## Kazan Federal University

### Introduction to the course:

# *«High resolution nuclear magnetic resonans (NMR) of crude oil and petrochemical synthesis products”*

**Research laboratory «NMR-structure»**

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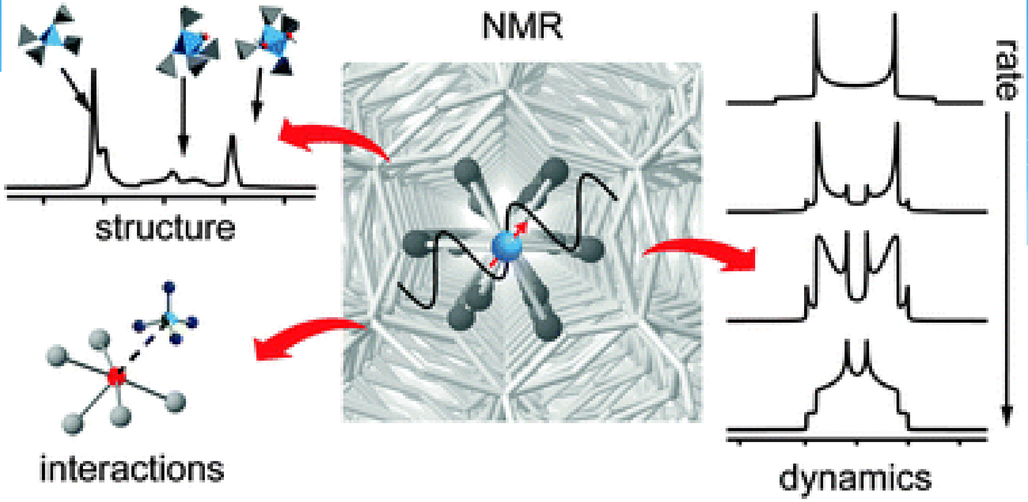
# Outline

* History of NMR
* Physical basics of high-resolution NMR spectroscopy
* The main parameters of NMR spectra
* Analysis of quality and quantity composition of oil samples

# Application field of NMR spectroscopy




* Identification of the chemical composition of the organic and bioorganic compounds in various phases
* Study of the spatial structure, conformational properties and intramolecular mobility of compounds in various solvents
* Study of the spatial structure of compounds in solid phase

# History of NMR

Isador Rabi (1938):

detected NMR absorption in a molecular beam

Nobel Prize in Physics in 1944

Felix Bloch (1945):

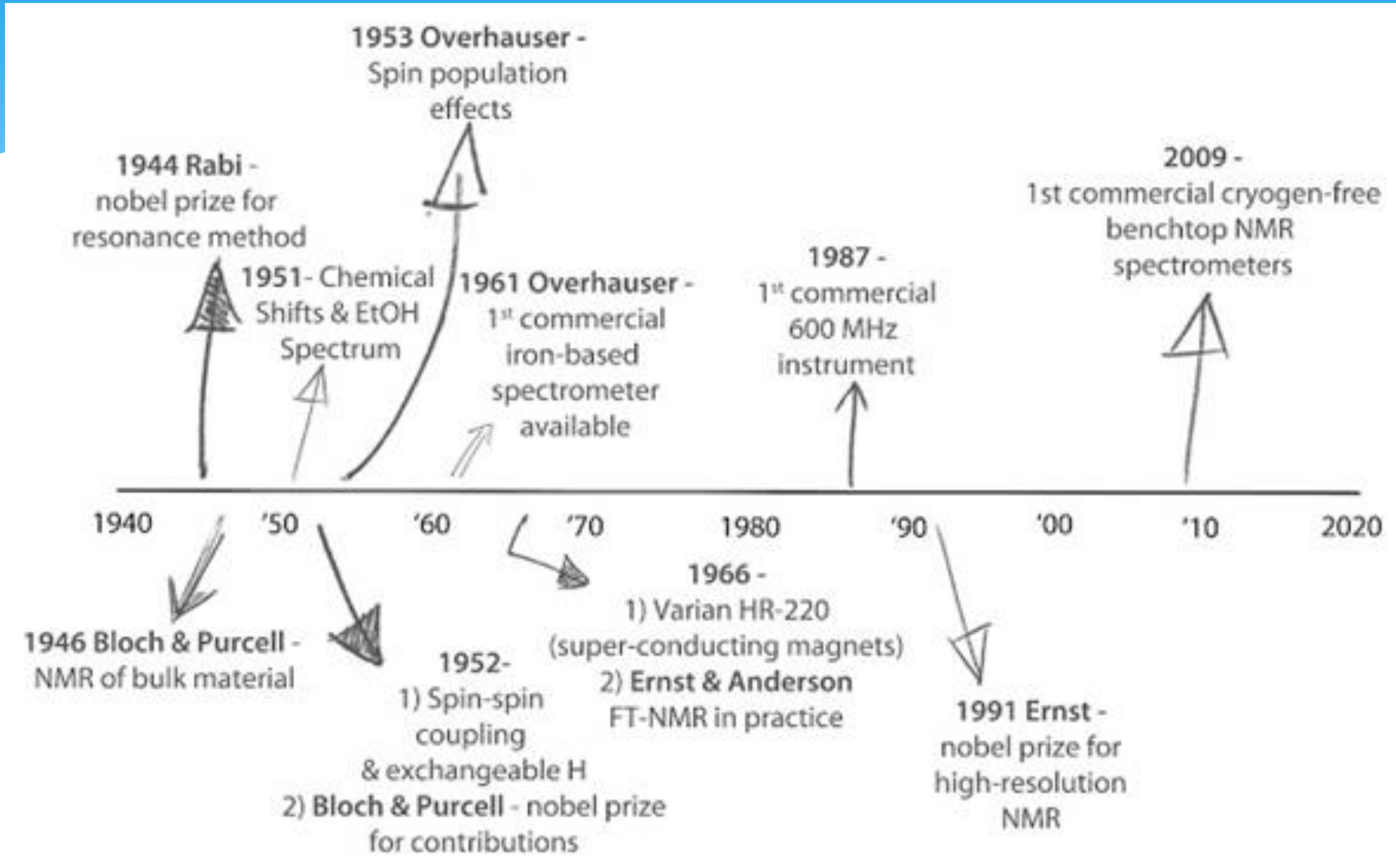
detected nuclear induction signal in water

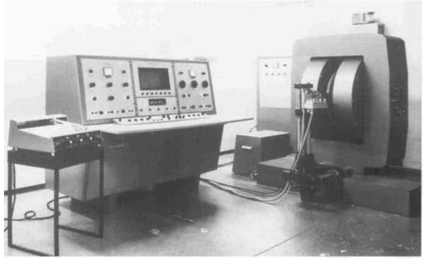
Edward Purcell (1945):

detected NMR absorption in paraffin

Nobel Prize in Physics in 1952

# Development of NMR spectroscopy

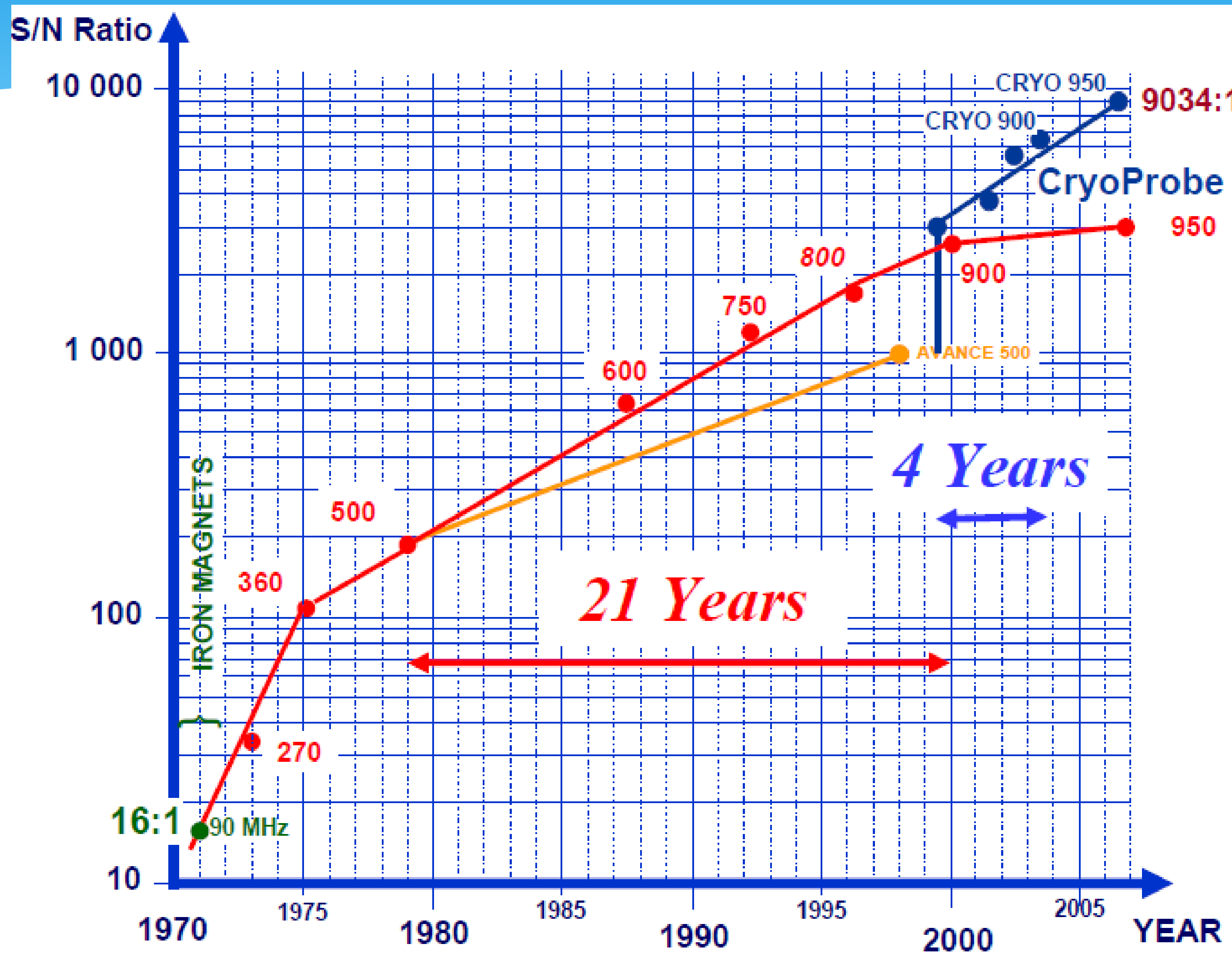


"Bruker" – 60 MHz; Germany, 1967


"Varian" – 900 MHz; USA, 2009

# Growth of sensitivity of NMR spectrometers



# Basics of NMR

Nuclei have an angular momentum L and a magnetic momentum μ

$$\vec{L} = \hbar\sqrt{I(I+1)}$$
$$\vec{\mu} = \gamma\hbar I$$

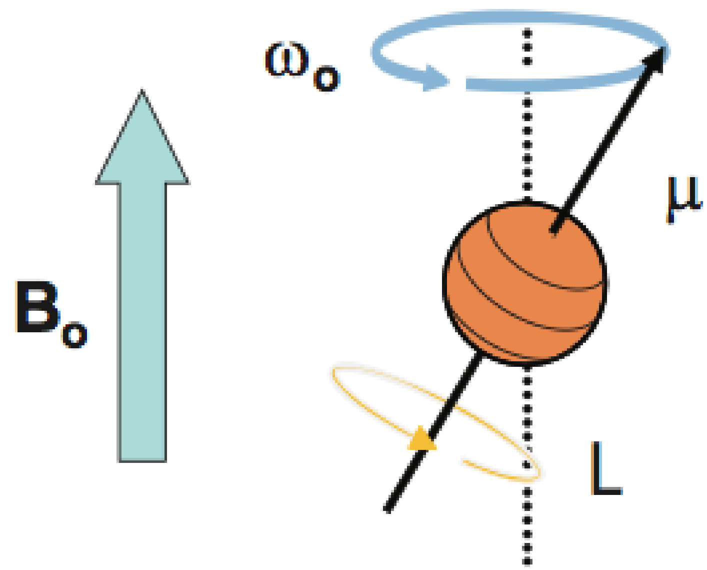
In magnetic field $B_o$ the nuclear will precess around the field direction

with frequency: $\omega_o = \gamma * B_o$

I – nuclear spin

γ - gyromagnetic ratio

$\hbar = \frac{h}{2\pi}$ - reduced Plank's constant



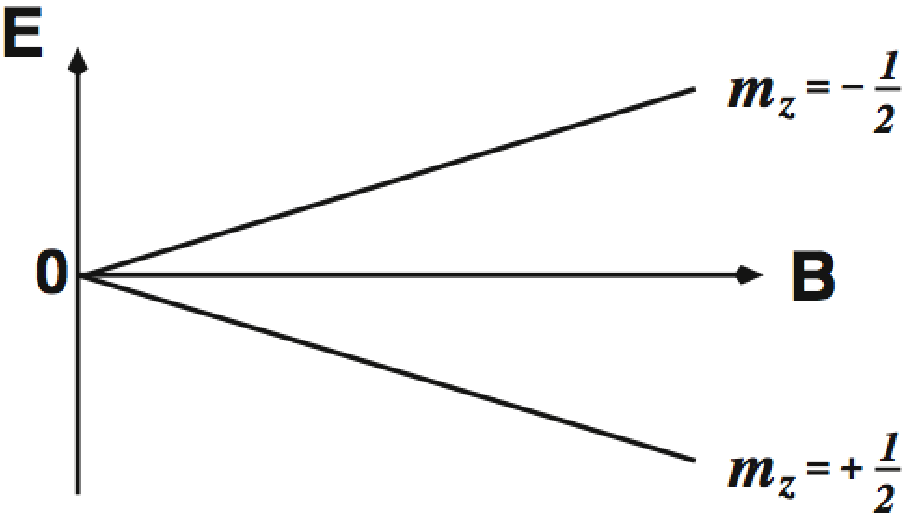
# Basics of NMR

Nucleus in a magnetic field

has an energy $E = -\gamma\hbar B m_z$

The energy difference between the two states is:

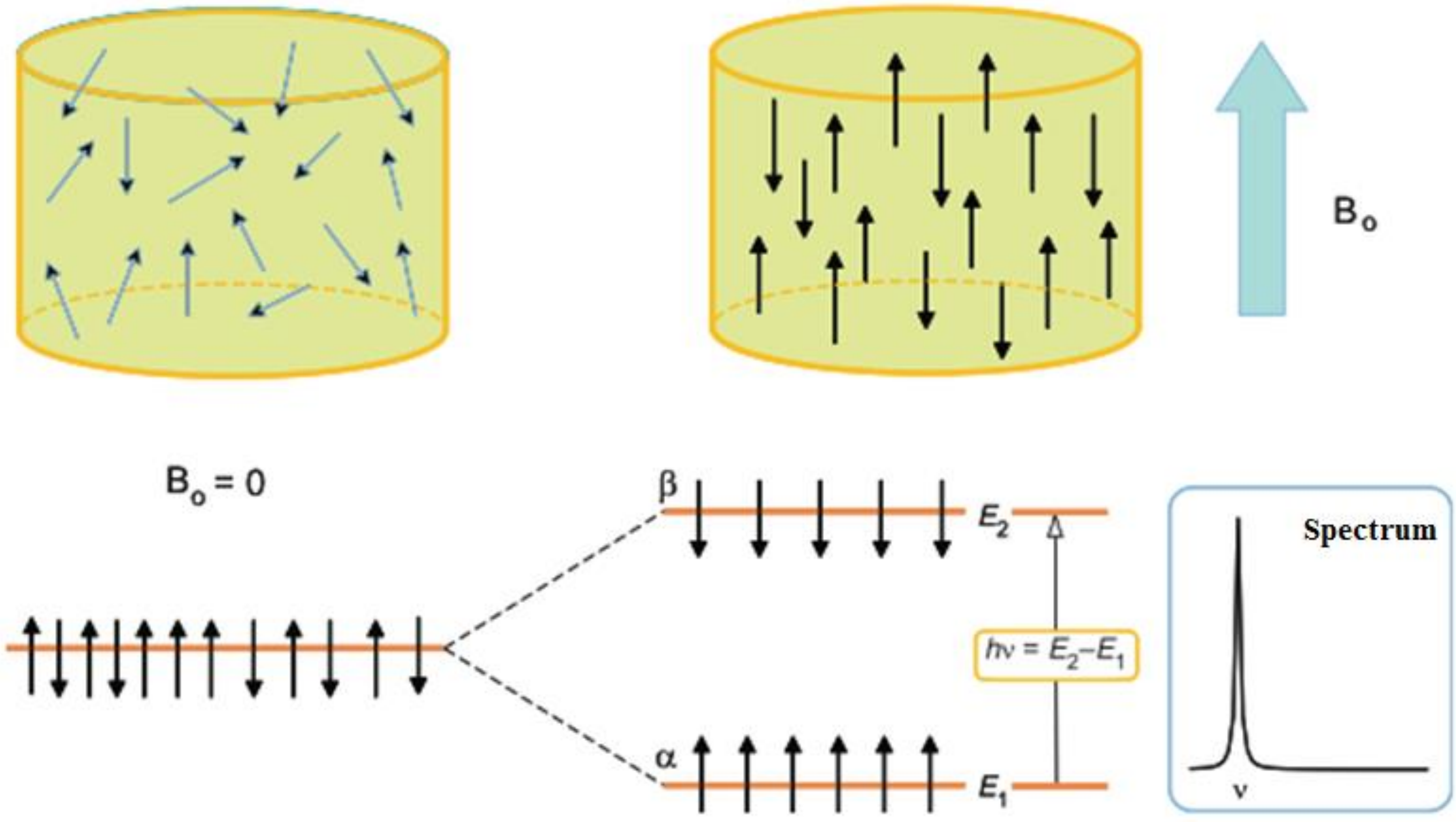
$$\Delta E = E_{-1/2} - E_{+1/2} = 2\gamma\hbar B I$$




Splitting of nuclei spin states in an external magnetic field

$m_z = -I, \ldots, +I$ - z-projection of magnetic quantum number

# Basics of NMR




if the substance is in a magnetic field it is possible to resonant absorption of electromagnetic energy!

