UNESCO/IUPAC Postgraduate Course in Polymer Science

Lecture:

NMR spectroscopy of polymers in solution

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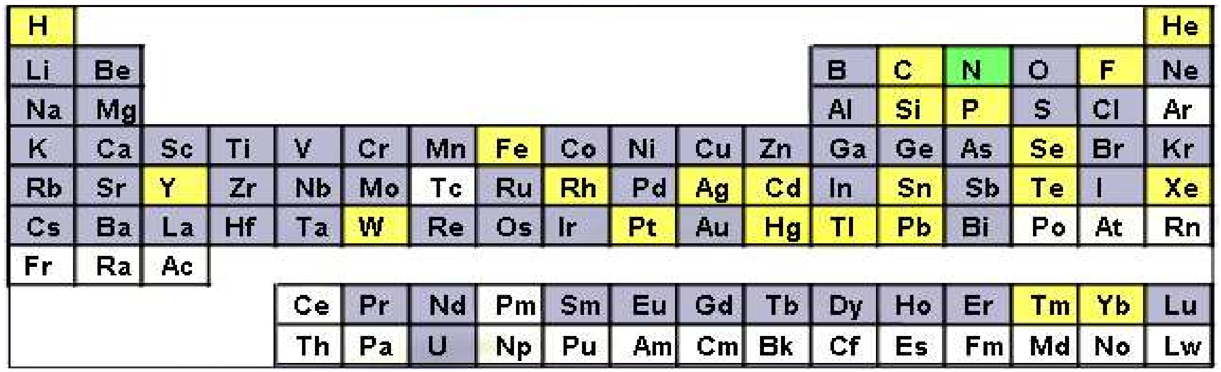
Basic conditions

Atoms active in NMR experiment

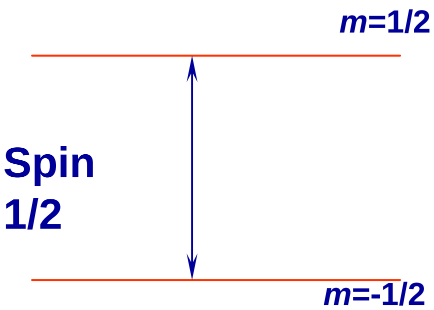
22 spins *I*=1/2

77 spins *I*=3/2, 5/2,9/2

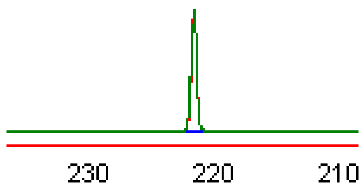
1 spin *I*=1



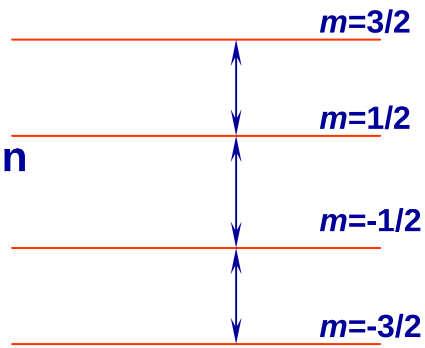
Spin 1/2



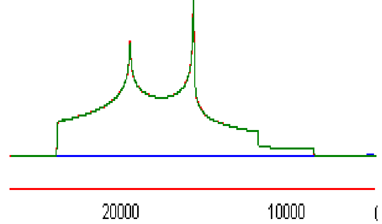
Spectrum: narrow signal 0,1-100 Hz



Spin 3/2



Spectrum: broad signal 1000-100000 Hz



Basic conditions

NMR active nuclei ⇒ Spin-quantum number, $I \neq 0$ ⇒ Magnetic-quantum number

$I = 1/2$ ⇒ $m = \pm 1/2$ (^{1}H, ^{13}C ^{29}Si, ^{119}Sn)

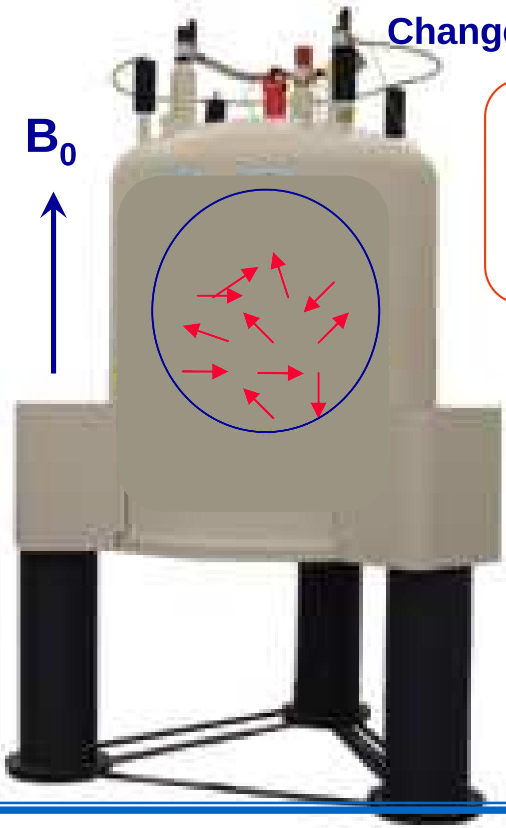
$I = 3/2$ ⇒ $m = \pm 3/2, \pm 1/2$ (^{23}Na, ^{27}Al)

Angular momentum: $\vec{\mathbf{I}}$ ⇒ Nuclear magnetic moment: $\vec{\boldsymbol{\mu}}$ $\quad \vec{\boldsymbol{\mu}} = \gamma \vec{\mathbf{I}} h / 2\pi$

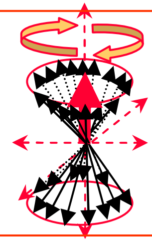
In a static magnetic field: $\vec{\mathbf{B}}_0$ ⇒ torque: $\vec{\boldsymbol{\tau}}$ $\quad \vec{\boldsymbol{\tau}} = \vec{\boldsymbol{\mu}} \times \vec{\mathbf{B}}_0 = \frac{d}{dt}\vec{\mathbf{I}}$

