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Tema -4

Data Acquisition

Data acquisition parameters: "the key"

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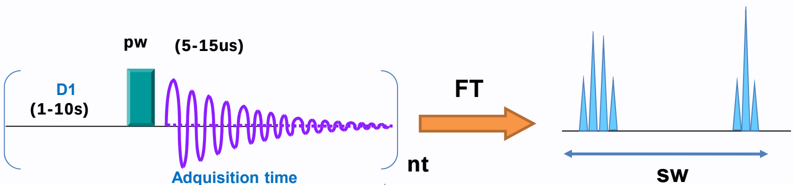
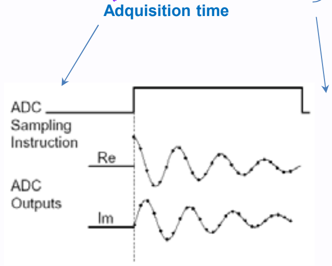
Basic 1D NMR sequence





- Sampling: ADC
- Folding
- Acquisition Time: Digital resolution
- Quadrature detection
- Truncation
- Zero filling
- Dynamic Range
- ADC Overflow
- Transients

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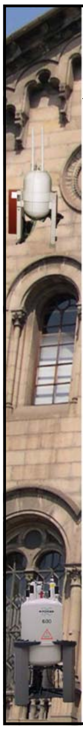

Signal detección

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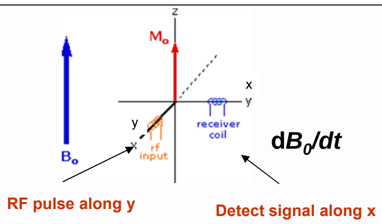
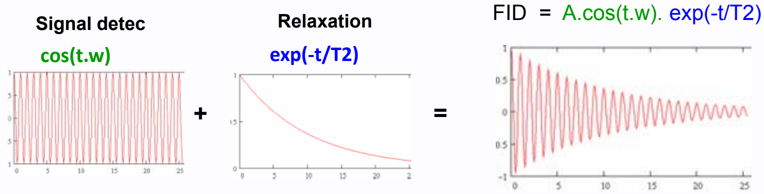


Free Induction Decay

FID = A.cos(t.w). exp(-t/T2)



The magnetization does not precess infinitely in the transverse plane but returns back to the equilibrium state by a process called *relaxation.* Two different time-constants describe this behavior:

T_2 Transverse relaxation (spin-spin)
T_1 Longitudinal (spin-lattice)

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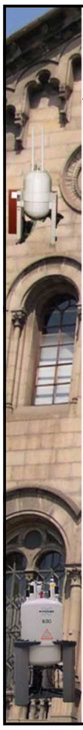

Sampling the NMR (Audio) Signal

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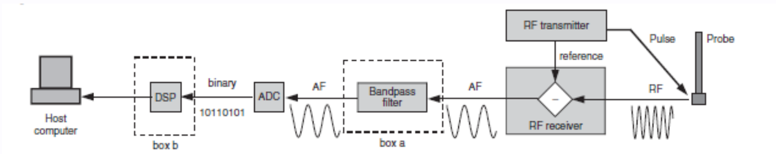
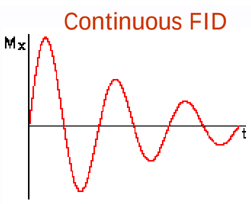
Collect *Digital* data by periodically sampling signal voltage

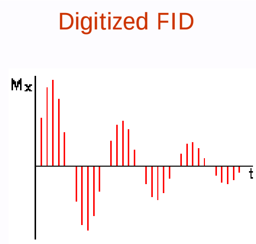
ADC – analog to digital converter





$Mx(t)=M_0\ sen(w_o t)\ e^{(-t/T_2)}$ Detec in x axis

$My(t)=-M_0\ cos(w_o t\ )\ e^{(-t/T_2)}$ Detec in y axis



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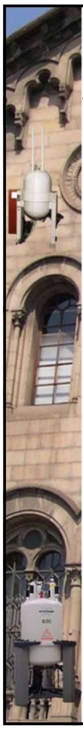

Sampling the NMR (Audio) Signal

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To correctly represent Cos/Sin wave, need to collect data at least twice as fast as the signal frequency

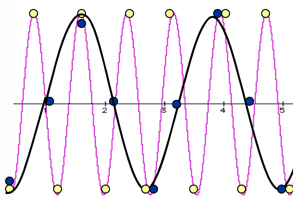
The ***Nyquist Theorem*** says that we have to sample at least twice as fast as the fastest (higher frequency) signal.