# Basics of NMR

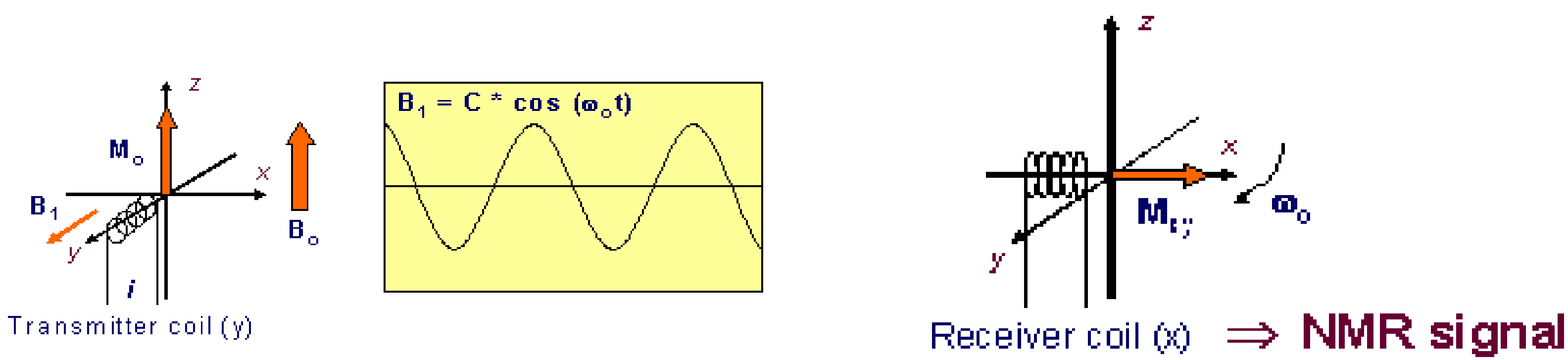
To get the NMR signal must be:

1) The nucleus with the magnetic moment

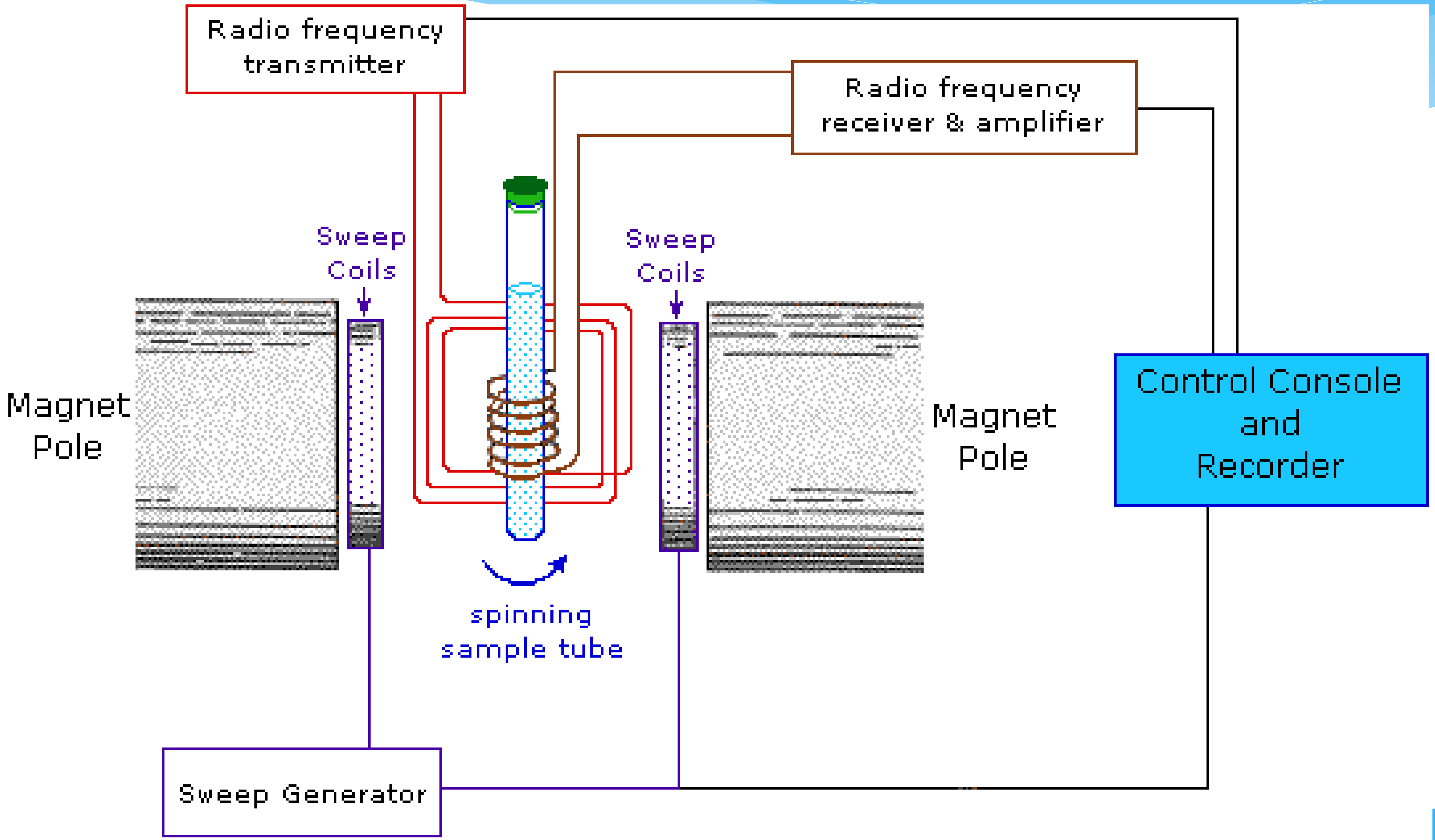
2) Magnetic field

3) Electromagnetic radiation of appropriate frequencies:

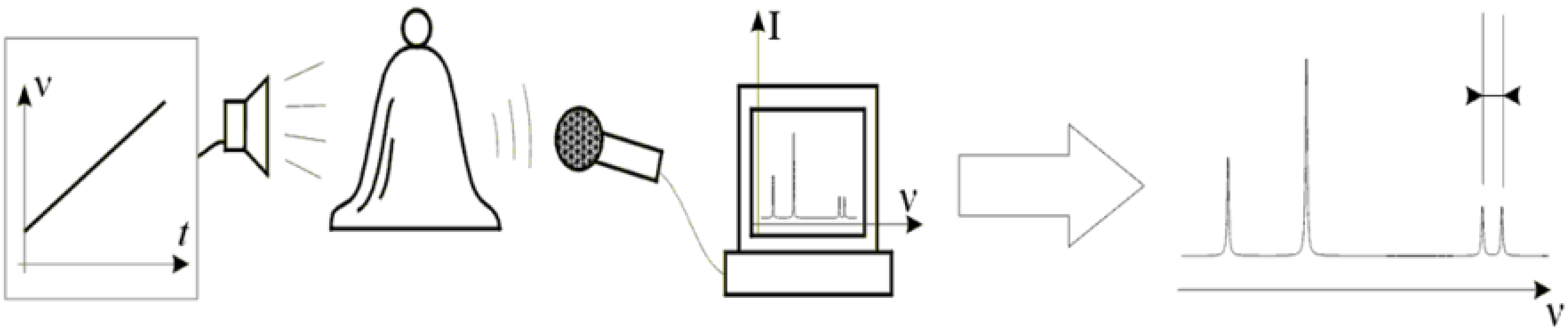
radio frequency electromagnetic waves
(from 30 MHz to 300 MHz)



# Block diagram of NMR spectrometer



# Continuous scan

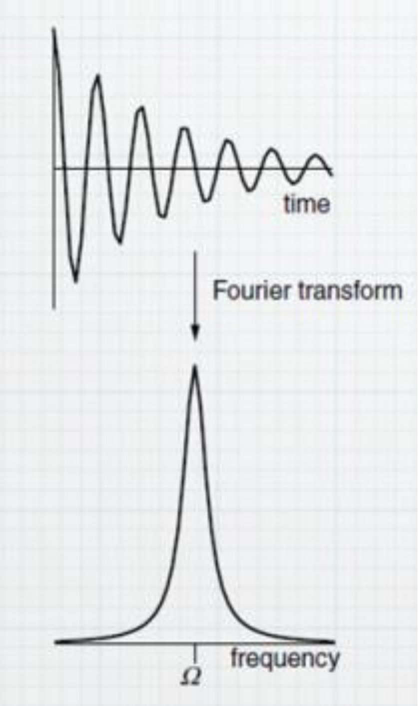


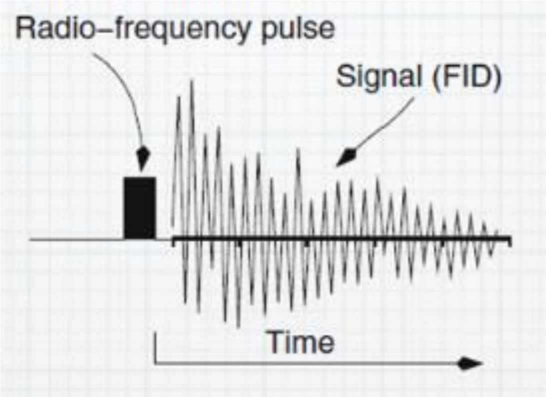

1000 Hz ~ 1000 sec

Disadvantages of spectrometers with a continuous scan:

1) Too much time for recording the spectrum
2) low sensitivity

# Principles of pulsed NMR experiment



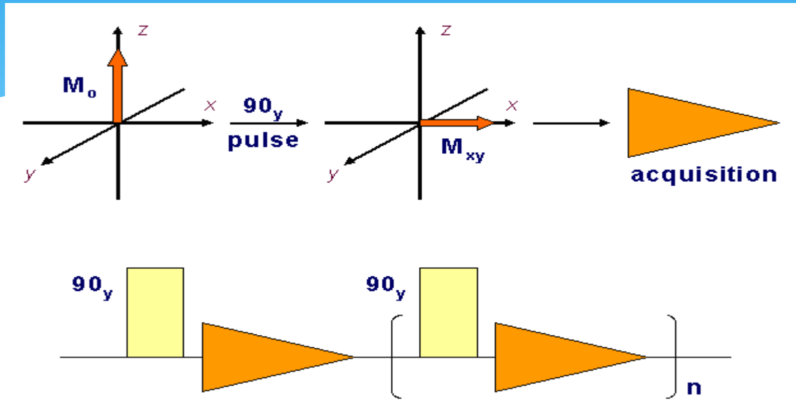

Richard Ernst

Nobel Prize in Chemistry in 1991

Pulse spectrometer:

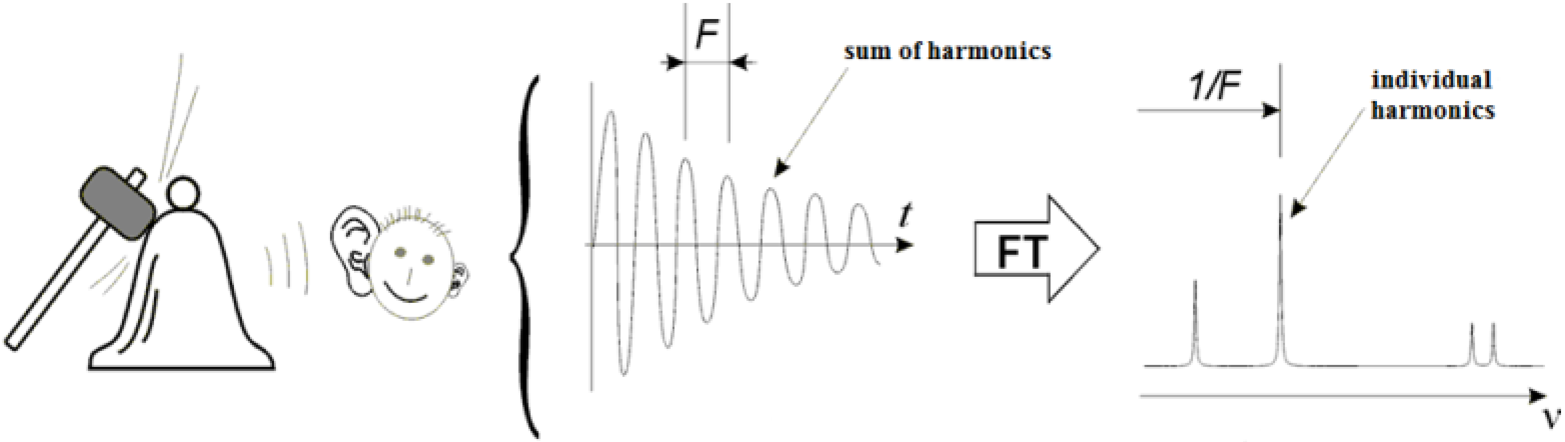
1) stimulation of system
2) check the FID (free induction decay)
3) Get spectra after Fourier transform

# Principles of pulsed NMR experiment




Fourier transform

$$S(w) = \int s(t) \exp(-iwt)\, dt$$

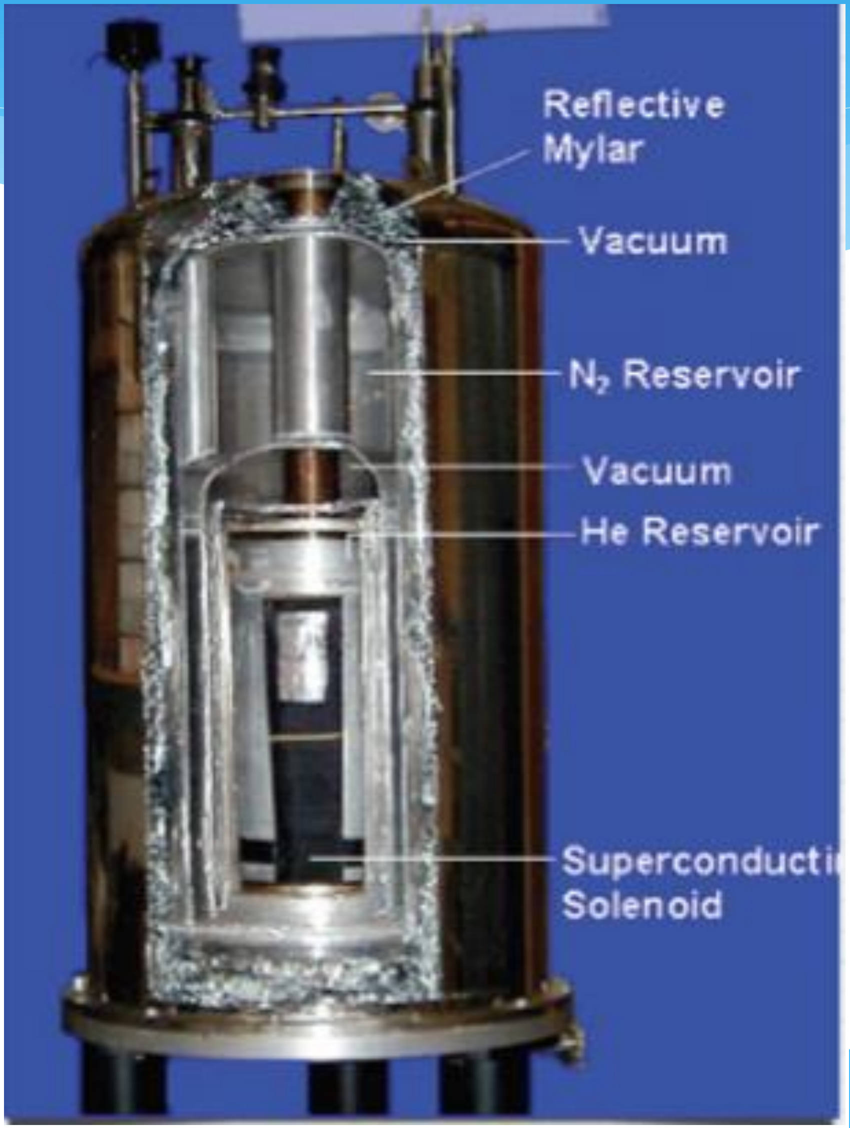



1000 Hz ~ 1 sec
to accumulation of FID

# Modern NMR spectrometer

## superconducting magnet

- It does not require a current source
- high stability of magnetic field
- it requires regular pouring of liquid helium and nitrogen
- the main parameter is the resonance frequency of $^{1}H$ nuclei
- very expensive