Change of orientation of the vector of magnetic moment: $\frac{d\vec{\boldsymbol{\mu}}}{dt} = \gamma \vec{\boldsymbol{\mu}} \times \vec{\mathbf{B}}_0$

B_0



Precession of spins around magnetic field:



with frequency $\omega_0 = \gamma \vec{\mathbf{B}}_0$

Larmor or resonant frequency

The frequency of the excitation field must be the same

m=1/2 β

B_0=0

$\Delta E = h\nu = \omega_0 / 2\pi$

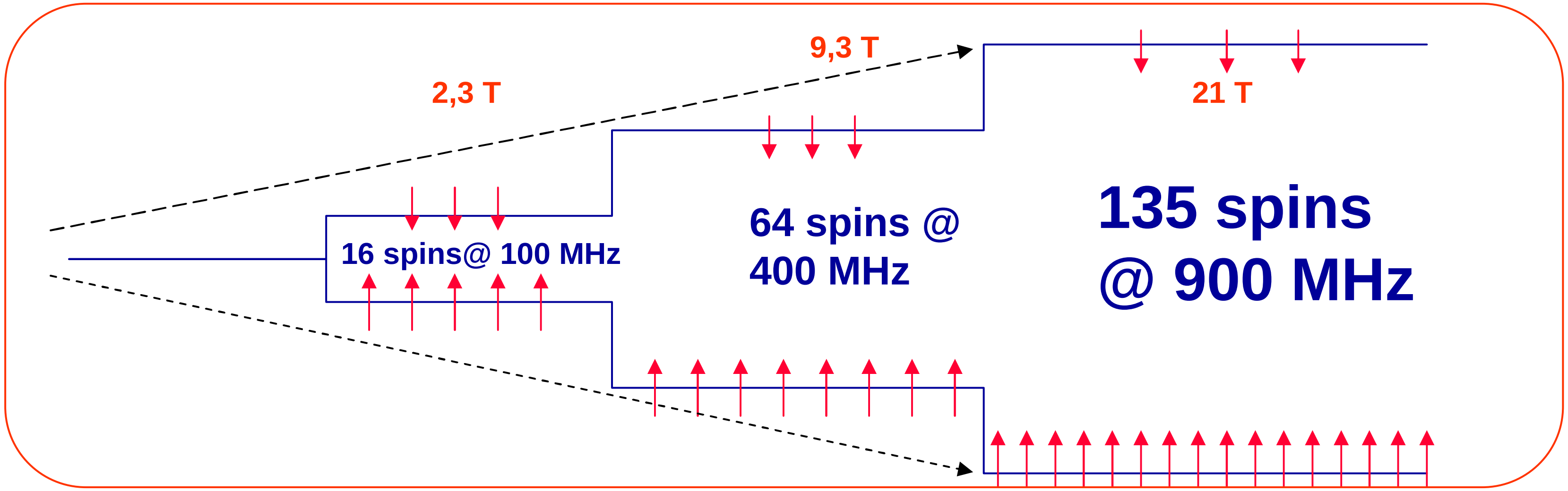
m=-1/2 α

$$N_\alpha / N_\beta = e^{\Delta E / kT} = 1.000064.......(400\text{MHz})$$

Basic condition – sensitivity

Increasing difference at energy levels with increasing intensity of magnetic field

The difference for 1 000 000 spins is:



$$N_\alpha / N_\beta = e^{\Delta E / kT} = 1.000064.......(400\text{MHz})$$

Basic condition – sensitivity

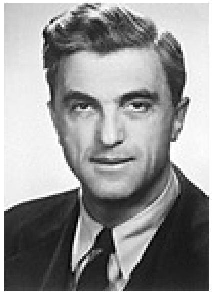
300 MHz
7,02 T
0,2 Mil €

600 MHz
14,04 T
1 Mil €

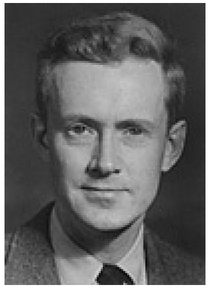
950 MHz
22,23 T
8-10 Mil € ??

History – the first NMR signal (1949)

