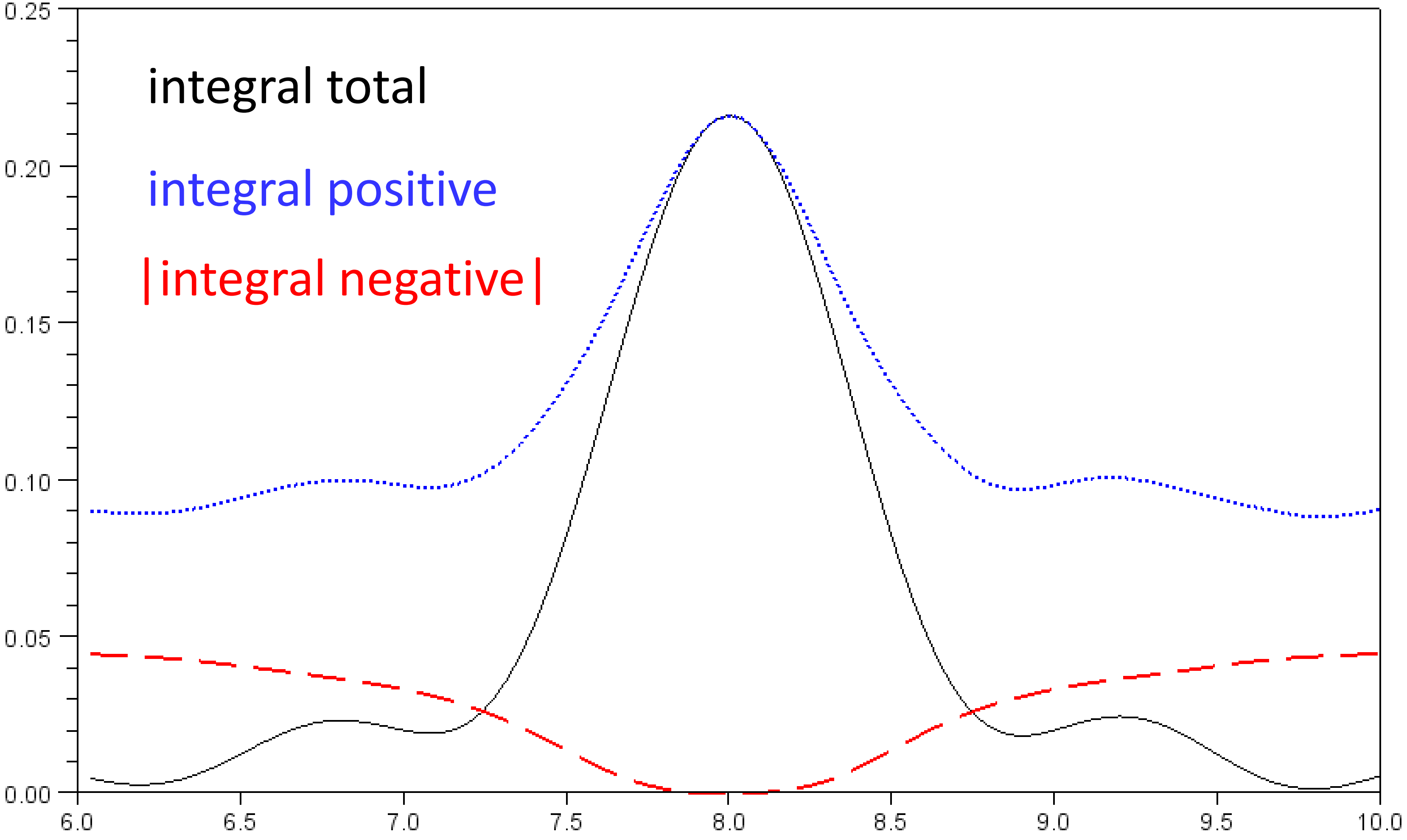


We often use ν in place of ω.

The $\omega = 2\pi\nu$ (units rad/s) is a more convenient variable for formal calculus, whereas ν (units s^{-1}= Hz) is more used to represent spectroscpic data

The two functions $S(\omega)$ and $S(\nu)$ are not strictly equal because of the 2π factor in the argument

the signal in the frequency domain



Time Domain and Frequency Domain

- Both can be exploited for acquisition, manipulation and the rappresentation of spectroscopic data
- it is a general concept, not exclusive for FT spectroscopy, but is common to many measurement techniques
- Il dominio dei tempi e quello delle frequenze portano la stessa informazione, sebbene in forma diversa.
- Può essere più conveniente considerare ora l’uno ora l’altro dominio, a seconda della particolare situazione.