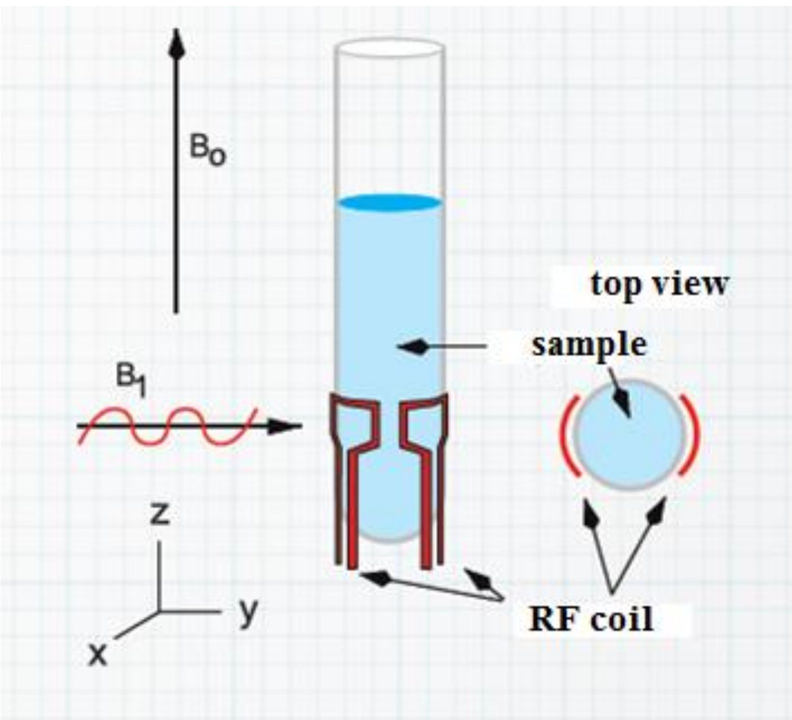


# NMR probe

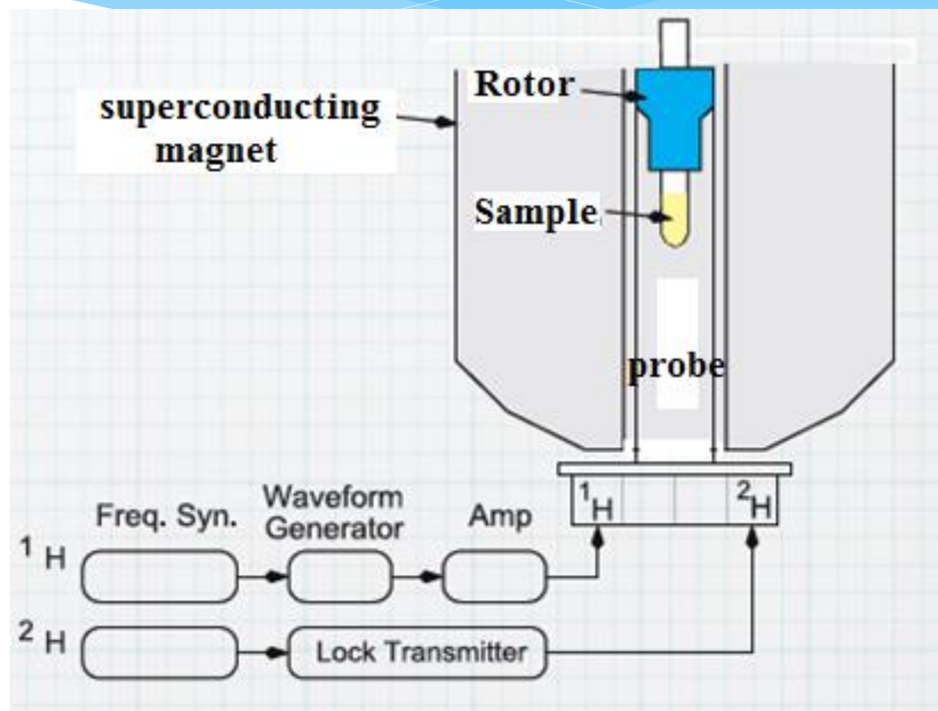
It allows to record signals from several types of nuclei

| nucleus | spin | natural content, % | NMR frequency, MHz |
|---|---|---|---|
| $^{1}H$ | 1/2 | 99,98 | 500 |
| $^{2}H$ | 1 | 0,016 | 76,77 |
| $^{12}C$ | 0 | 98,9 | - |
| $^{13}C$ | 1/2 | 1,108 | 125,75 |
| $^{15}N$ | 1/2 | 0.37 | 50.69 |
| $^{17}O$ | 5/2 | 0.037 | 67.8 |
| $^{19}F$ | 1/2 | 100 | 470.592 |
| $^{31}P$ | 1/2 | 100 | 202.45 |

# NMR probe



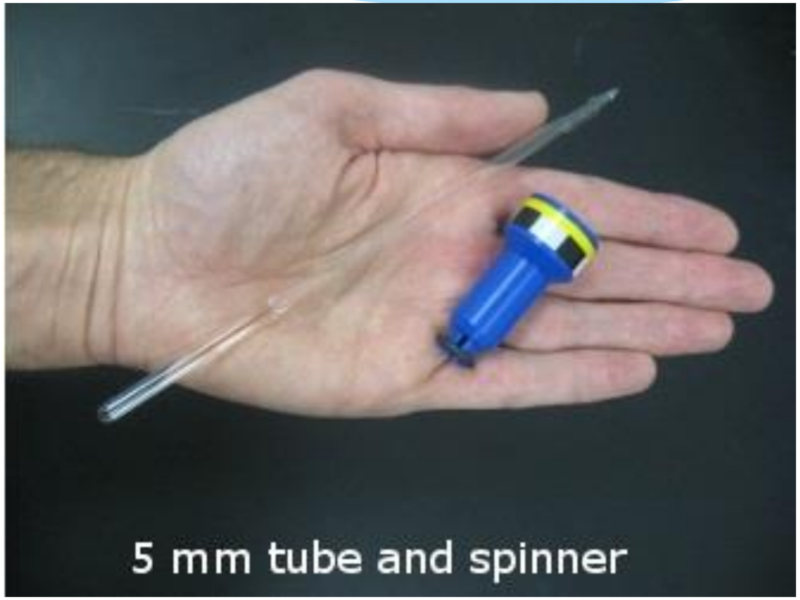
Bo
B1
top view
sample
z
y
x
RF coil

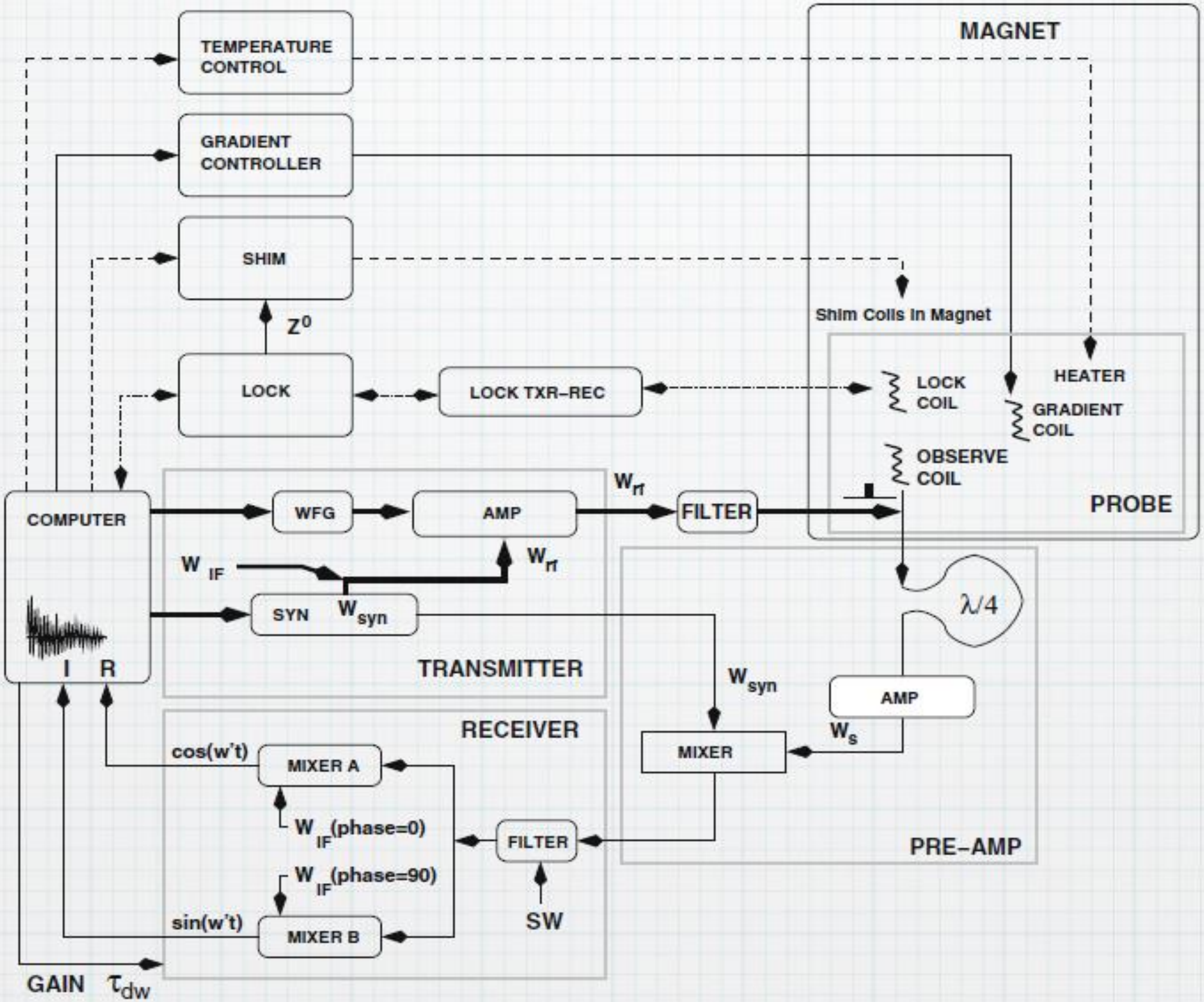
Rotor
superconducting magnet
Sample
probe
Freq. Syn.
Waveform Generator
Amp
1H
2H
Lock Transmitter

# NMR sample

- needed to use special ampoule
- needed deuterium-solvents
- volume: 0.6-0.7 ml
- concentration: 0.6-0.7 mM
- the sample must be homogeneous



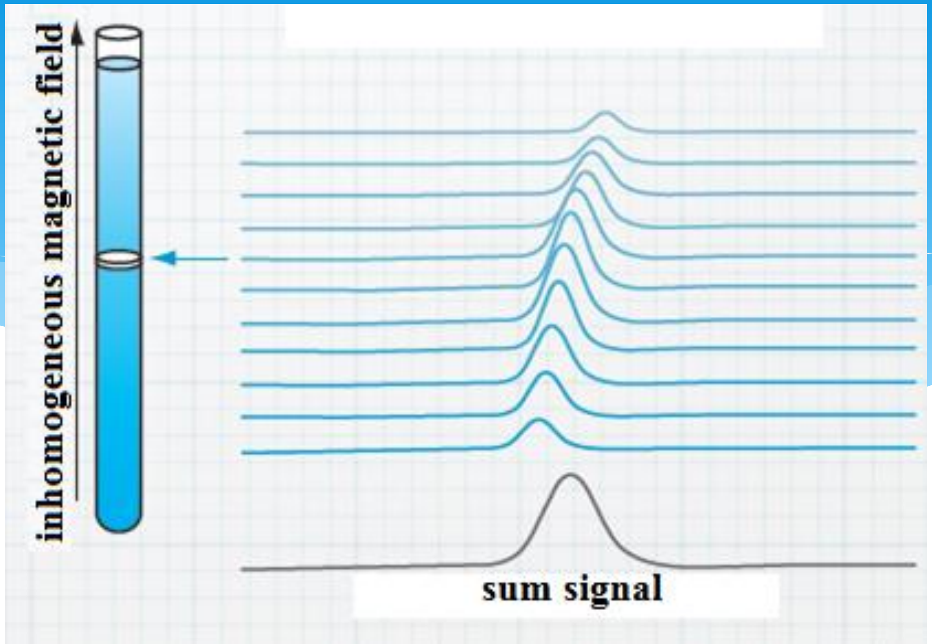
# Radio circuit of modern NMR spectrometer



# NMR laboratory

# Magnetic field homogeneity

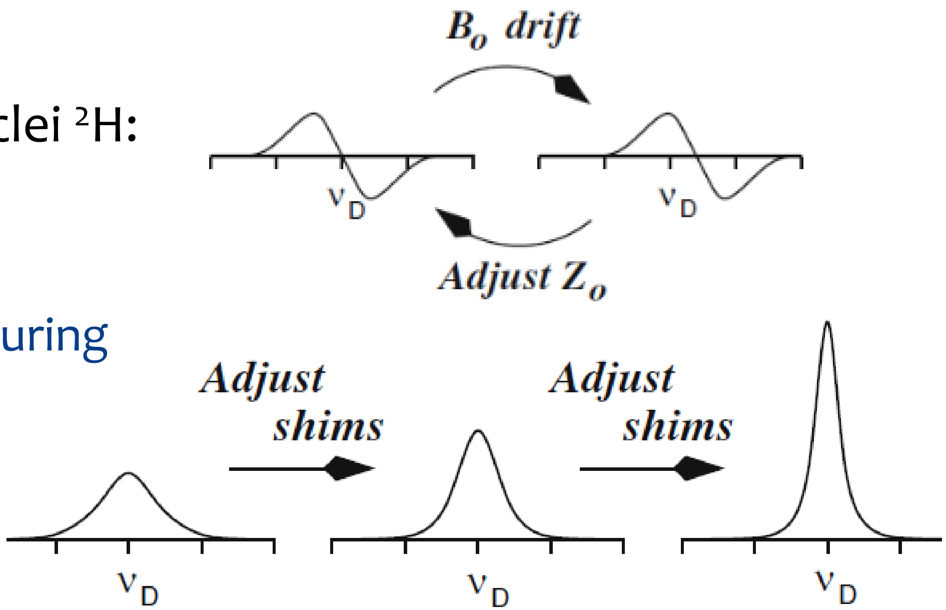
in order to obtain a line width of 0.5 Hz at 500 MHz the resonance field should be the same within $10^{-9}$




The signal from the deuterium nuclei $^2H$:

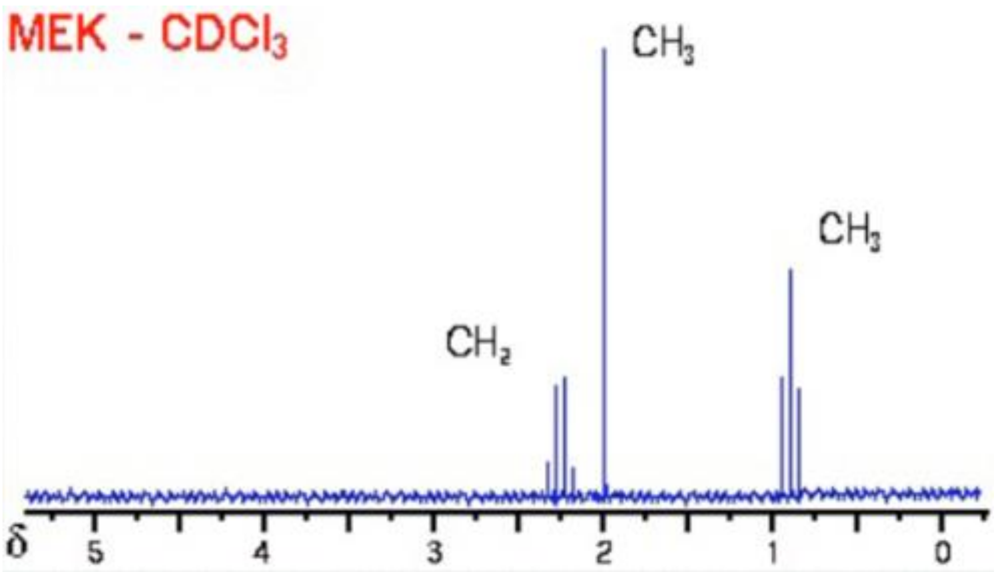
- adjusting of homogeneity

- stabilization of the magnetic field during the experiment



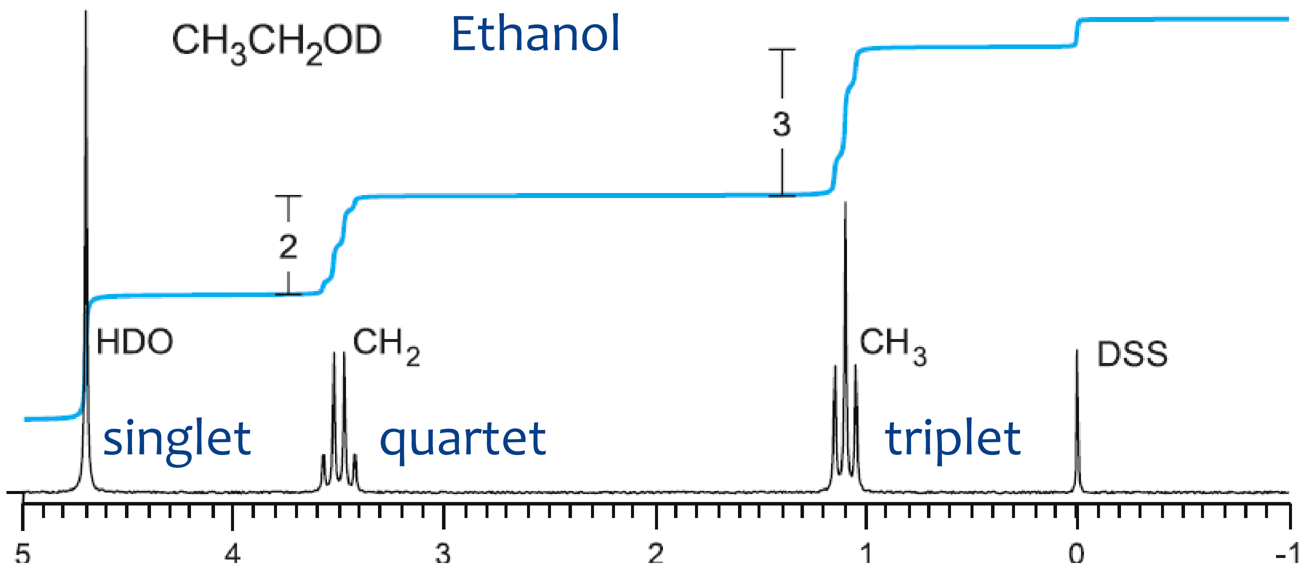
# Problem of noise in NMR spectroscopy

- especially important for rare nuclei, e. g. $^{13}C$
- Solution: multiple signal accumulation !