Bloch's laboratory

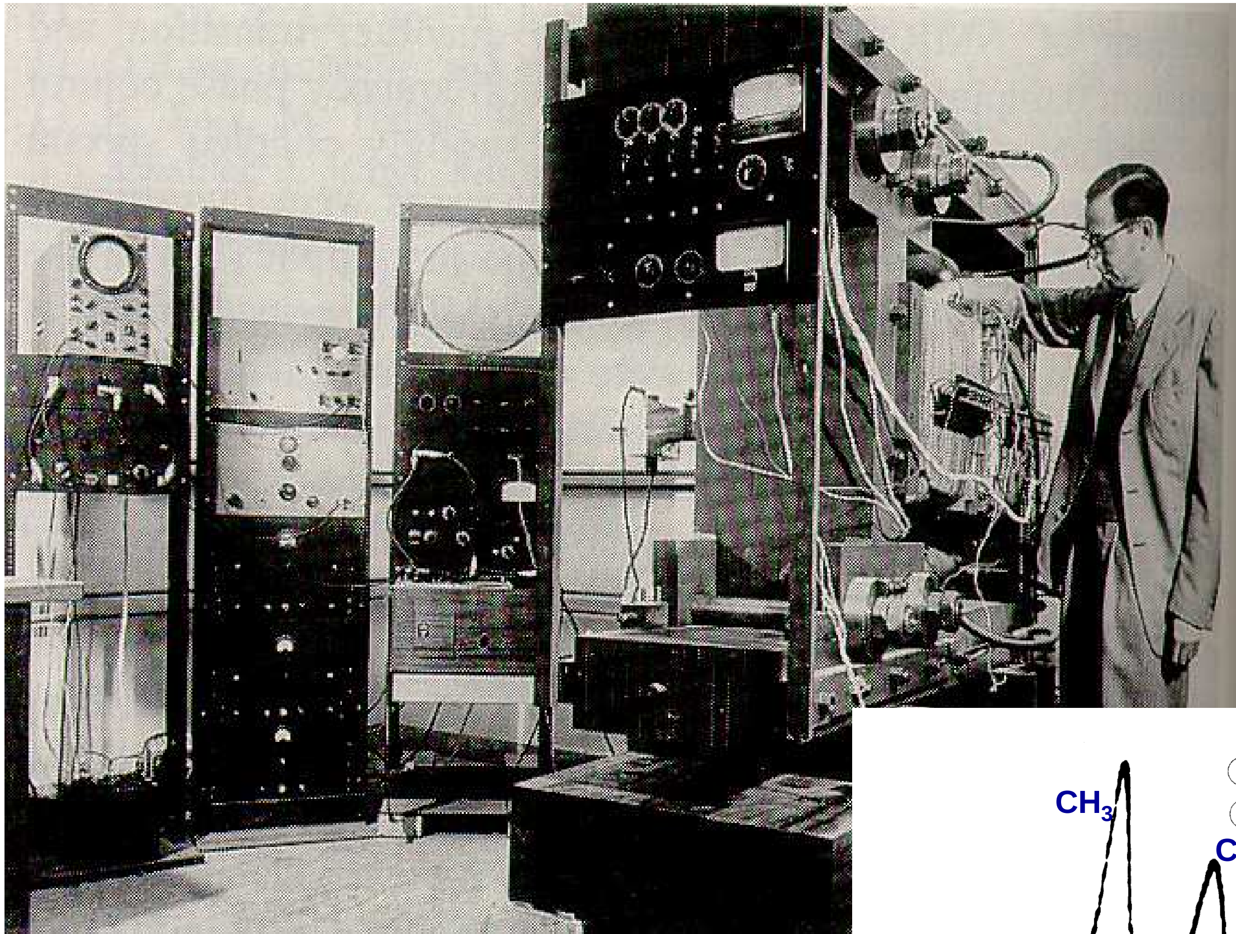


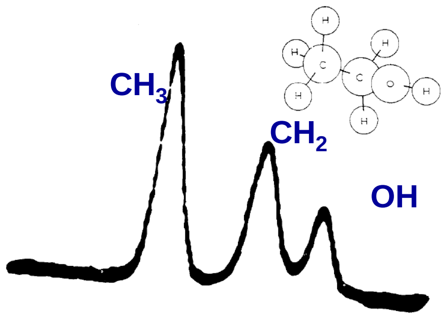
Felix Bloch
1905-1983



Edward M. Purcell
1912-1997

1952 – Nobel Prize