DW=SR = 1 / (2 * SW)

If sampling is too slow, get folded or aliased peaks

Sample Rate

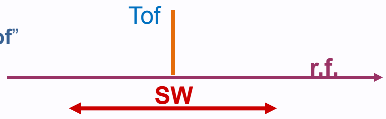
- ○ - Correct rate, correct frequency
- ● Wrong phase! -½ correct rate, ½ correct frequency Folded peaks!



SR – sampling rate
SW – sweep width
DW – Dwell Time

DW= $\frac{1}{2*SW}$

Carrier Offset or **Transmitter Offset** or "**tof**" is the frequency of the irradiating field. It is also the "**Reference**" or "**Rotating Frame**" frequency



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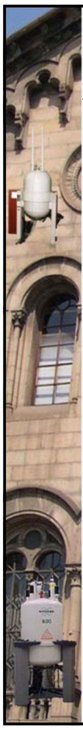

Folding : Incorrect Sampling

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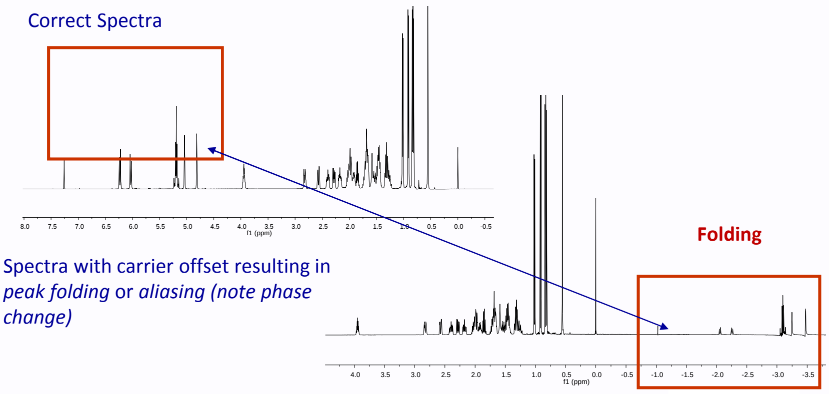
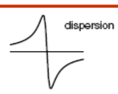
If SW is too small or sampling rate is too slow, than peaks are folded or aliased
The solvent selected is not right or the spectral window is small

Correct Spectra



Spectra with carrier offset resulting in *peak folding* or *aliasing (note phase change)*

The phase of folded peaks can vary: positive, negative phase or dispersive
The intensity of the folded signals can be attenuated



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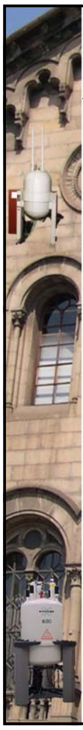

Acquisition times and digital resolution

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If Maximum Frequency to be sampled is f_{max} = SW

We must sample at a rate no less than $\frac{2 * SW}{sec.}$

Digital Resolution

The amount of memory limit the accuracy of the signal to be recorded

For a given **# of memory** (**# Points -> TD (time domain)**), one obtain:

$\frac{NP}{2}$ (*real*) & $\frac{NP}{2}$ (*Imaginary*)

Digital Resolution = **D.R.** = **Df** (Separation between 2 points)

$$D.R. = \frac{2 * SW}{NP}$$

Acquisition Time => AQ or AT

$$AQ = NP * rate^{-1} = \frac{NP}{2*SW}$$

D.R. = **1** / **AQ** = 2 * **SW** / **TD**

To collect a well digitized spectrum is necessary use a long Acquisition time

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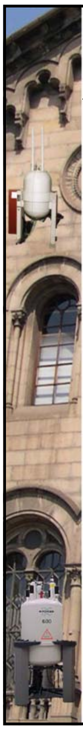

Example

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At 200 MHz If: { **SW=2000 Hz (10 ppm)**, **TD = 16,000 points (16K)** }

What is the **Digital Resolution**:

D.R. = 2***SW**/**TD** = 4000 / **16,000** = 1 / 4 = **0.25 Hz**

What is the **Acquisition Time AQ**:

AQ = **TD** * **DW** = **TD** / (2 * **SW**) = **4 seconds**

D.R. = 1 / **AQ** = 2 * **SW** / **TD**

If the acquisition times used are very large, the "noise" is introduced in the spectrum

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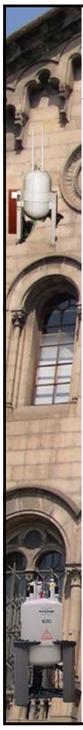

Acquisition time

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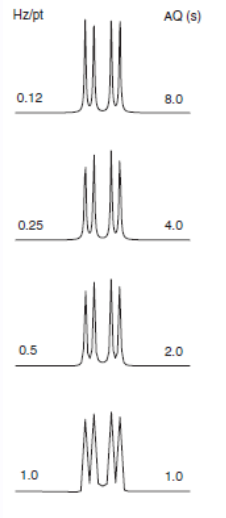
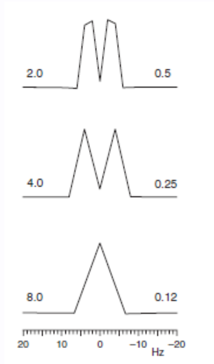
Good digital resolution



Poor digital resolution



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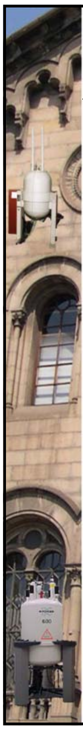

Quadrature detección

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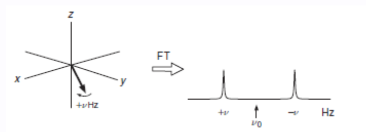
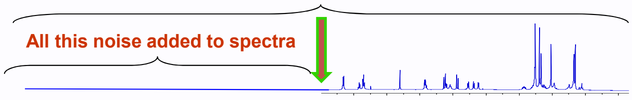
If NMR signal is detected on a single axis (*x or y), the* Fourier Transform cannot distinguish between signals that are larger than or smaller than the reference frequency by the same amount

A magnetization vector moving to vHz produce two resonances with same frequency but opposite *direction*



- to differentiate the two possibilities the carrier must be placed at edge at the end of the spectrum, then peaks are all positive or negative relative to carrier



Is necessary use PW more short pulse (more power) add more Noise that causes a reduction in SN

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Quadrature detección

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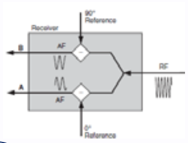
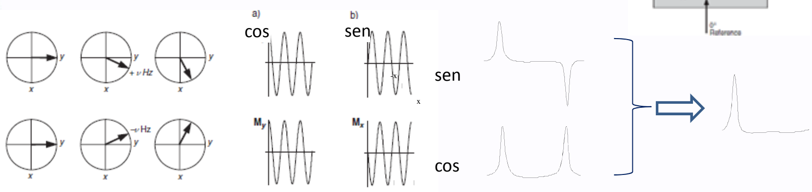
- Quadrature detection permits discrimination between positive and negative signals (below)
- Use two detectors 90º out phase





- Quadrature detection permits a smaller SW, improved digital resolution and, an increase in S/N of $2^{1/2}$