[Signal / noise] ration grows as $\sqrt{number\_of\_scans}$

# The main parameters of NMR spectrum

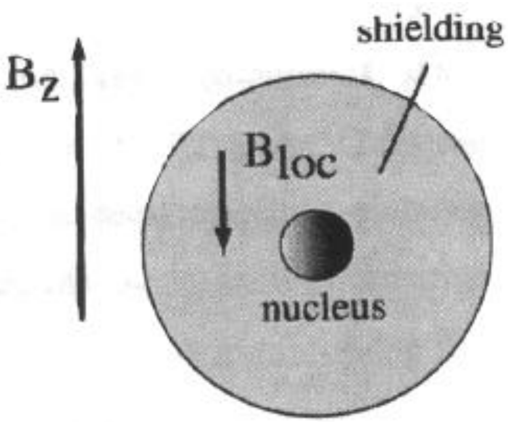



ppm – parts per million

1) Chemical shifts: position of signal (in ppm scale)
2) spin-spin interaction constants: the multiplicity of the spectrum
3) Integral intensities of signals: the area under the resonance line is proportional to the number of nuclei

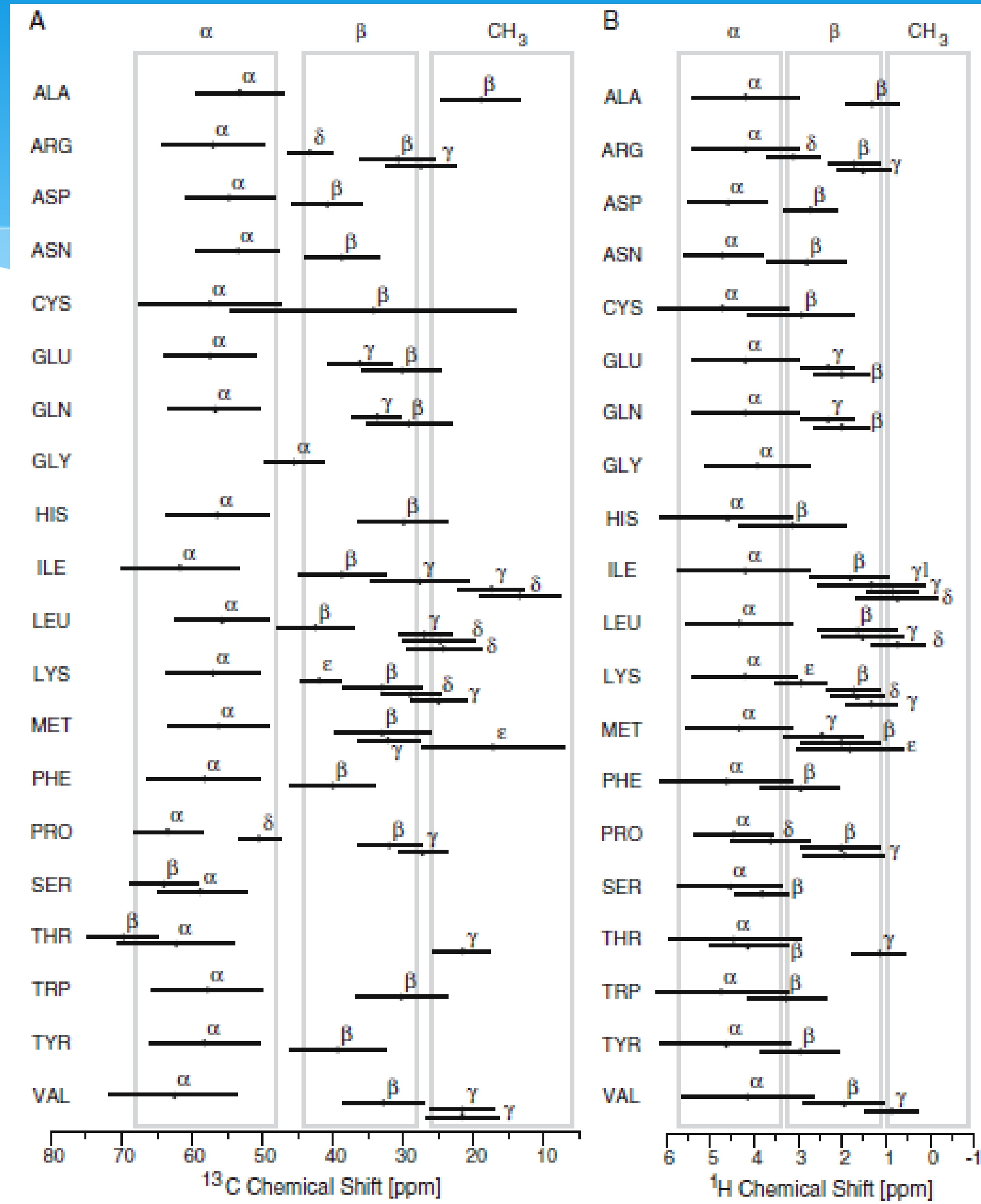
# Chemical shift

the electron cloud around the nucleus reduces the magnetic field



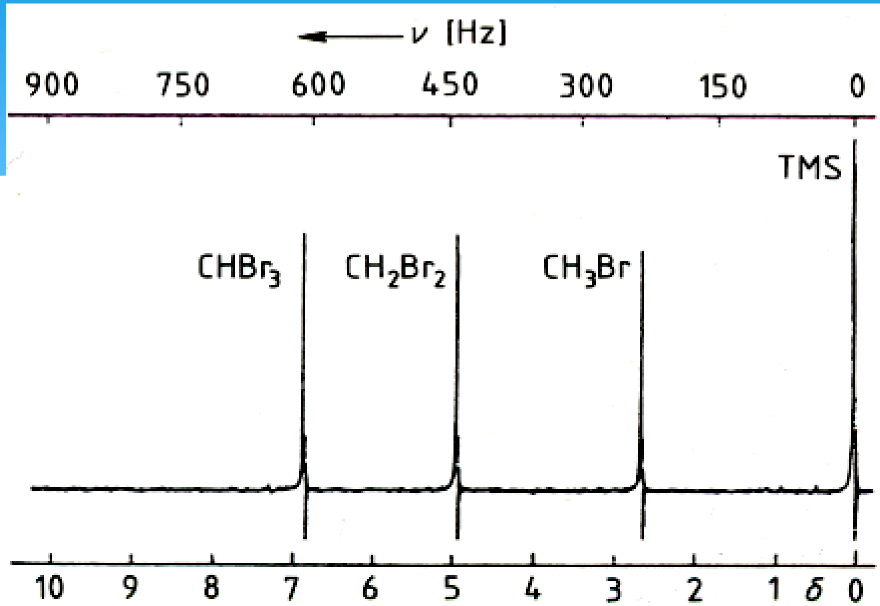

For each chemical environment there are characteristic chemical shift values !

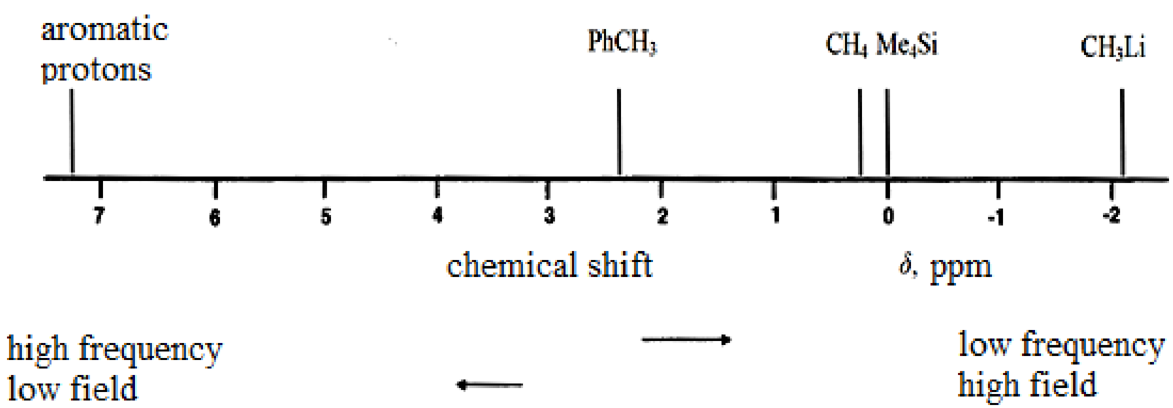
$$B_{loc} = B_0 - \sigma B_0 = (1-\sigma)B_0$$



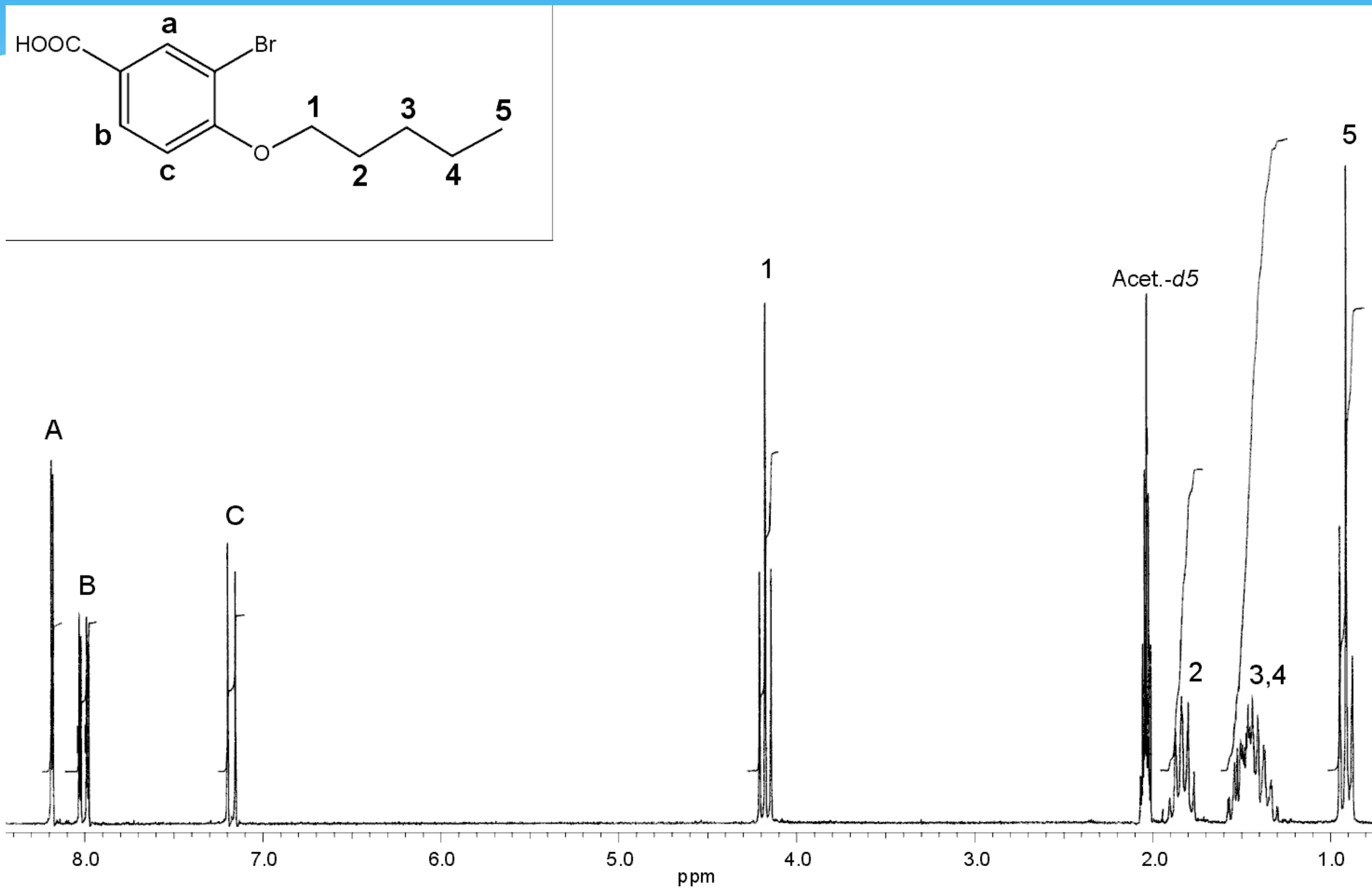

$^1H$ and $^{13}C$ chemical shifts of amino acids

# Chemical shifts (examples)

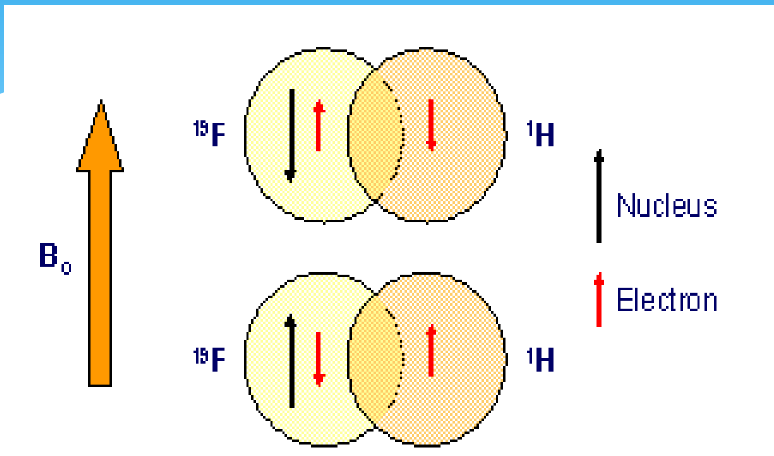


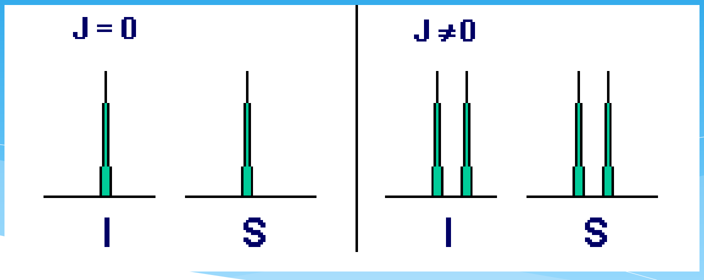
# Chemical shifts (examples)