History - NMR spectrometer at 1964

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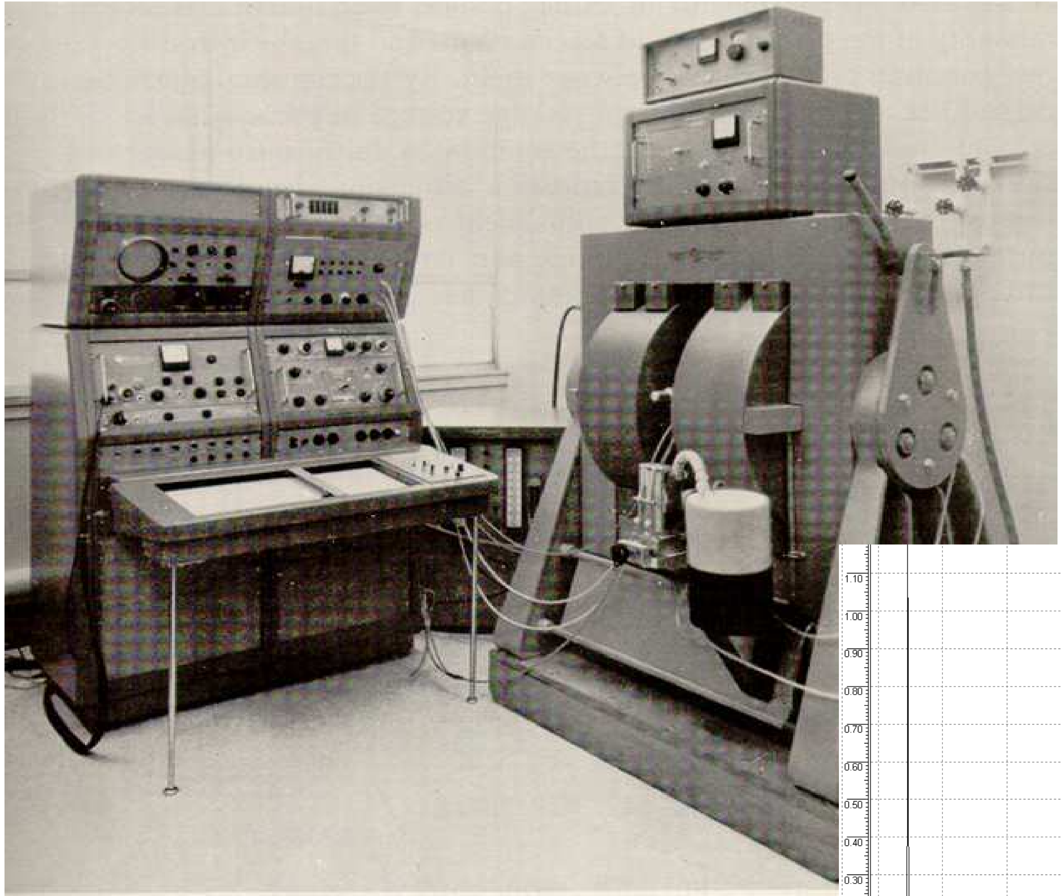
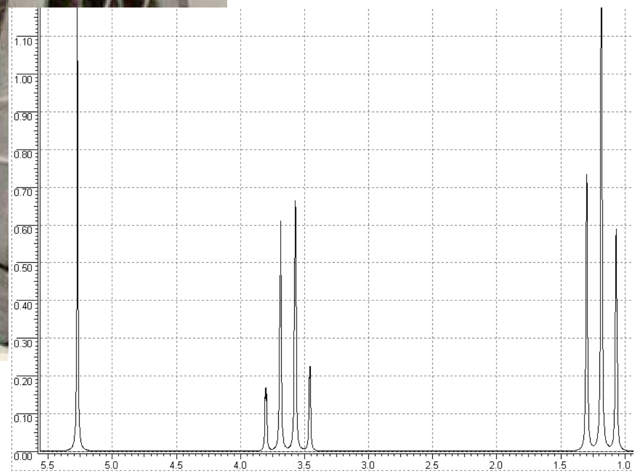
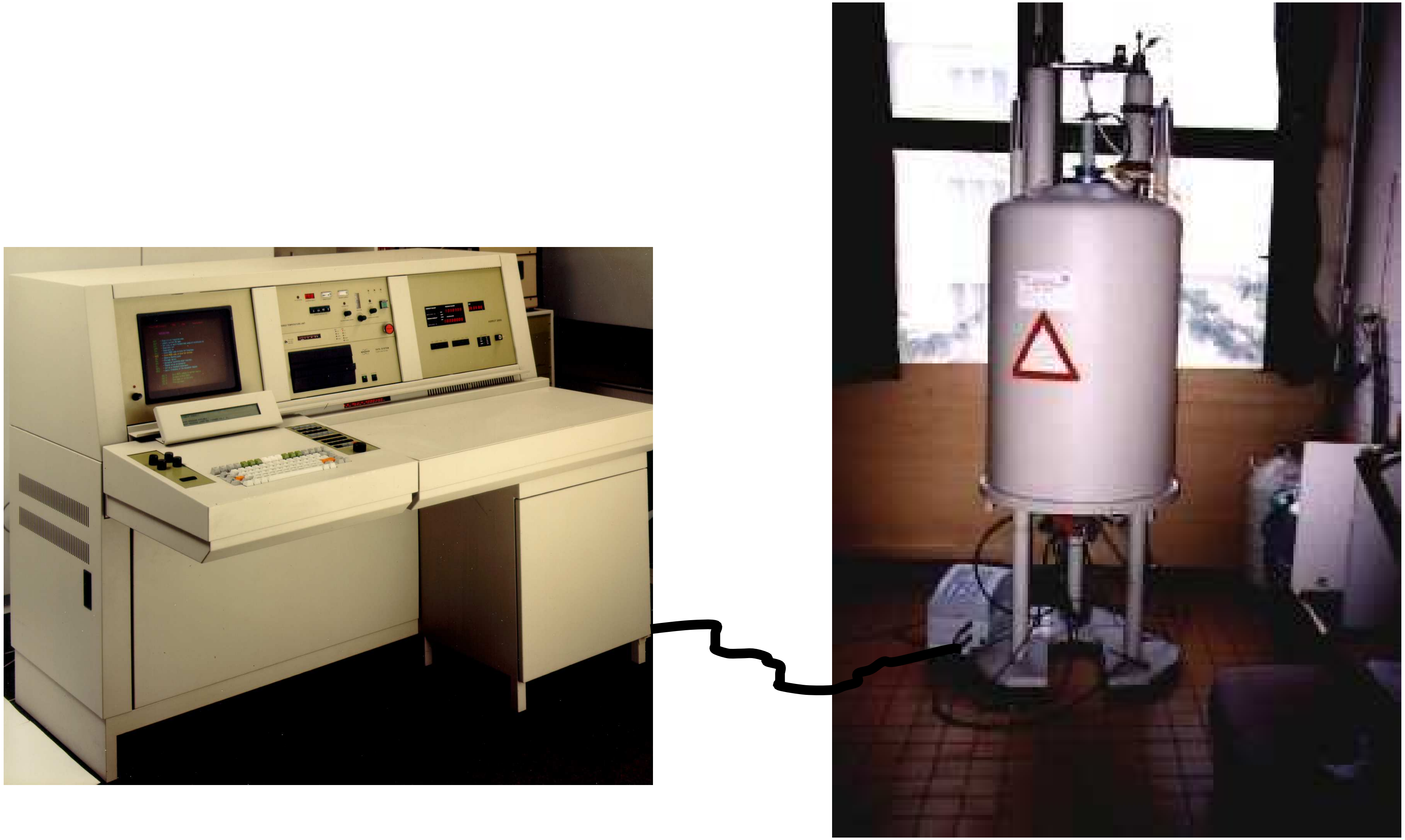