Two ways for quadrature detection

Simultaneous sampling

$$DW = \frac{1}{SW} \qquad AQ = DW\frac{TD}{2} = \frac{TD}{2SW}$$

$$DR = \frac{SW}{SI} = \frac{2SW}{TD} \qquad DR = \frac{1}{AQ}$$

Sequential sampling

$$DW = \frac{1}{2\,SW} \qquad AQ = DW * TD = \frac{TD}{2SW}$$

$$DR = \frac{SW}{SI} = \frac{2SW}{TD} \qquad DR = \frac{1}{AQ}$$

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Truncation error

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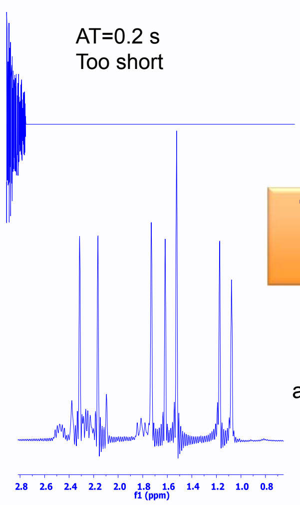
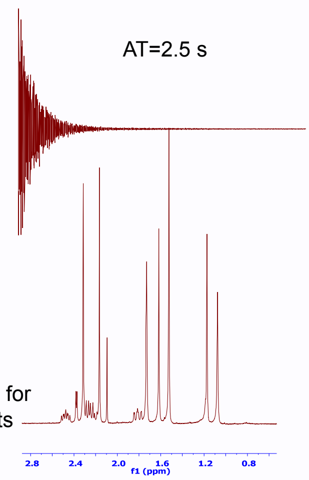
The data set is truncated: when the FID has not decay to zero at the end of acquisition time

The truncation of the FID produces a symmetrical ringing at the base of the peaks



Truncated FID with spectra "wiggles"



Use a decaying apodization function for remove this effects

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Zero filling

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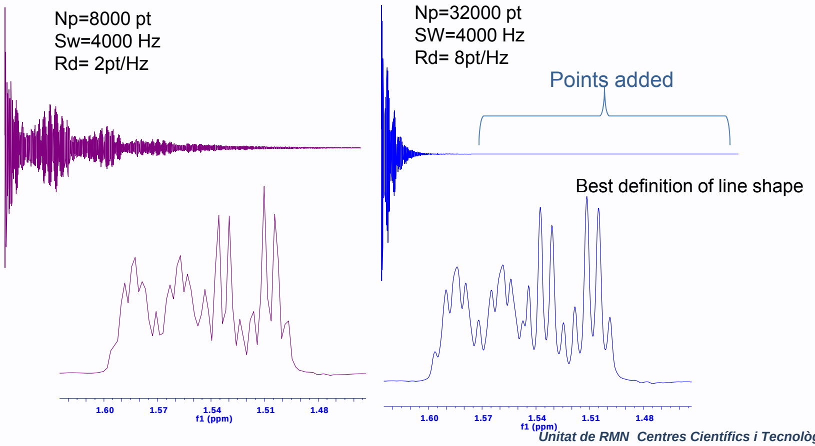
Addition of points (zero val) at the end of the fid

Provide the FID has fallen to zero, when the acquisition stops, is possible artificially improve the resolution by append zeros in to the end FID.
Usually doubling number of data points (increase de Digital Resolution)



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Dynamic Range

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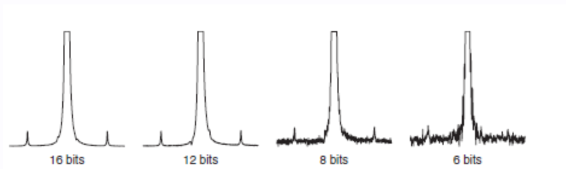
The capability of ADC converter limits the frequency range to observe and also the amplitudes of signals that can be measured

The ADC can be operated at 14 or 16 bits

- The 16 bits ADC is able to represent values in the range 32.767 (or 2^{15}-1)
- The ratio between the largest and smaller signals is 32.767:1



Digitiser resolution

Reduction of dynamical range limits the observation smaller signals when the thermal noise is low.

When used H2O/10% D2O 90% the high intensity of water signal may be to prevent the observation of signals of product: It is necessary to use some solvent suppression techniques

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Dynamic Range II

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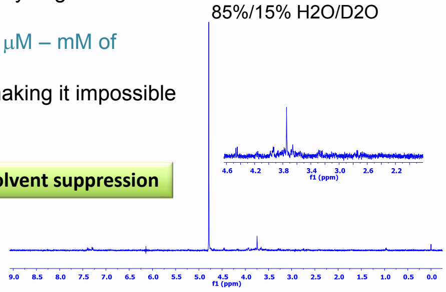
Solvent suppression