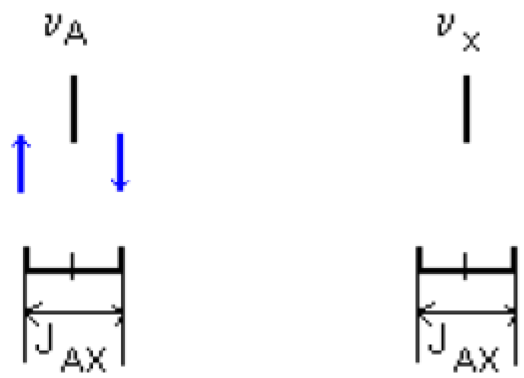


# Spin-spin interaction constants



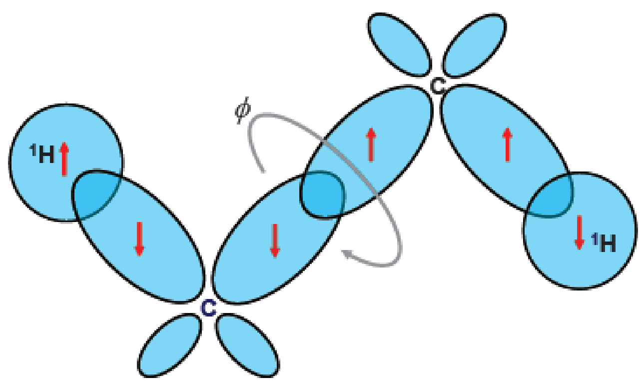

Nuclear interaction scheme throught electronic bonds in HF molecule

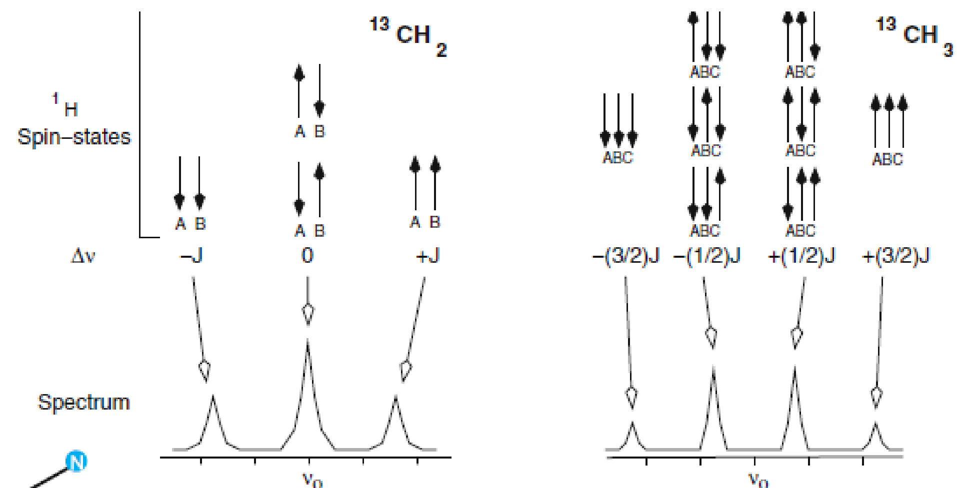


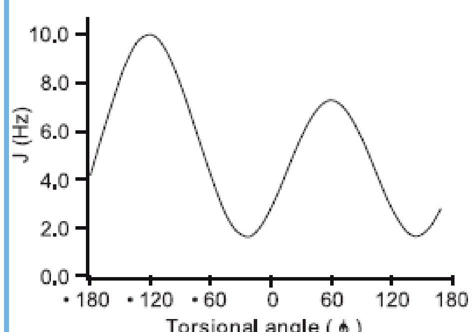



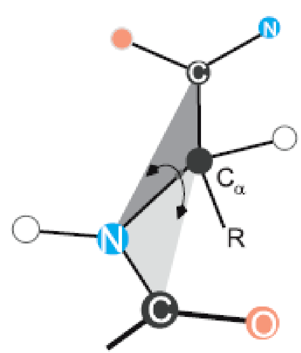

| | $J_{HH}$, Hz | Sign | $J_{CH}$, Гц | Sign | $J_{CC}$, Hz | Sign |
|---|---|---|---|---|---|---|
| $^{1}J$ | 276 | + | 125-250 | + | 30-80 | + |
| $^{2}J$ | 0-30 | - | -10 +20 | +/- | < 20 | +/- |
| $^{3}J$ | 0-18 | + | 1-10 | + | 0-5 | + |
| $^{3+n}J$ | 0-7 | +/- | < 1 | +/- | < 1 | +/- |

# Spin-spin interaction constants



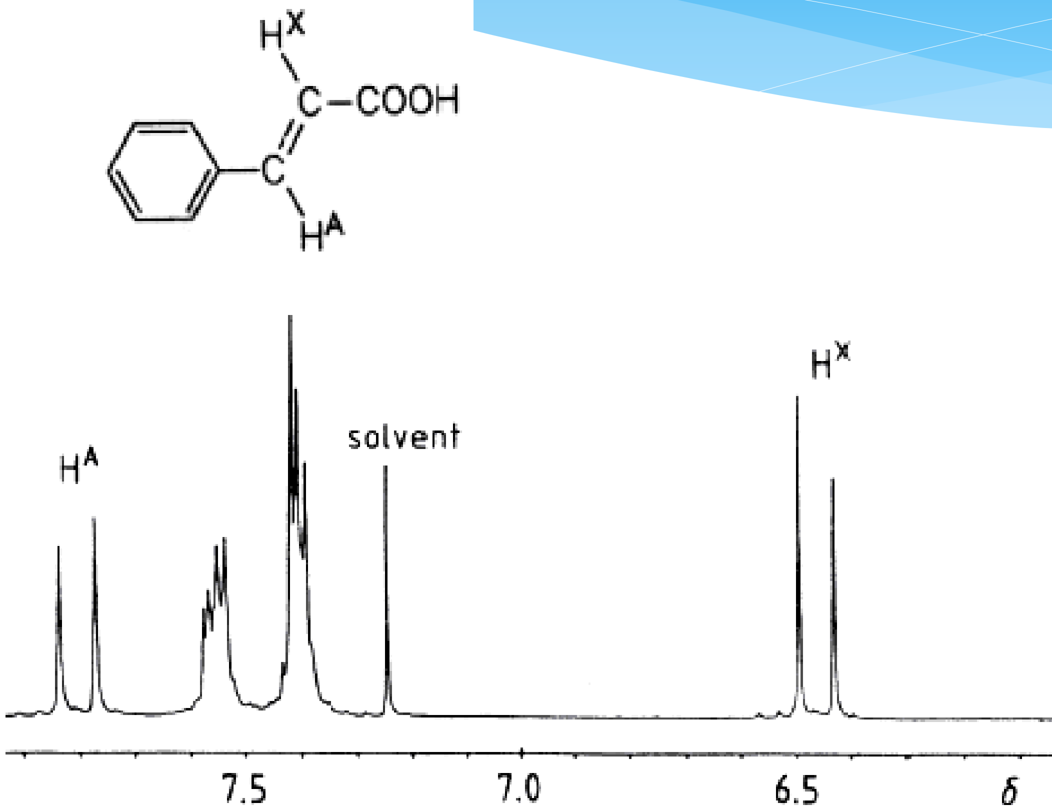



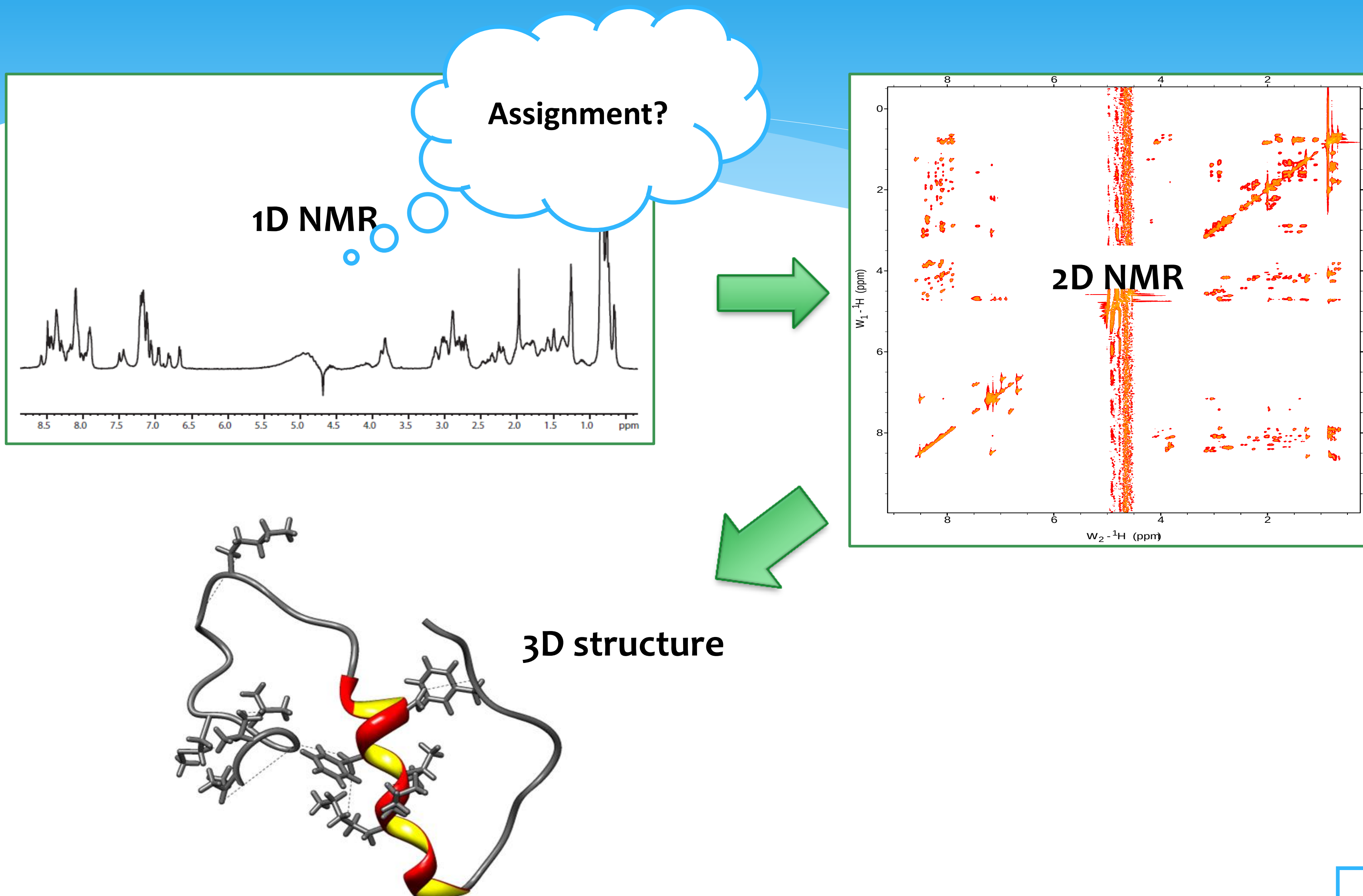




Interaction throught chemical bonds are stereospecific !

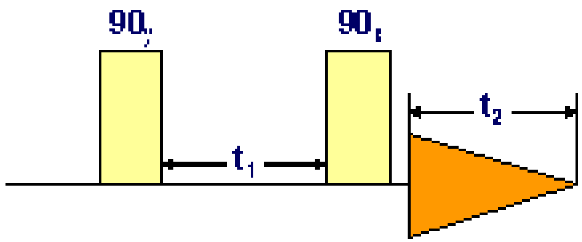
# Spin-spin interaction constants (examples)

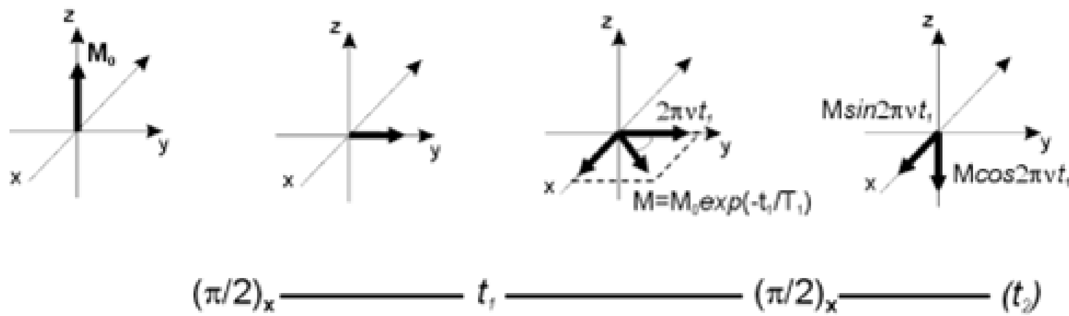


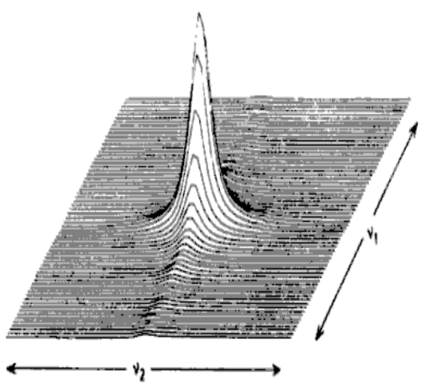
# NMR spectroscopy of complex compounds

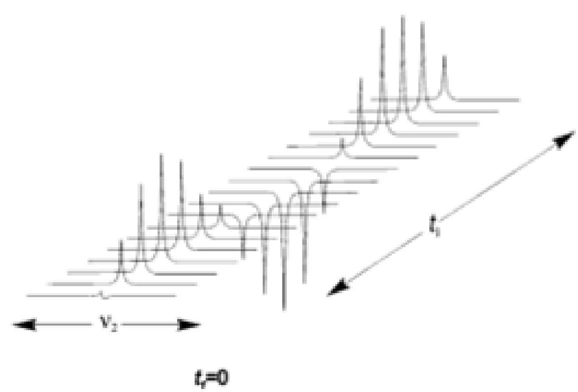


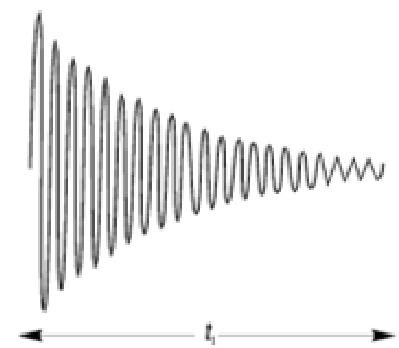
# 2D correlation NMR experiment: COSY



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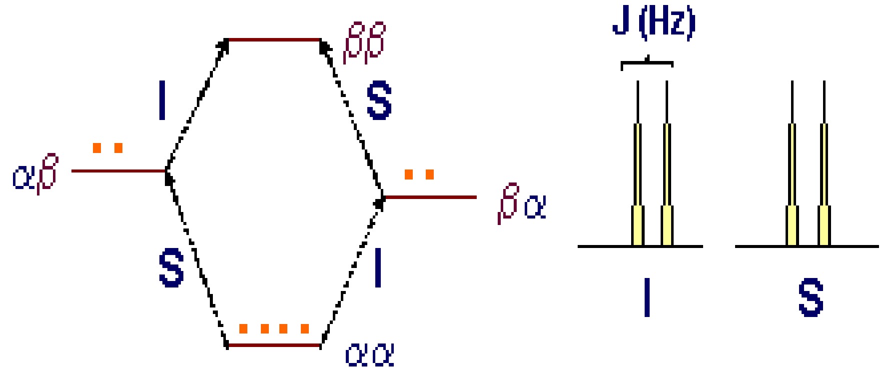