History - NMR spectrometer at 1970

History - NMR spectrometer at 1985



AM console with cryomagnets

History - NMR spectrometer at 2000

Current routine

Present - NMR spectrometer at 2002

The application laboratory, Bruker GmbH

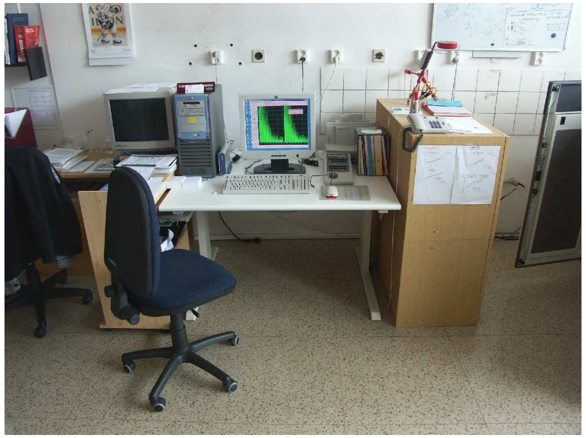
AVANCE 750 WB

17.6 T;
Supercooled He - 1,8K

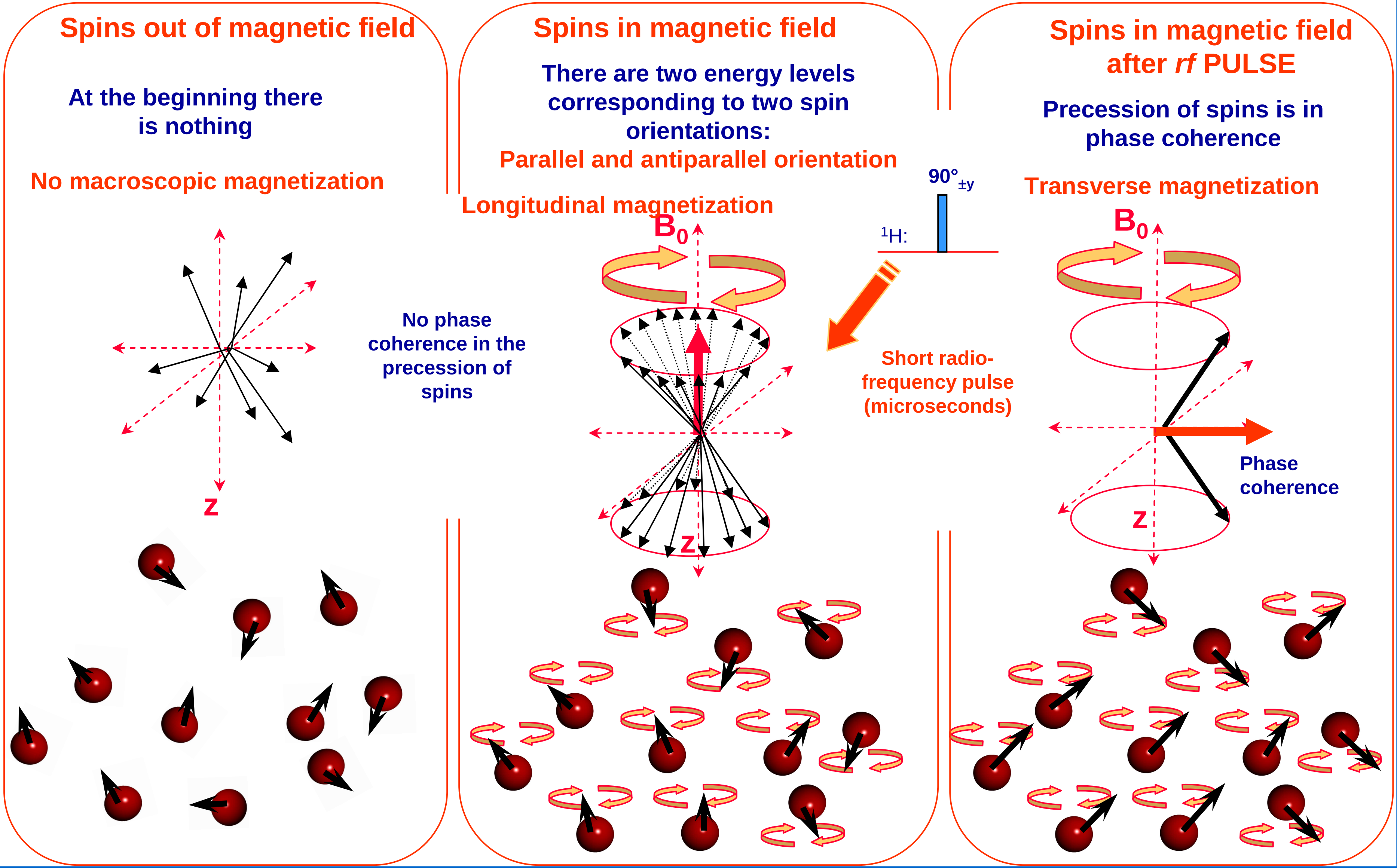
Boiling temperature 4,7K (Joule-Thompson)

Present - NMR spectrometer at 2006

AVANCE 500 WB/US, IMC AS CR



Basic NMR experiment



Basic NMR experiment

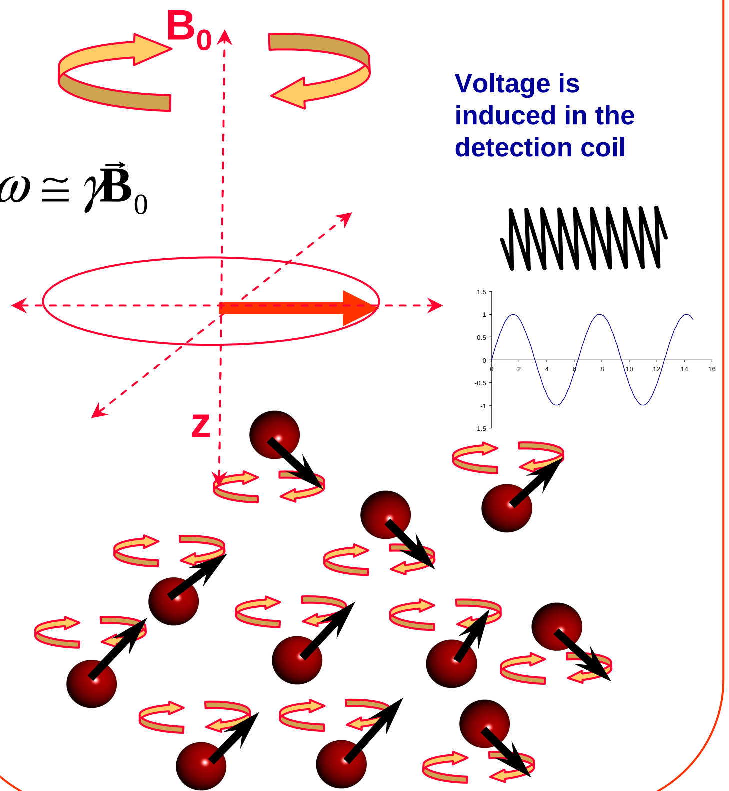
Spins in a magnetic field after an *rf* PULSE