Segnale nel dominio delle frequenze

Il risultato della FT complessa è una funzione complessa

$$S(\omega)=\int_0^{+\infty}\exp\left(i\omega_0 t\right)\exp\left(-\frac{t}{T_2}\right)\exp(-i\omega t)\,dt=\left|\frac{\exp\left[-i(\omega-\omega_0)t-\dfrac{t}{T_2}\right]}{-i(\omega-\omega_0)-\dfrac{1}{T_2}}\right|_0^{+\infty}=$$

$$=\frac{1}{i\left(\omega-\omega_0\right)+\dfrac{1}{T_2}}=\frac{T_2}{i\left(\omega-\omega_0\right)T_2+1}=\frac{i\left(\omega-\omega_0\right)T_2^2-T_2}{-\left(\omega-\omega_0\right)^2T_2^2-1}=$$

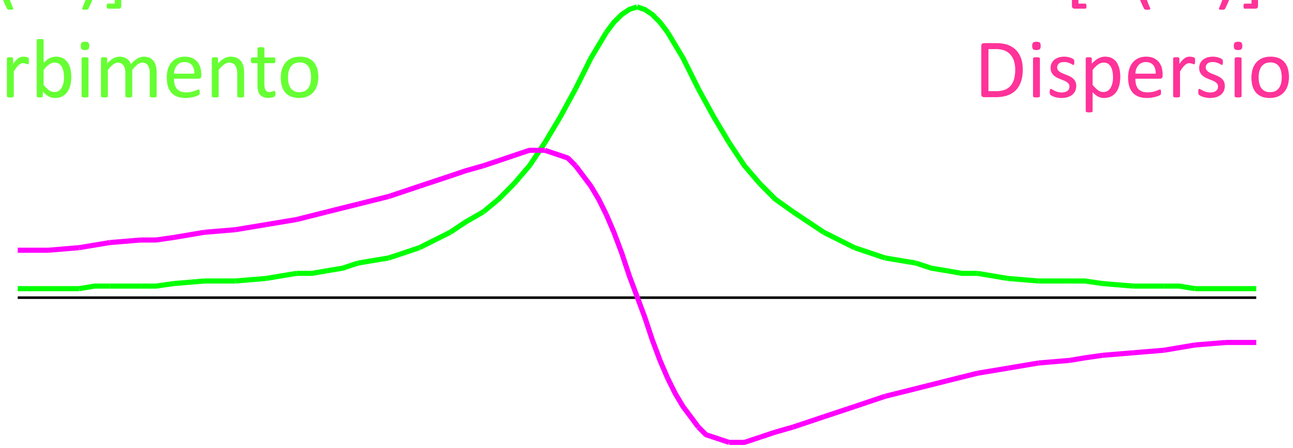
Funzione Lorentziana

Si introduce $\Delta\omega=\omega-\omega_0$

$$S(\omega)=\frac{T_2-i\Delta\omega T_2^2}{1+\Delta\omega^2T_2^2}$$

Re[S(ω)]
Assorbimento

Im[S(ω)]
Dispersione



Sensibilità della spettroscopia NMR

- Ogni punto del segnale nel dominio del tempo contiene informazione da tutte le frequenze presenti, è come avere un detector multicanale con un grandissimo numero di canali
- Il segnale è debole, la f.e.m. è dell’ordine dei mV. Il rumore dipende dall’elettronica dei circuiti. Si suppone che il *noise* sia “bianco”, cioè abbia la stessa intensità per tutte le frequenze.
- Il *noise* con frequenza superiore alla frequenza di Nyquist viene eliminato mediante un filtro analogico, che lavora a livello di audio-frequenze.