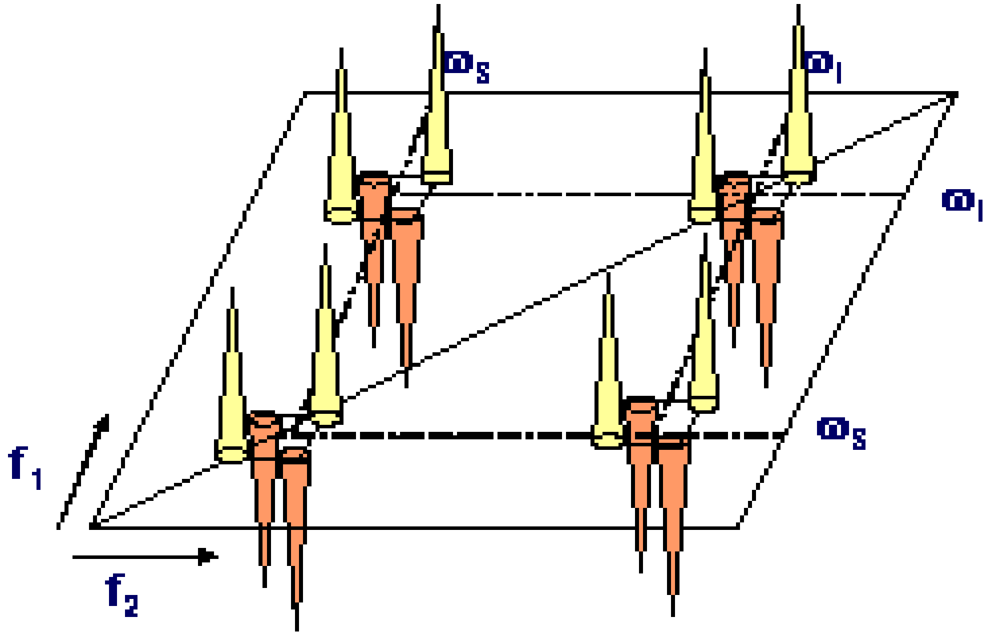

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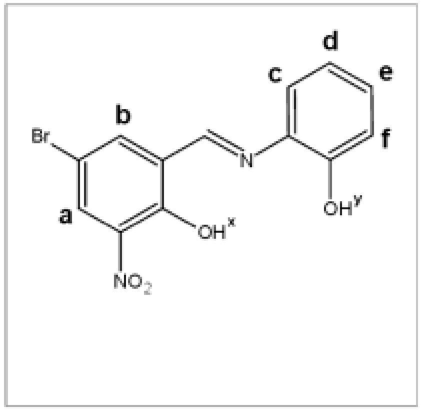
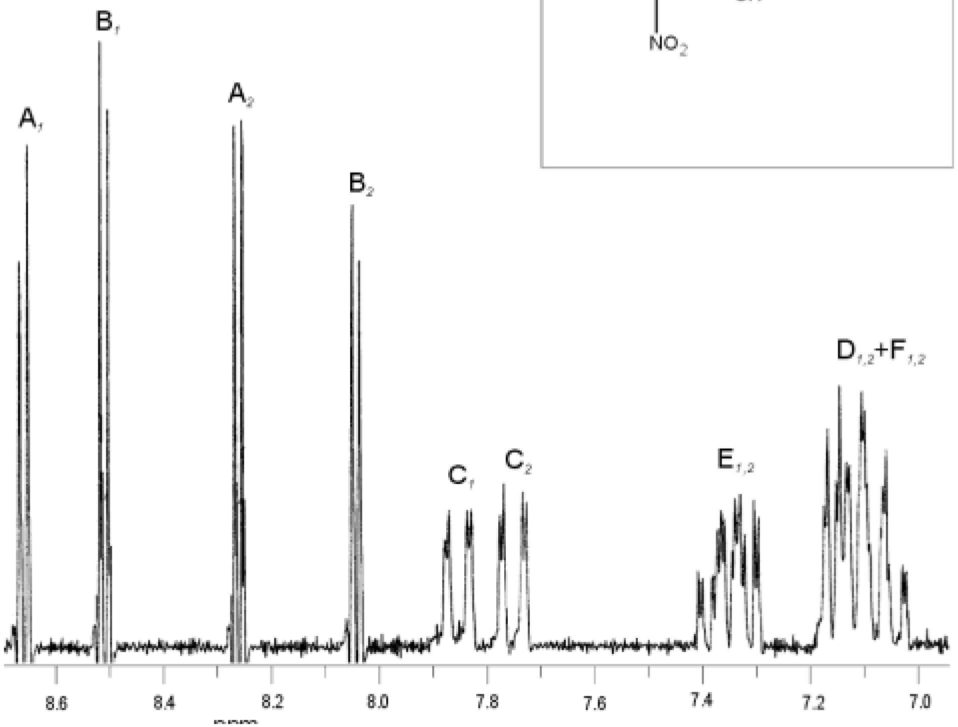
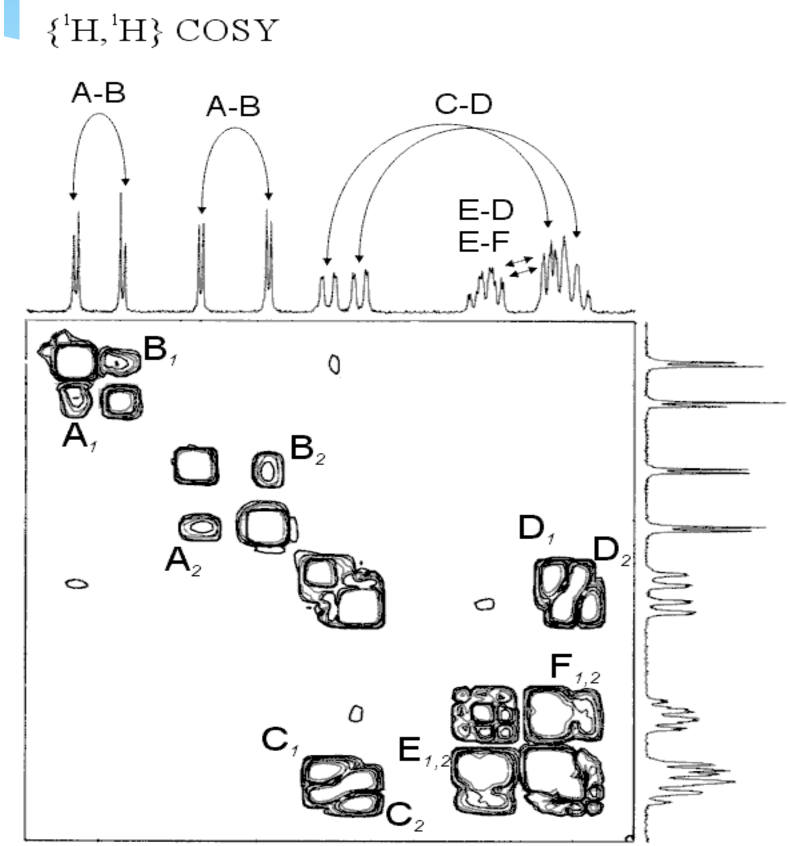


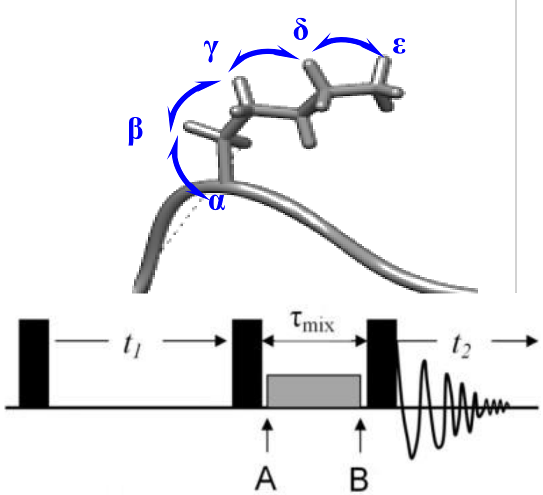



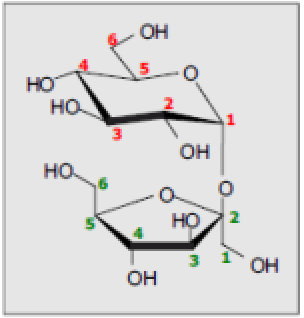
# 2D correlation NMR experiment: TOCSY

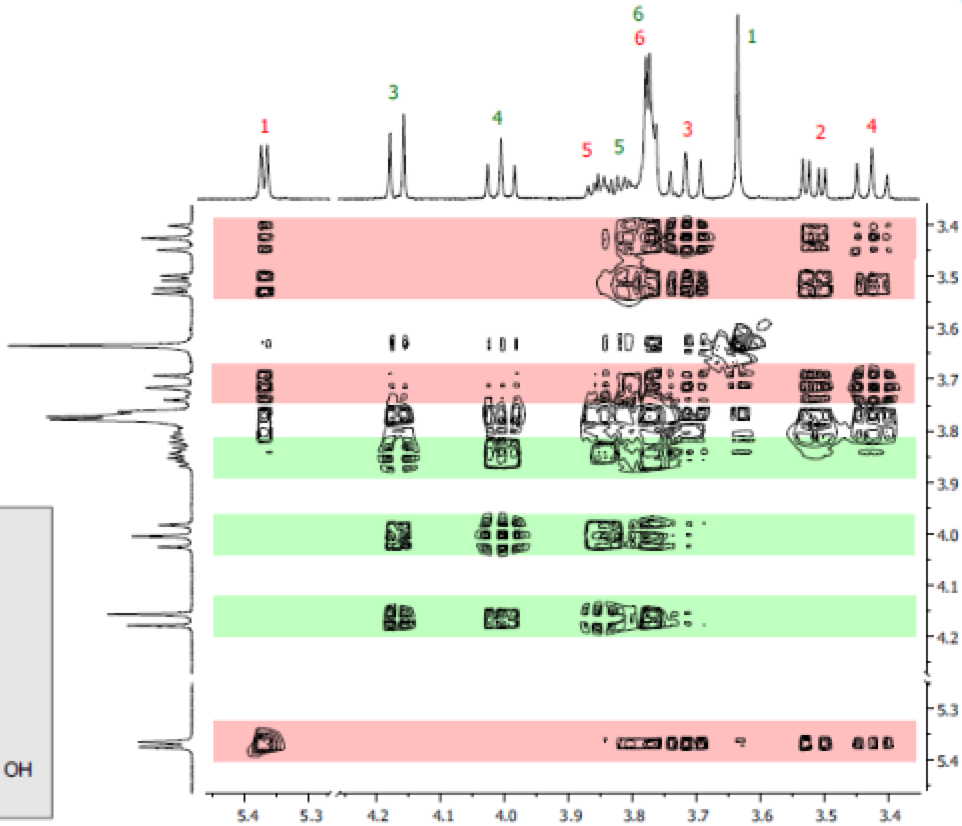
## $^1$H-$^1$H TOCSY

***(Total correlation spectroscopy)***



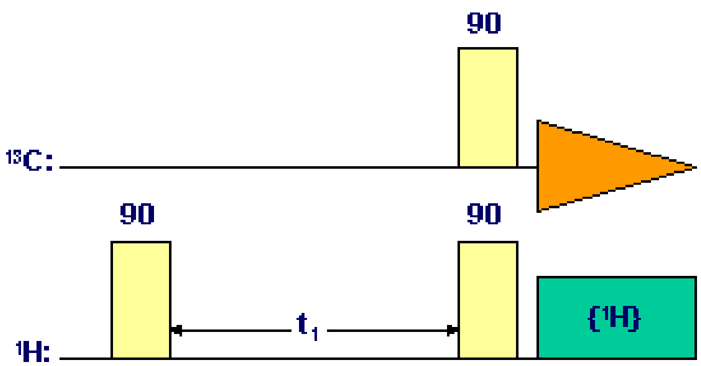

Pulse sequence of $^1$H-$^1$H TOCSY

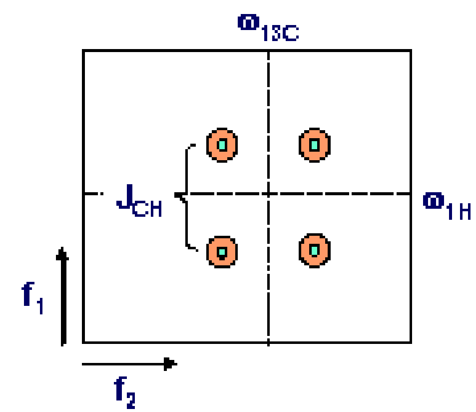


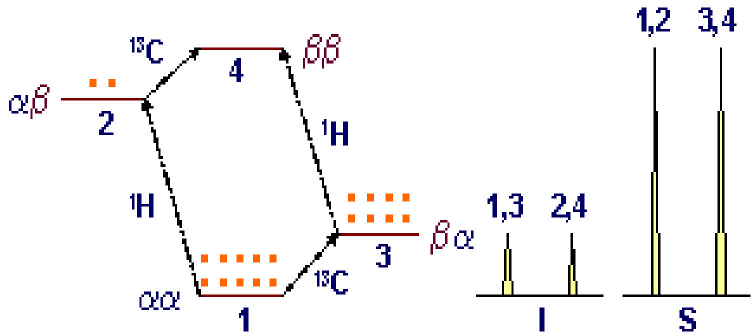



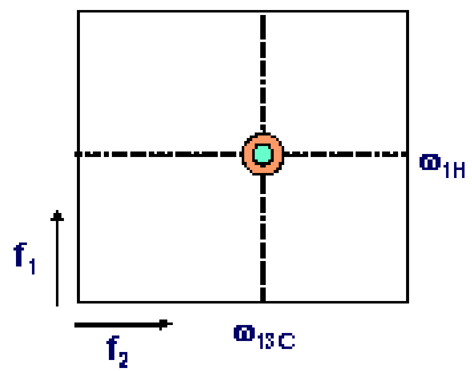
Example of $^1$H-$^1$H TOCSY NMR spectrum