The precession of spins is in the phase coherence

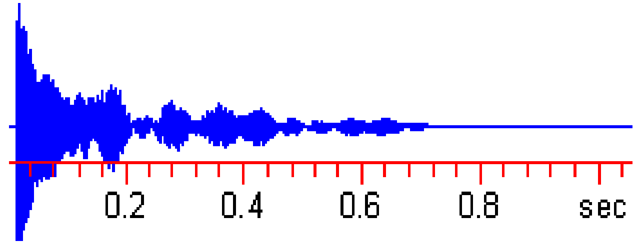
Transverse magnetization rotates around the magnetic field

Frequency of this oscillation corresponds to the chemical shift

$$\omega \cong \gamma \vec{\mathbf{B}}_0$$



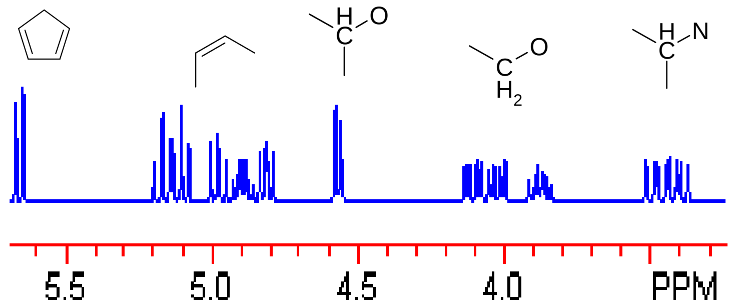
Free Induction Decay (FID) is detected



The FID contains all structural information – we cannot read it

$$F(\omega) = \int_{-\infty}^{\infty} dt.\, f(t)\, e^{-i\omega t}$$

Fourier transformation (FT)



There is a classical spectrum

Chemical shift

Influence of chemical surrounding – effective magnetic field B_{eff}

$$B_{eff} = B_0 - B_{loc} = B_0(1-s)$$

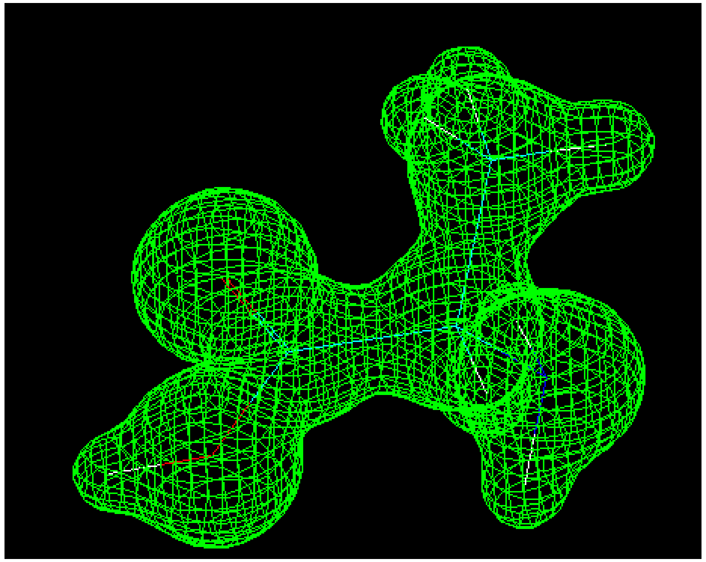
Electron density ➡ shielding of nuclei

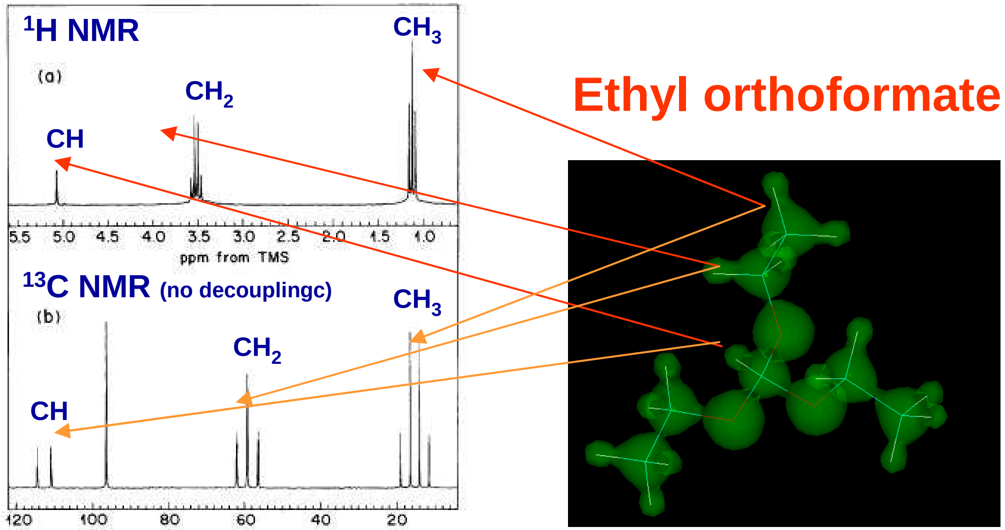
Differences in 1000-0.01 Hz

Increasing electronegativity of neighboring atom
Increasing strength of hydrogen bond