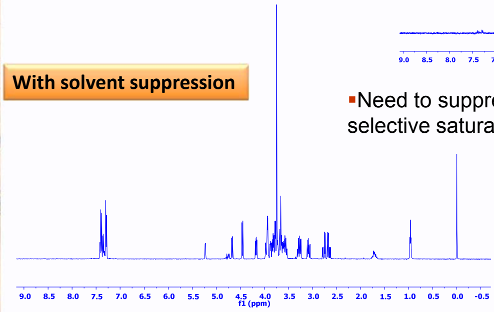
- The solvent concentration is significantly larger than the sample concentration
  - water is 55M compared to typical µM – mM of compound
- strong solvent signal can fill digitizer making it impossible to observe the sample signal

Aspartam sweetener
85%/15% H_2O/D_2O



Without solvent suppression

With solvent suppression



- Need to suppress intense solvent signals with selective saturation pulse

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ADC Overflow

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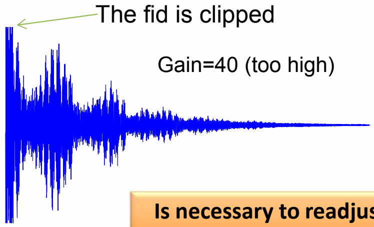
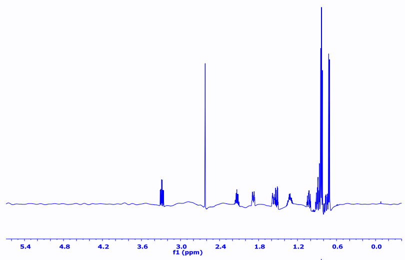
If a signal is too large to fit on the largest possible value of ADC record, the result is the emergence of a distortion in the spectra

The fid is clipped

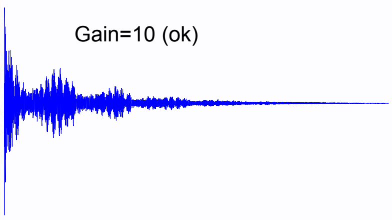
Gain=40 (too high)

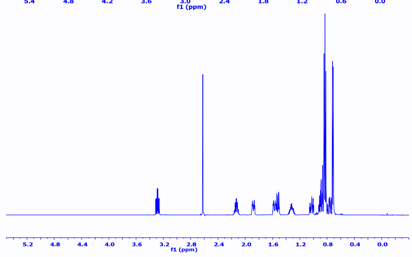




Is necessary to readjust the gain value

Gain=10 (ok)





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Ernst angle

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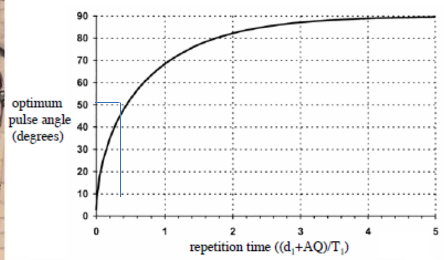
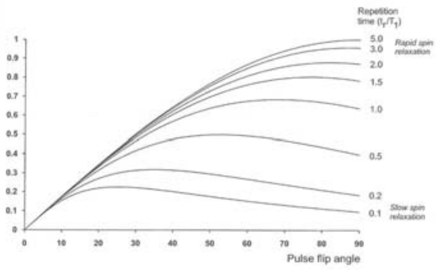
The highest signal-to-noise is achieved in a 1D by waiting less time between scans but using something less than a 90º pulse according to the Ernst equation:

$$\cos(\alpha_e) = e^{-tr/T1}$$



For medium-size molecules in proton T1 ≈2-8s

For an repetition rate equal to 3.5 s and T1 Max=6s α_e ≈50º



Dependence of signal-noise ratio on pulse angle for different repetition rates. The maximun for each curve corresponds to the Ernst angle . Use the maximun value T1 for

Which spectrometer Should I use for ^{13}C

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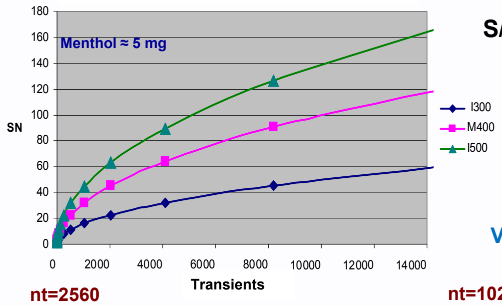