# 2D correlation NMR experiment: HSQC

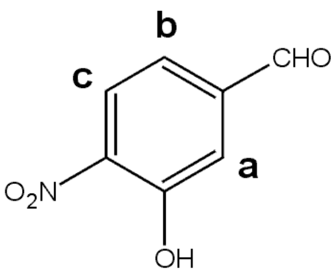


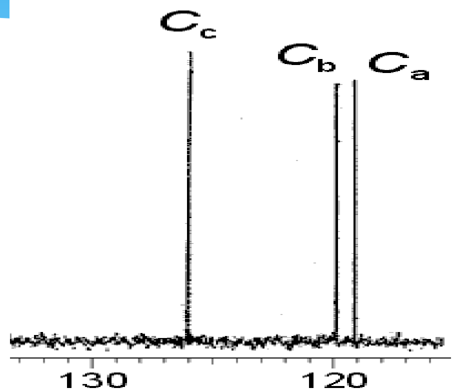



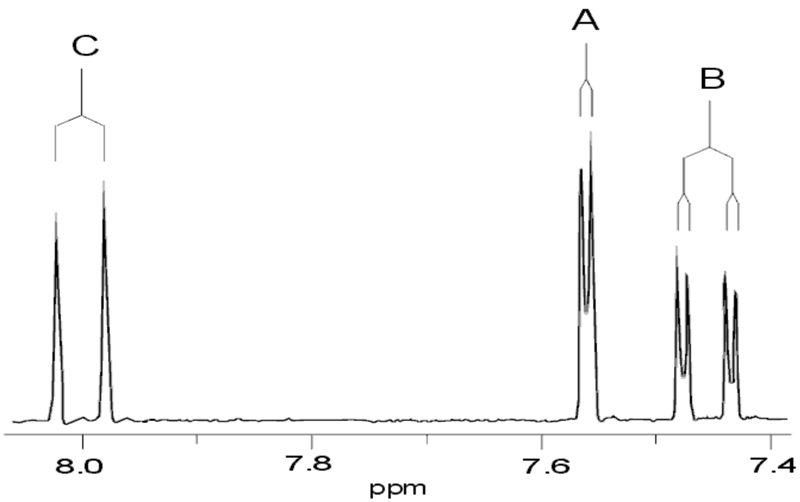



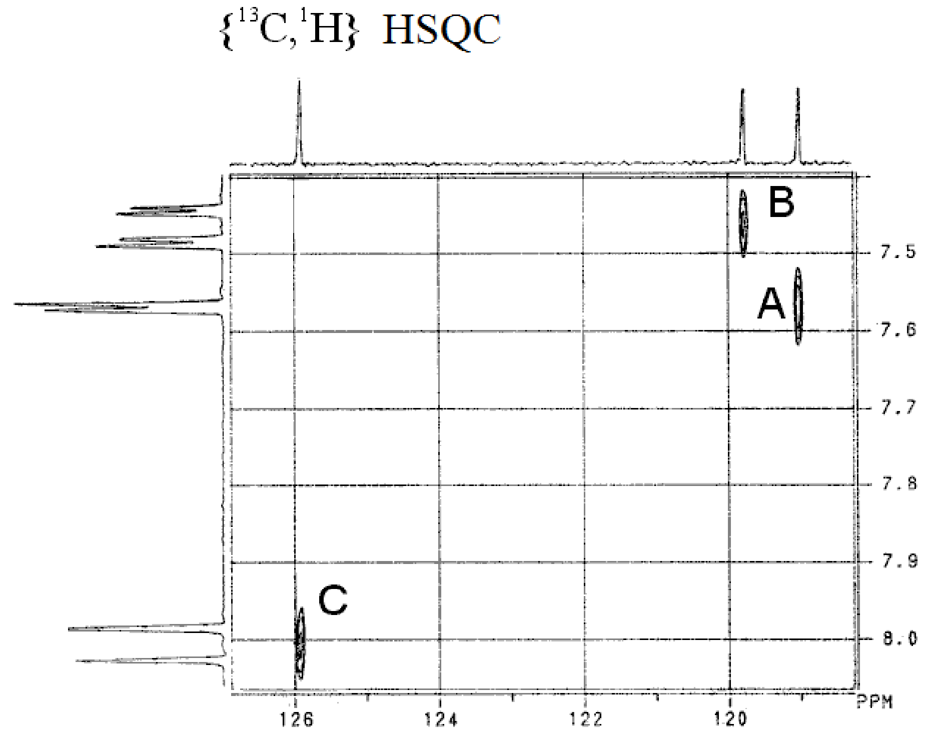



# 2D correlation NMR experiment: HSQC

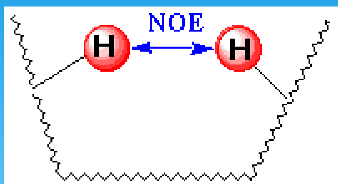


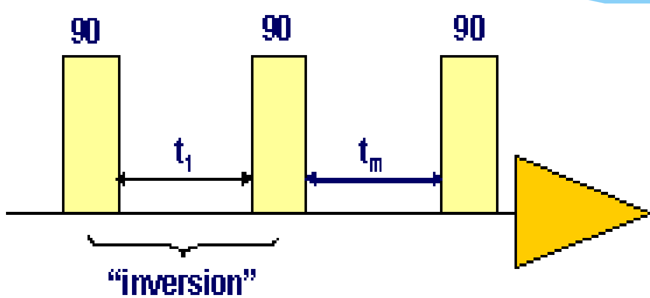



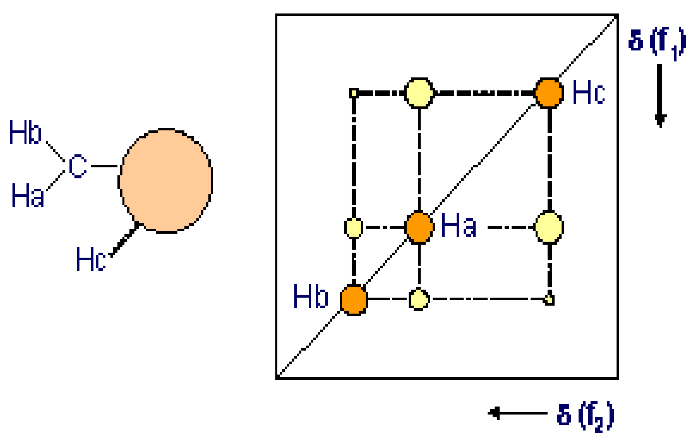



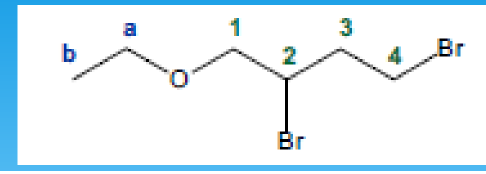
# 2D correlation NMR experiment: NOESY

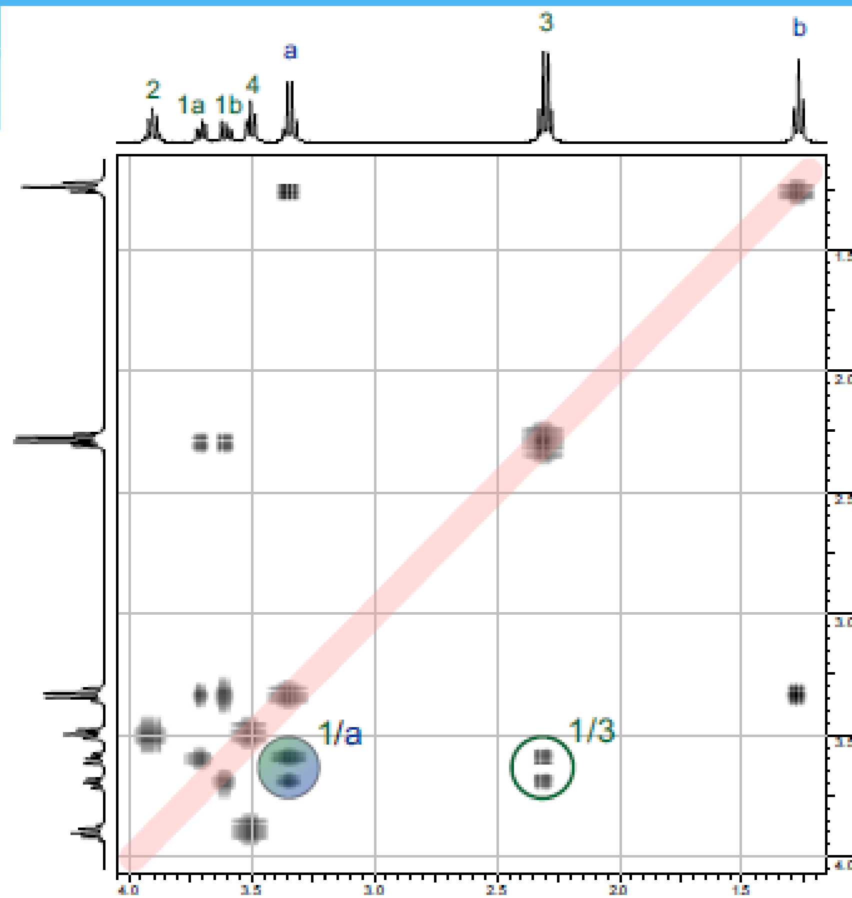



Pulse sequence of $^{1}H$-$^{1}H$ NOESY



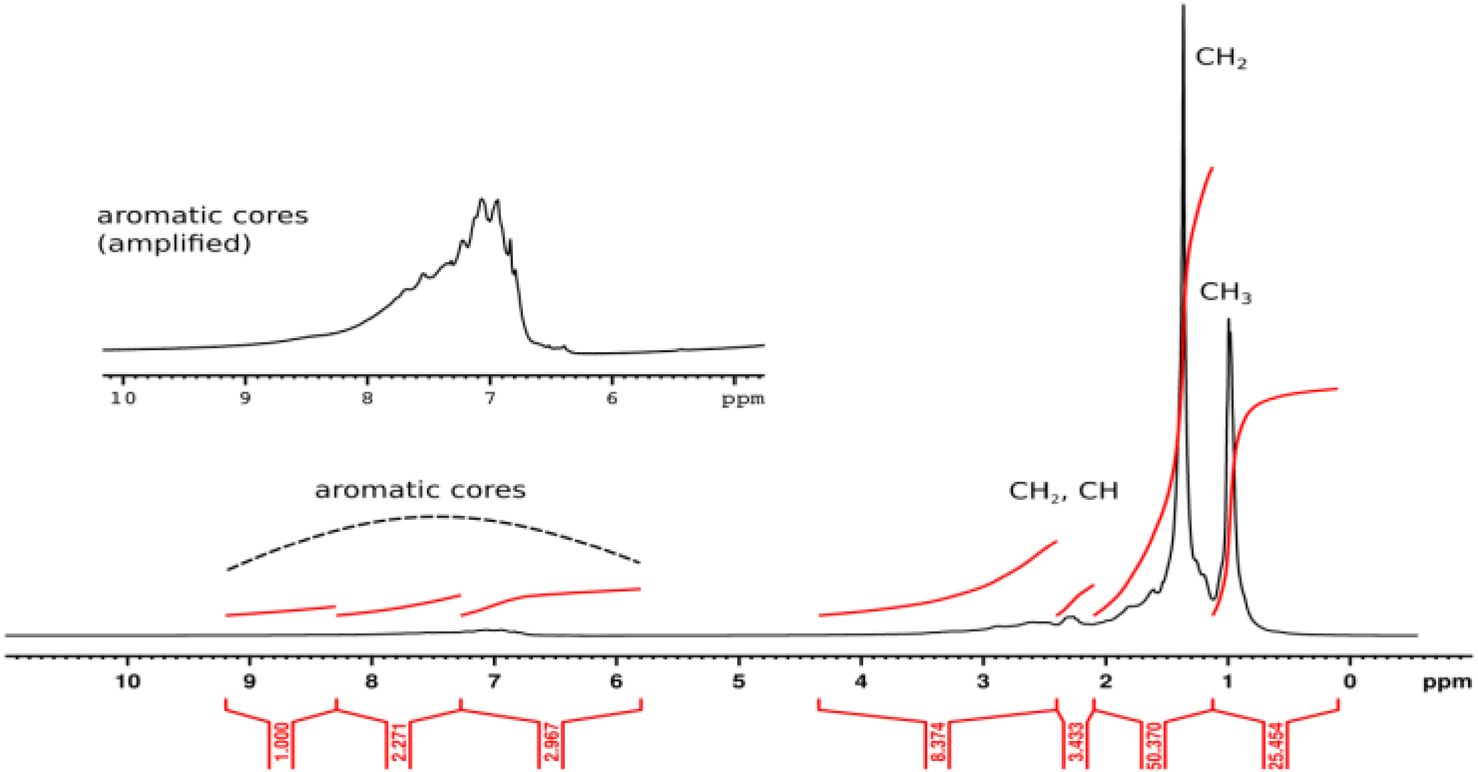




Example of $^{1}H$-$^{1}H$ NOESY NMR spectrum

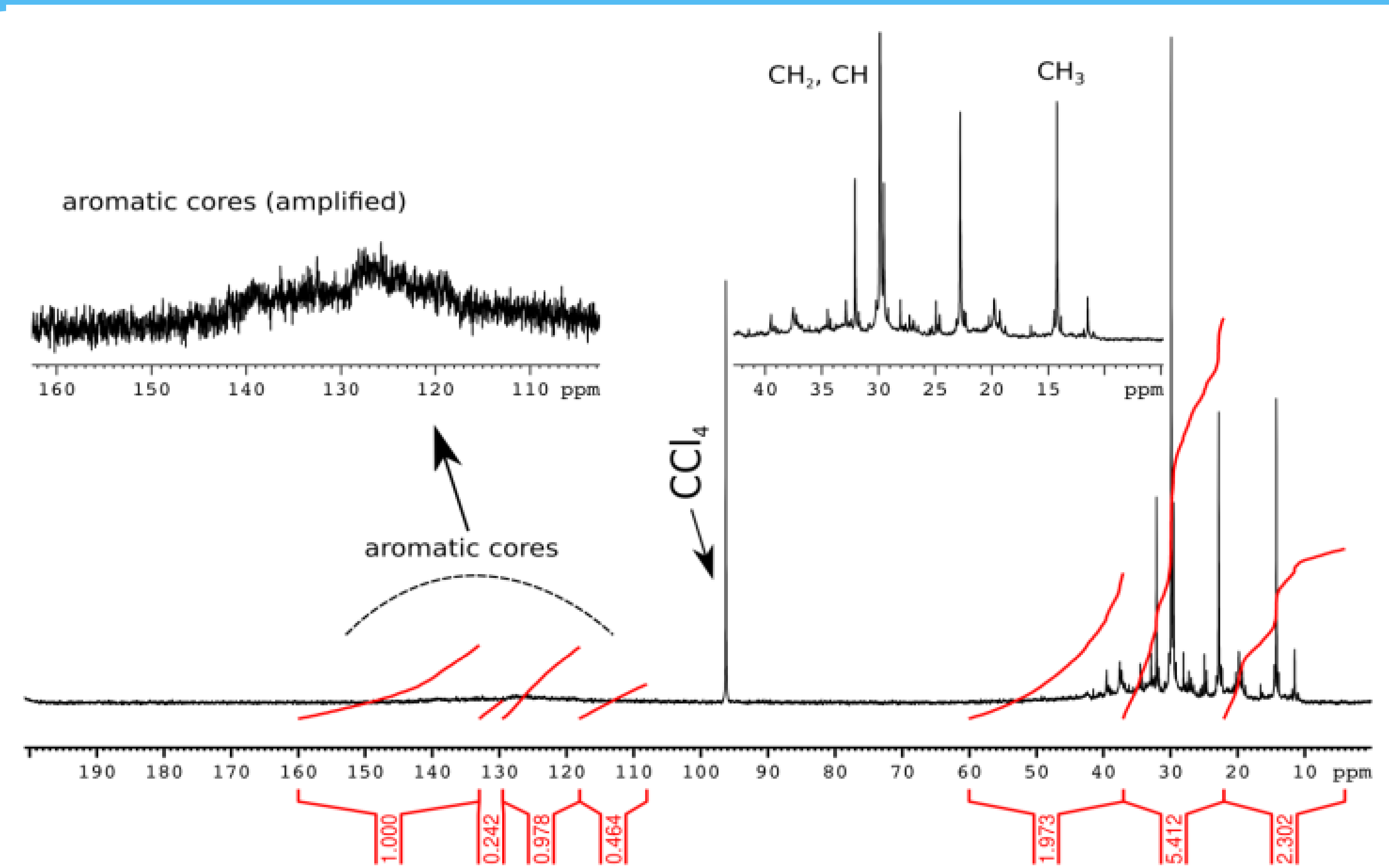
# Study of quality and quantity composition of oil samples by NMR spectroscopy

# Study of quality and quantity composition of oil samples by NMR spectroscopy



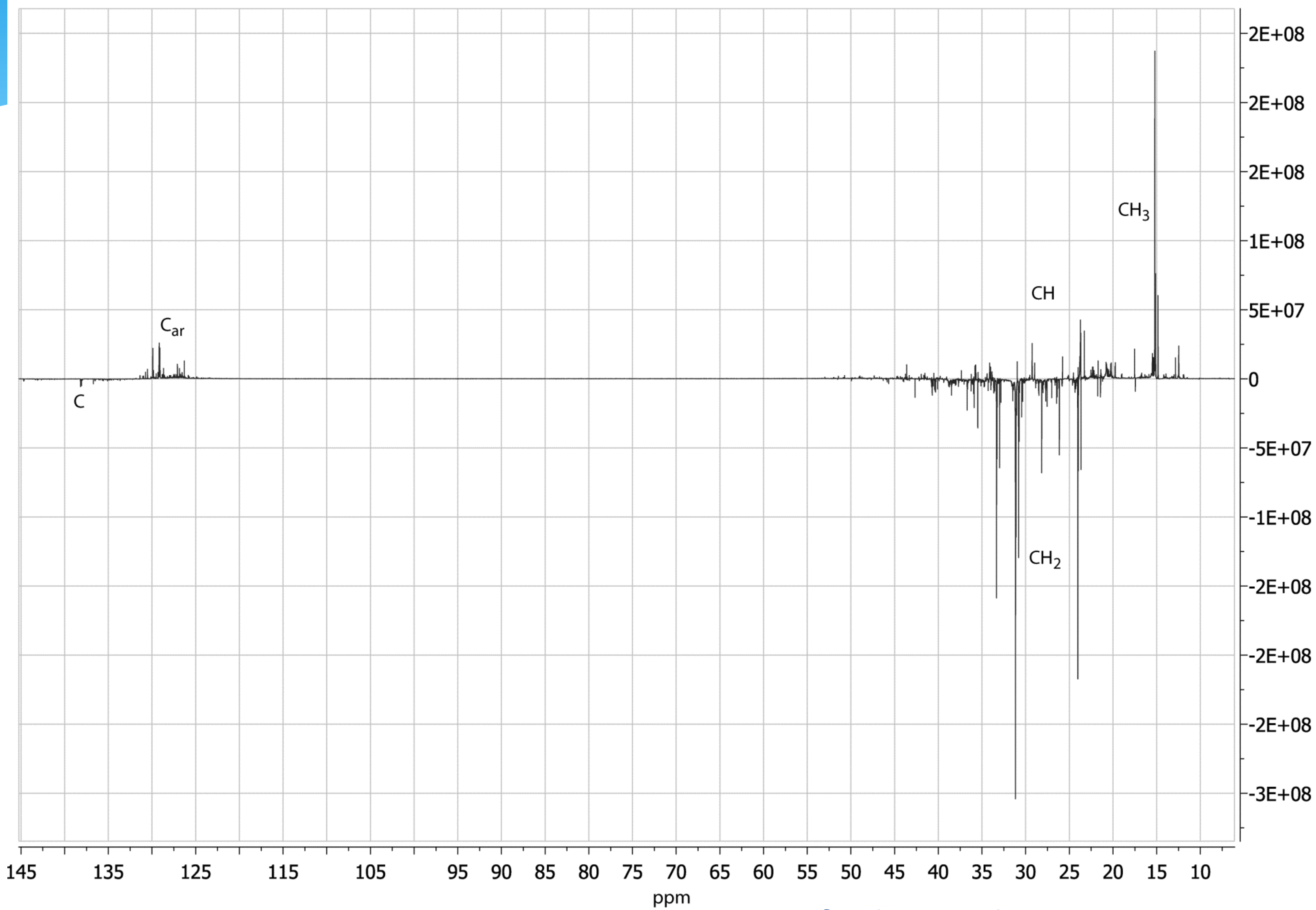

1H NMR spectrum and integral intensities of oil sample from Bashkirian horizon mixed with CCl4

# Study of quality and quantity composition of oil samples by NMR spectroscopy



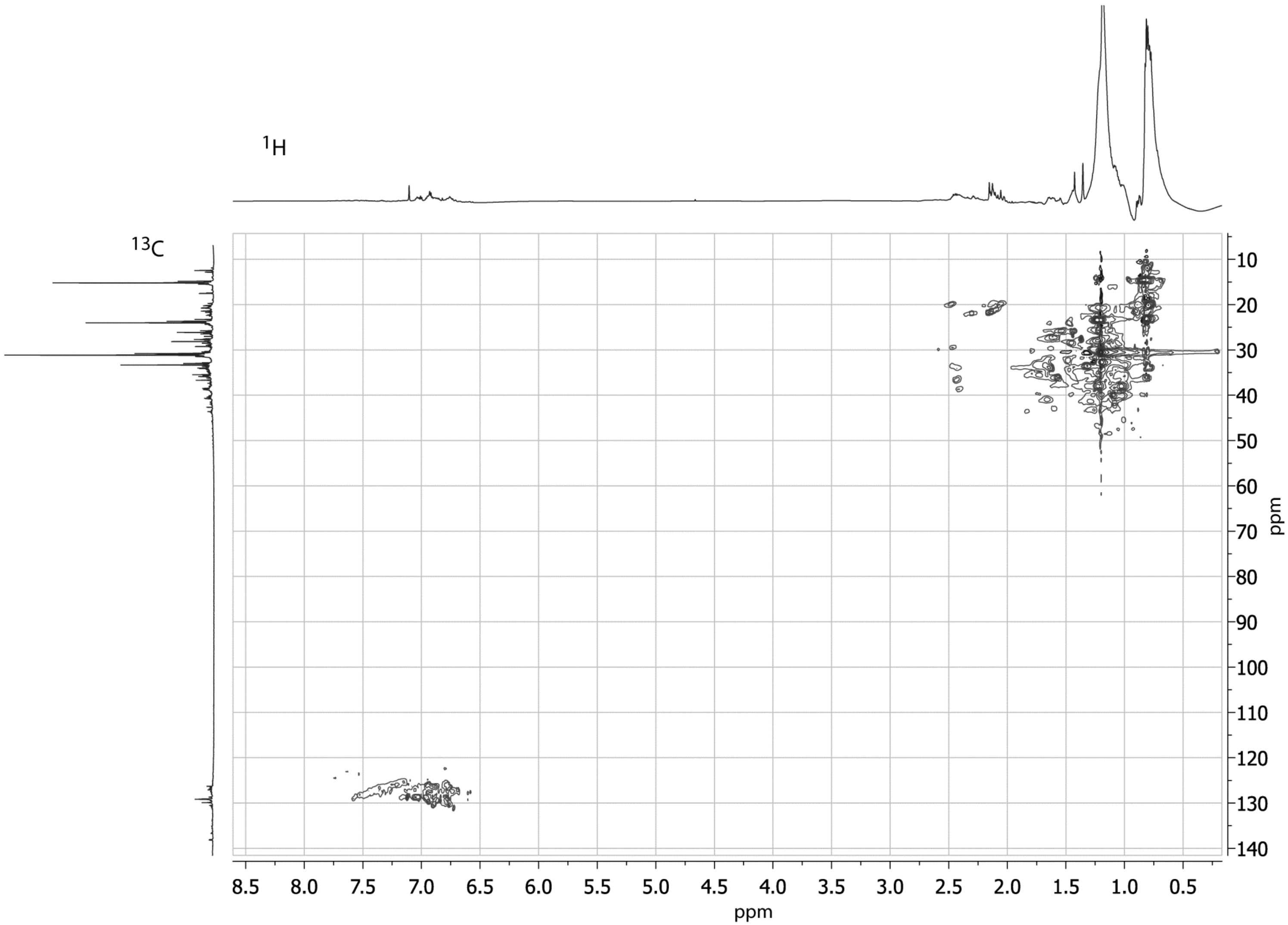

13C NMR spectrum of oil sample from Bashkirian horizon mixed with CCl4

# Study of quality and quantity composition of oil samples by NMR spectroscopy




13C NMR APT spectrum of oil sample

# Study of quality and quantity composition of oil samples by NMR spectroscopy




HSQC NMR spectrum of oil sample

# Study of quality and quantity composition of oil samples by NMR spectroscopy

Molar content (%) of functional groups of oil samples (I - VI) revealed by $^1$H NMR spectroscopy (percentage)

| | Chemical shift range, ppm | (I) | (II) | (III) | (IV) | (V) | (VI) |
|---|---|---|---|---|---|---|---|
| H1 | 0.1-1.1 | 20.9 | 21.1 | 18.9 | 18.6 | 18.1 | 19.1 |
| H2 | 1.1-2.1 | 50.7 | 54.9 | 52.3 | 53.3 | 53.9 | 54.1 |
| H3 | 2.1-2.4 | 3.0 | 2.5 | 2.4 | 2.6 | 2.3 | 2.3 |
| H4 | 2.4-4.4 | 13.6 | 10.7 | 13.4 | 13.3 | 14.2 | 13.5 |
| H5 | 5.8-7.3 | 6.7 | 6.3 | 5.2 | 6.0 | 5.7 | 5.8 |
| H6 | 7.3-8.3 | 4.8 | 4.3 | 6.4 | 5.7 | 5.2 | 4.9 |
| H7 | 8.3-9.2 | 0.3 | 0.2 | 1.4 | 0.5 | 0.6 | 0.3 |