Increasing electron density

← ppm →

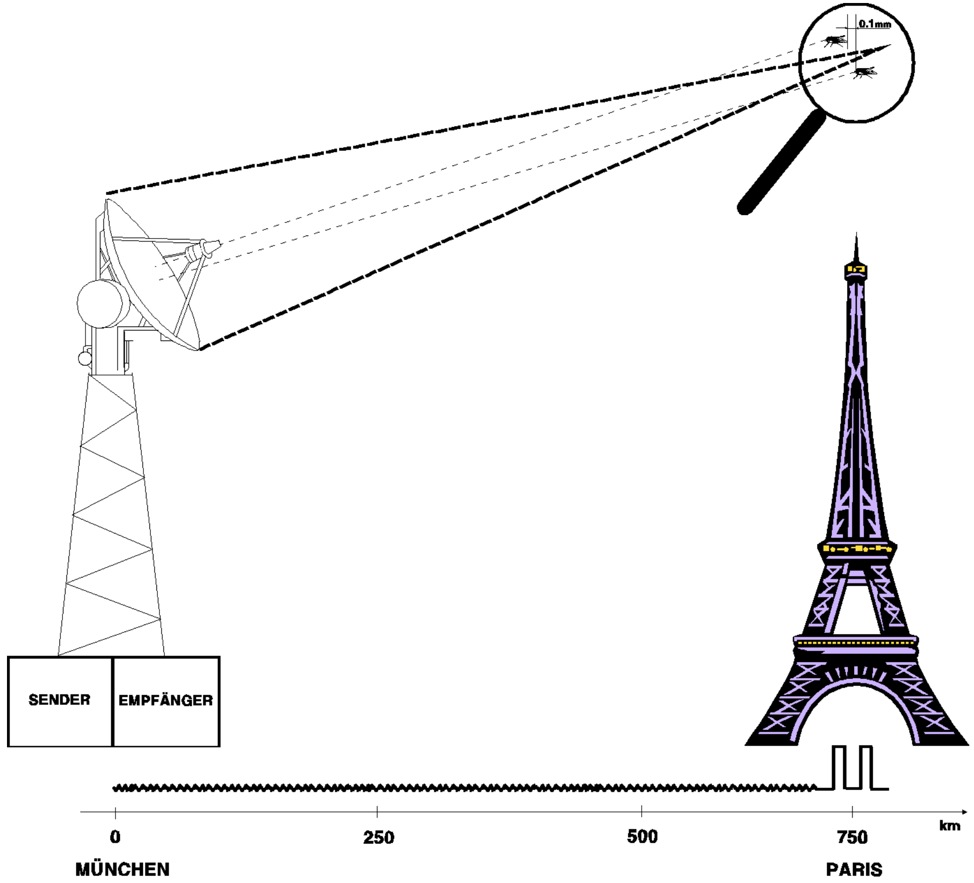




Basic problem - resolution

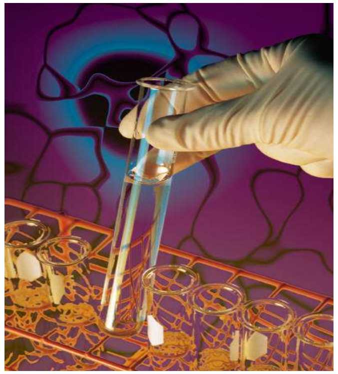
Required resolution (0,1 - 0,01Hz)

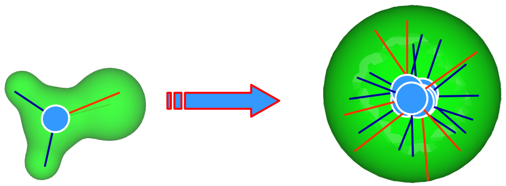
Currier frequency is ca. 750 MHz

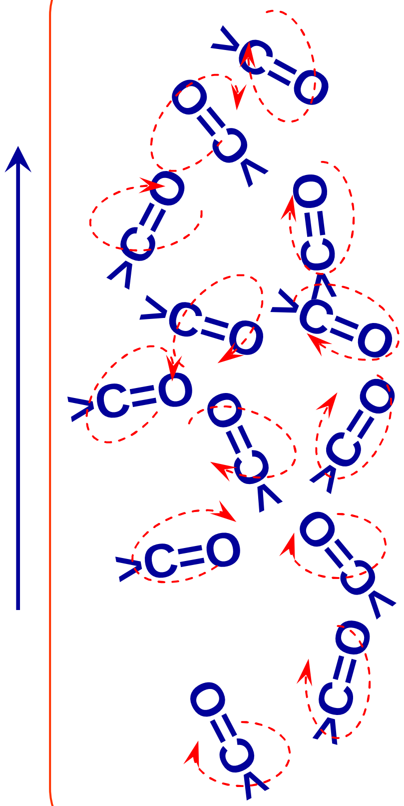


NMR in solution

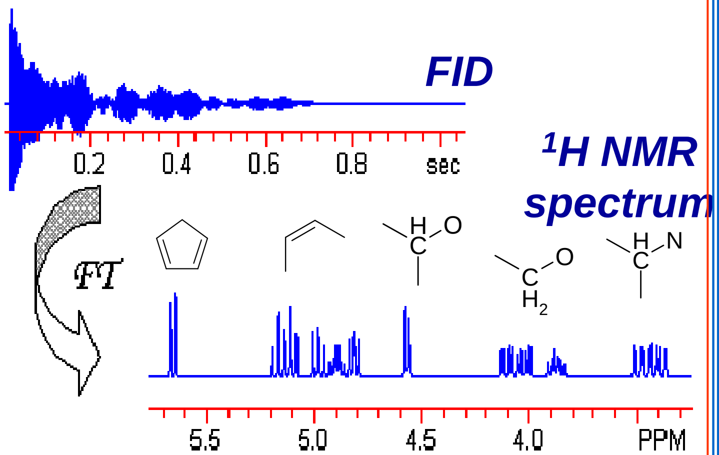
Solution → **Isotropic values of chemical shift**







Highly resolved NMR spectrum
Line-width < 0.1 Hz



The same groups have the same chemical shift. Molecules are magnetically equivalent.