S/N

- Siccome la media del N, essendo un *noise* bianco, è zero, allora si fa riferimento al *noise* picco-picco medio su cento campionamenti.
- Il rapporto segnale su rumore convenzionalmente in NMR è dato da:

$$\boxed{S/N = 2.5\frac{S}{\langle N_{pp}\rangle}}$$

E’ accettabile prima di calcolare il rapporto S/N, moltiplicare il segnale nel dominio dei tempi per una funzione di peso del tipo matched filter

$$\boxed{\exp\left(-\frac{t}{T_2}\right)}$$

$$\boxed{\frac{S}{N} \propto N_0 \frac{1}{T} B_0^{3/2} \gamma_{ecc} \gamma_{oss}^{3/2} T_2^* \sqrt{n}}$$

Contribuiscono a S/N

- N_0 il numero di spin per unità di volume (abbondanza isotopica, concentrazione)
- T^{-1} l'inverso della temperatura
- $B_0^{3/2}$ il campo magnetico strumentale
- γ_{exc} rapporto magnetogirico del nucleo che viene eccitato
- $\gamma_{obs}^{3/2}$ rapporto magnetogirico del nucleo che viene osservato
- T_2^* tempo di rilassamento trasversale effettivo
- $n^{1/2}$ radice quadrata del numero di accumuli

Il segnale aumenta proporzionalmente al numero degli accumuli, n, mentre il noise, essendo assolutamente random aumenta con

$$\sqrt{n}$$

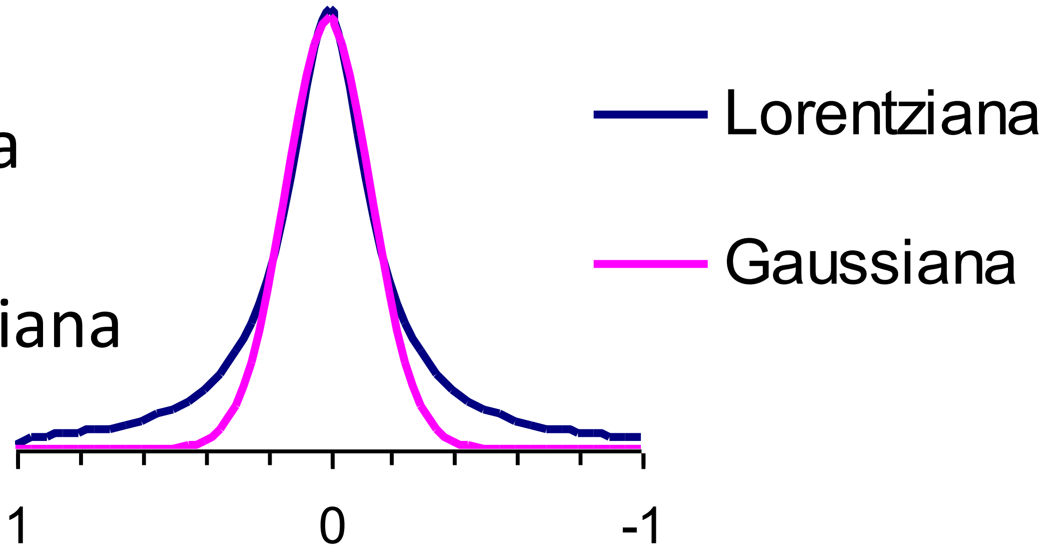
NB per raddoppiare il S/N bisogna quadruplicare n

Filtri matematici (finestre)

- E’ molto raro che uno spettro ottenuto dalla FT di un FID soddisfi tutti i requisiti di un’ottima presentazione
- Nella maggior parte dei casi si sottopone i dati ad una procedura di filtro per migliorare l’aspetto dello spettro
- Molto spesso in pratica questo corrisponde a moltiplicare il FID nel dominio dei tempi per una funzione del tempo.
- La spettroscopia in trasformata di Fourier permette tutte queste manipolazioni

Gli scopi delle funzioni filtro sono molteplici:

1. Matched filtering per massimizzare la sensibilità, cioè il rapporto S/N
2. Aumento della risoluzione diminuendo artificialmente la larghezza di riga delle risonanze
3. Trasformazione della forma della riga da Lorentziana a Gaussiana



4. Apodizzazione del FID per sopprimere le oscillazioni alla base del segnale nello spettro in funzione della frequenza: oscillazioni di Gibbs

di solito si usa un’esponenziale che decade, anche una Hamming window

Nel contesto della spettroscopia NMR in trasformata di Fourier i filtri matematici sono spesso chiamati finestre