# Study of quality and quantity composition of oil samples by NMR spectroscopy

Molar content (%) of functional groups of oil samples (I - VI) revealed by $^{13}C$ NMR spectroscopy (percentage)

| | Chemical shift range, ppm | (I) | (II) | (III) | (IV) | (V) | (VI) |
|---|---|---|---|---|---|---|---|
| C1 | 4-22 | 23.1 | 24.5 | 20.1 | 20.2 | 18.6 | 17.7 |
| C2 | 22-37 | 48.8 | 53.8 | 53.5 | 52.5 | 43.7 | 43.0 |
| C3 | 37-60 | 12.5 | 10.9 | 11.4 | 14.7 | 15.9 | 16.5 |
| C4 | 108-118 | 0.8 | <0.1 | 0.1 | 0.6 | 3.8 | 3.8 |
| C5 | 118-129 | 8.7 | 5.6 | 7.7 | 7.5 | 7.9 | 7.9 |
| C6 | 129-133 | 1.6 | 1.4 | 1.5 | 1.6 | 2.0 | 2.0 |
| C7 | 133-160 | 4.5 | 3.7 | 5.7 | 3.9 | 8.1 | 9.1 |

# Study of quality and quantity composition of oil samples by NMR spectroscopy

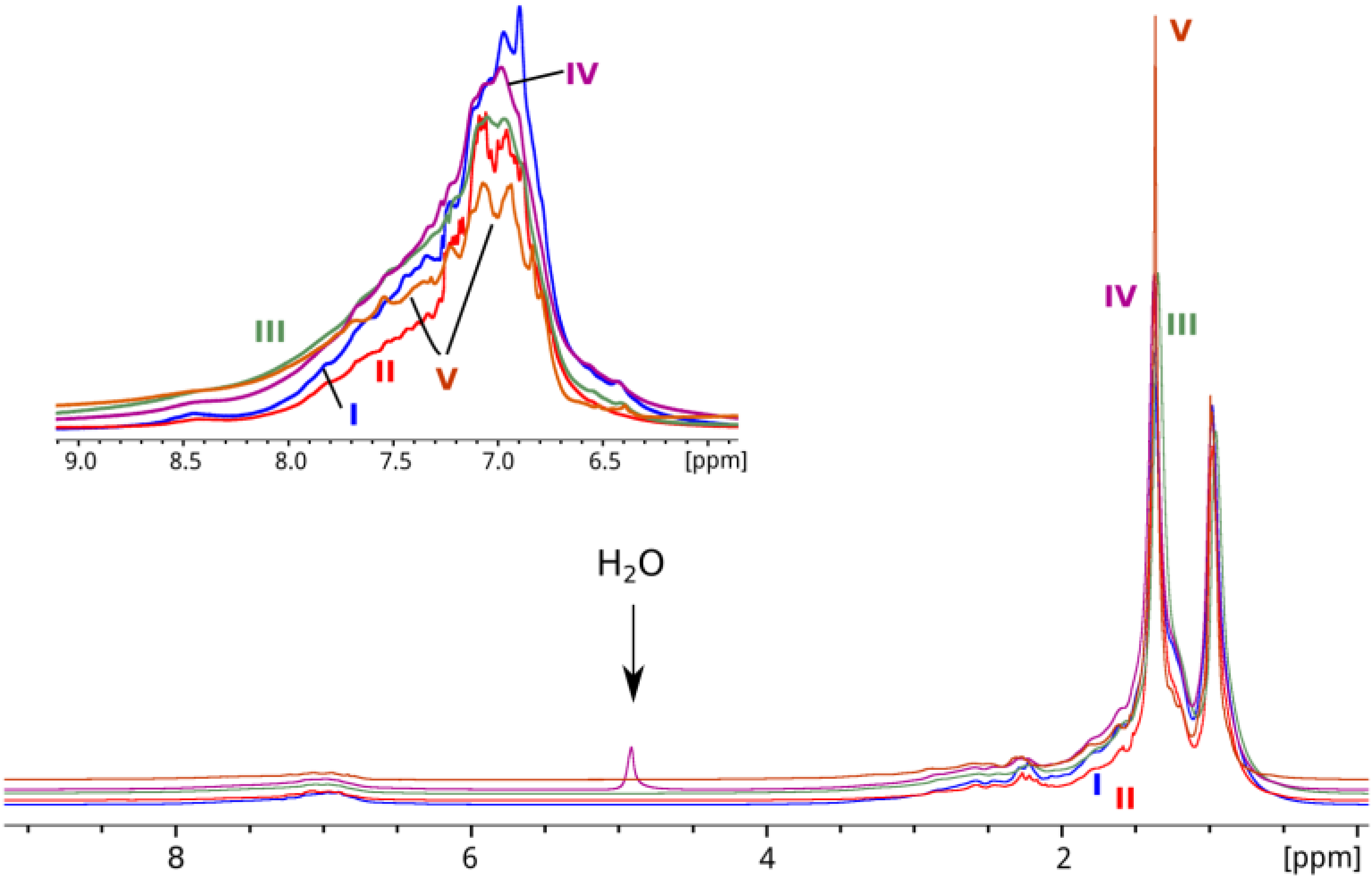
| | (I) | (II) | (III) | (IV) | (V) | (VI) |
|---|---|---|---|---|---|---|
| $C_p$ | 22.8 | 24.3 | 19.8 | 19.9 | 18.2 | 17.4 |
| $C_{sq}$ | 50.5 | 55.6 | 55.4 | 54.3 | 45.3 | 44.6 |
| $C_t$ | 12.0 | 9.4 | 9.9 | 13.8 | 18.5 | 19.1 |
| $C_{ar}$ | 14.7 | 10.7 | 14.8 | 12.0 | 17.9 | 19.0 |

$$C_p = ((1.02I_p - 0.006I_{sq}) / (I_t + I_{sq} + I_p))(1 - C_{ar})$$

$$C_{sq} = ((1.04I_{sq} - 0.04I_t - 0.02I_p) / (I_t + I_{sq} + I_p))(1 - C_{ar})$$

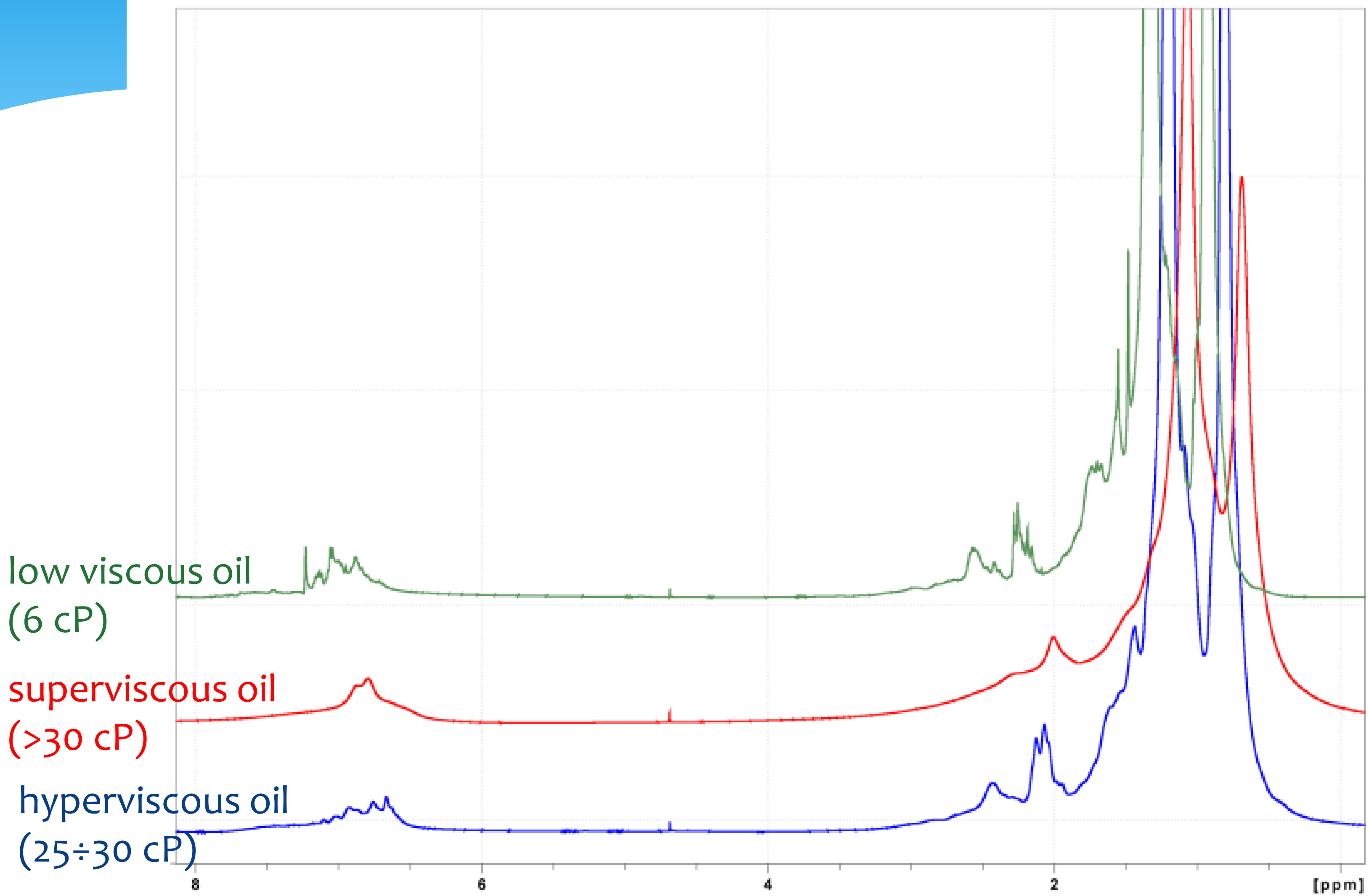
$$C_t = ((1.04I_t - 0.034I_{sq}) / (I_t + I_{sq} + I_p))(1 - C_{ar})$$

# Study of quality and quantity composition of oil samples by NMR spectroscopy



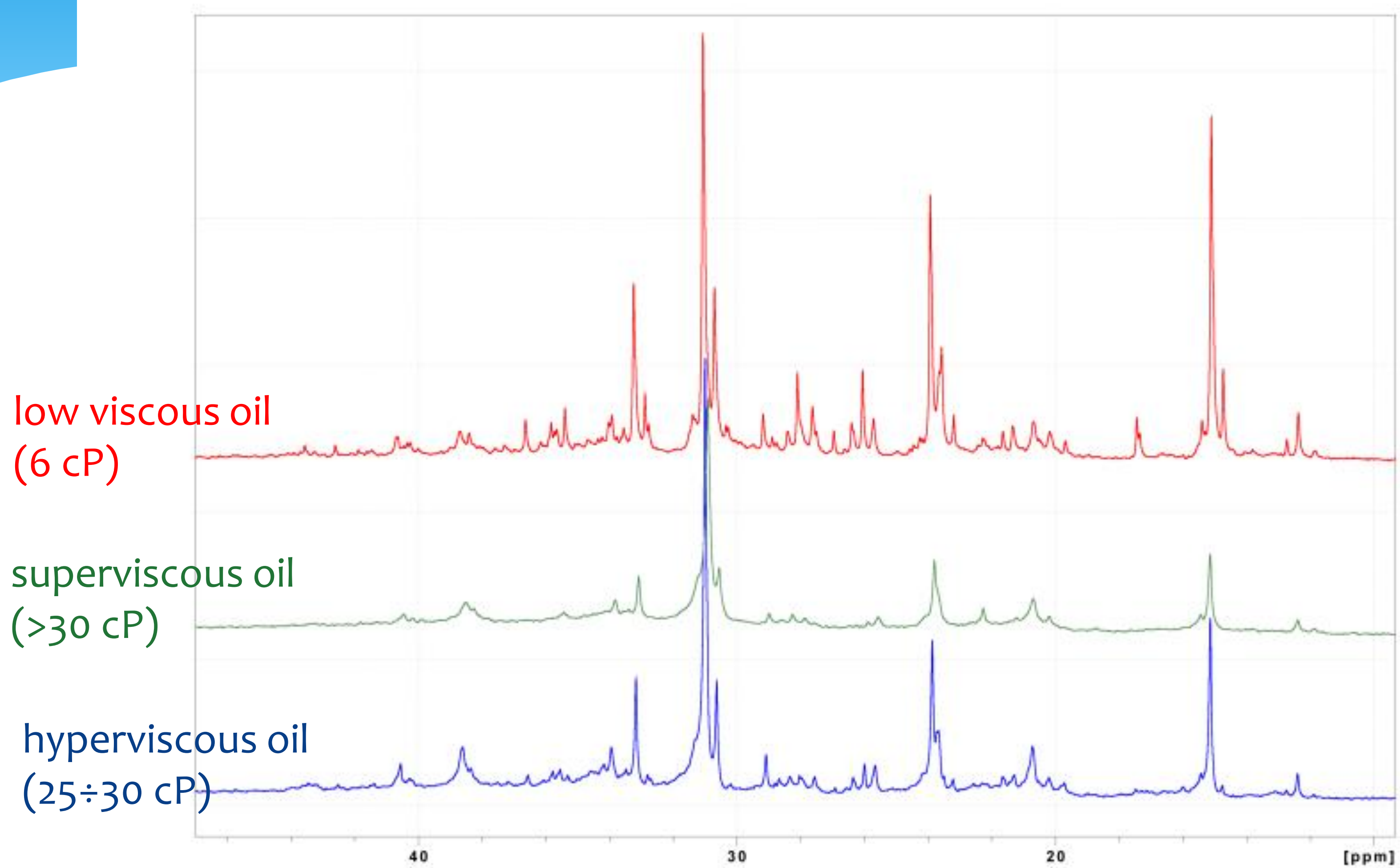

Comparison of $^1$H NMR spectra (500 MHz) of five oil samples

# Study of quality and quantity composition of light and heavy oil samples by NMR spectroscopy




$^{1}$H NMR spectra of oil samples

# Study of quality and quantity composition of light and heavy oil samples by NMR spectroscopy




$^{13}C$ NMR spectra of oil samples

# Study of quality and quantity composition of light and heavy oil samples by NMR spectroscopy

| | Low viscous oil (401) | Low viscous oil (3002) | Hyperviscous oil | Superviscous oil |
|---|---|---|---|---|
| $C_p$ | 33.4 | 34.7 | 25.8 | 21.6 |
| $C_{sq}$ | 48.4 | 53.8 | 53.0 | 48.9 |
| $C_t$ | 12.1 | 4.8 | 10.0 | 12.8 |
| $C_{ar}$ | 6.4 | 6.9 | 12.5 | 19.3 |

# THANK YOU FOR ATTENTION

**Research laboratory**

**«NMR-structure»**

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