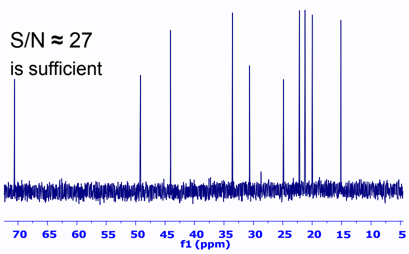
$$S/N \propto (N\,A\,T^{-1}\,T^{*}_{2})\,\gamma_e \sqrt{\gamma^{3}_{d}\,B_0^{3}}$$

$$S/N_x = S/N_i\sqrt{nt_x}$$

VNMRS-500 ≈ 1.5mg/ml Menthol

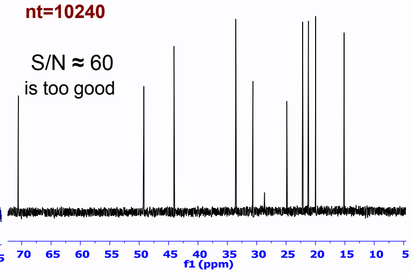
nt=2560

S/N ≈ 27
is sufficient



nt=10240

S/N ≈ 60
is too good



^{13}C Spectra

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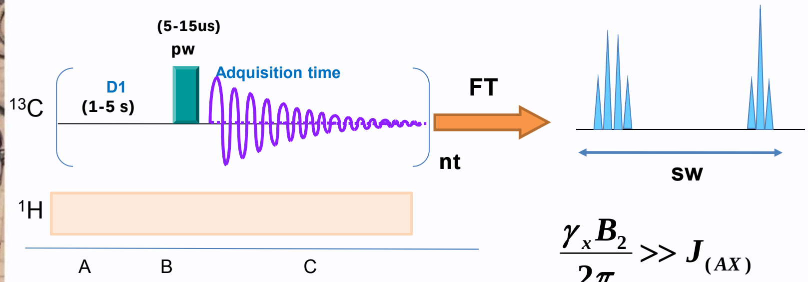
Heteronuclear Decoupling



$$\frac{\gamma_x B_2}{2\pi} >> J_{(AX)}$$

Full Decoupled and Full NOE

Apply a second strong radiofrequency field (B_2)

For a decoupled ^{13}C spectra, pulse is at ^{1}H frequency

^{1}H nuclei continually precess about B_2 → M_z averages to zero!

If M_z =0, coupling vanishes and ^{13}C resonances reduce to singlet

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^{13}C NMR spectra

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^{13}C Spectra are acquired with 1H decoupling

All signals are singlets → Increase the sensitivity, spectra are less complicated

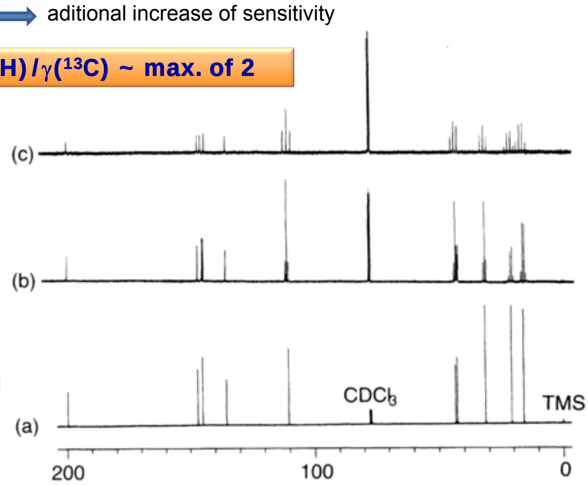
NOE 1H-13C → aditional increase of sensitivity

$1 + \eta = 1 + 1/2 \cdot \gamma(^1H)/\gamma(^{13}C)$ ~ max. of 2

Decoupler off

Off Resonnace

Completely 1H decoupled (WALTZ)



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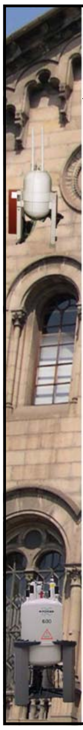

Required information before to programming the NMR experiments

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- Chemical characteristics of the analyt
  - Molecular weight
  - Functional groups
- Sample available in the active volume (mass and solubility)
- Is a mixture or a single compound
- Is necessary obtained information about;
- Check the reaction, Identification, Structure determination,
  - Qualitative
  - Quantitative

Select: spectrometer, experiment and parameters

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