Fast isotropic motion

Symmetrical distribution of electron cloud

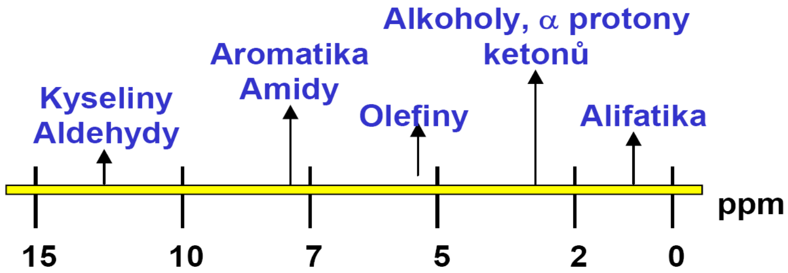
Fast isotropic motion – fast reorientation of molecules : distribution of electrons seems to be symmetrical

^{1}H NMR spectra (basic parameters)

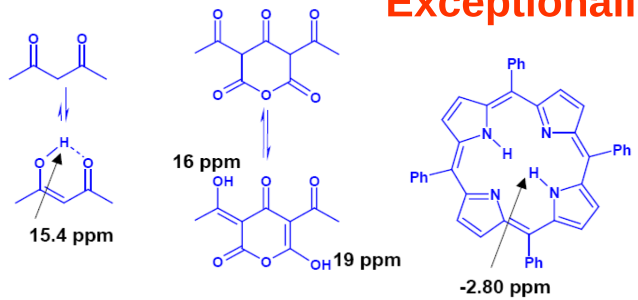
1. Number of signals.
2. Integral intensity (depends on number of atoms in one structure unit).
3. Chemical shift (position of signal depends on chemical surrounding).
4. Multiplicity (signals have fine splitting which depends on the number interacting spins).

Chemical shift

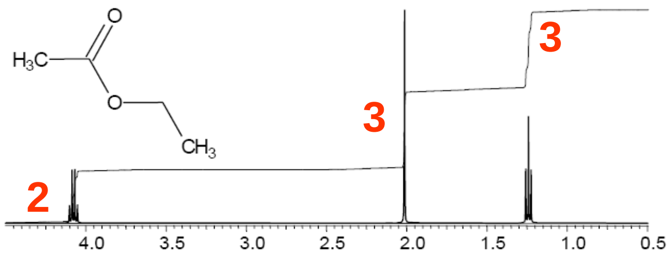
Usually



Exceptionally



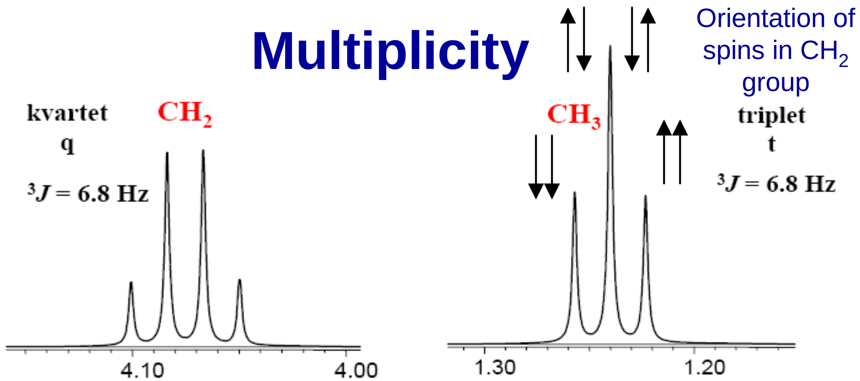
Integral intensity



CH_2 bond to O: 4 ppm
CH_3 bond to carbonyl: 2ppm
CH_3 bond CH_2: only 1,3 ppm

Intensity: 3H CH_3, 3H CH_3 a 2H CH_2

Multiplicity



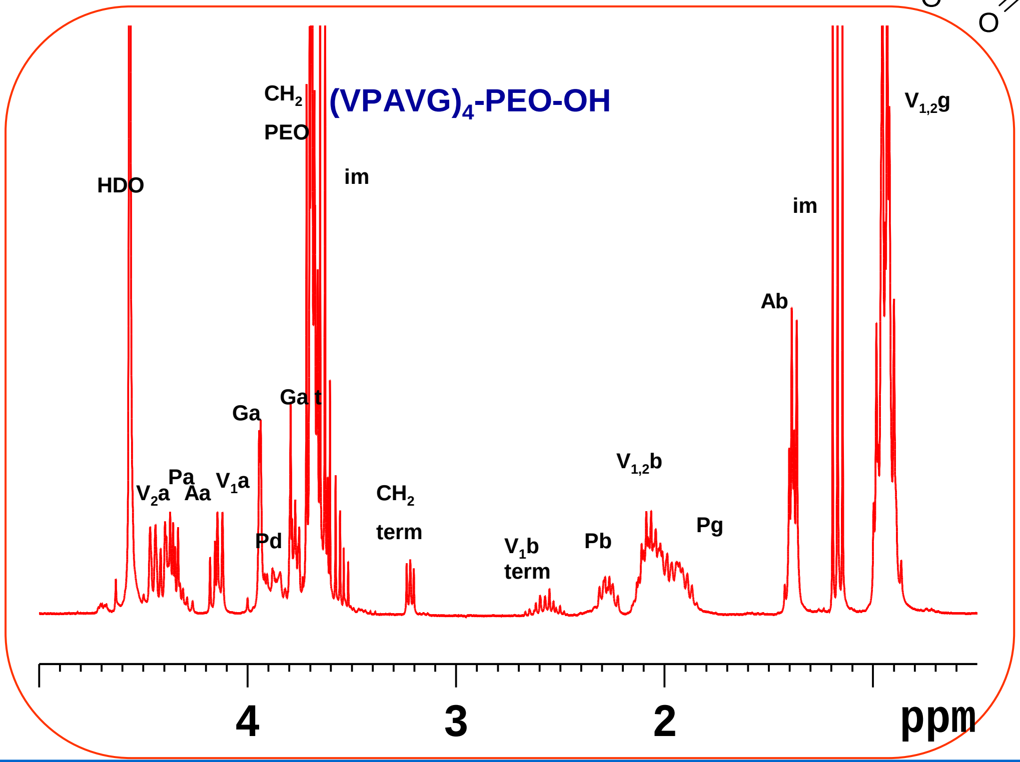
Number of signal = number of neighboring ^{1}H atoms plus 1 (n+1)

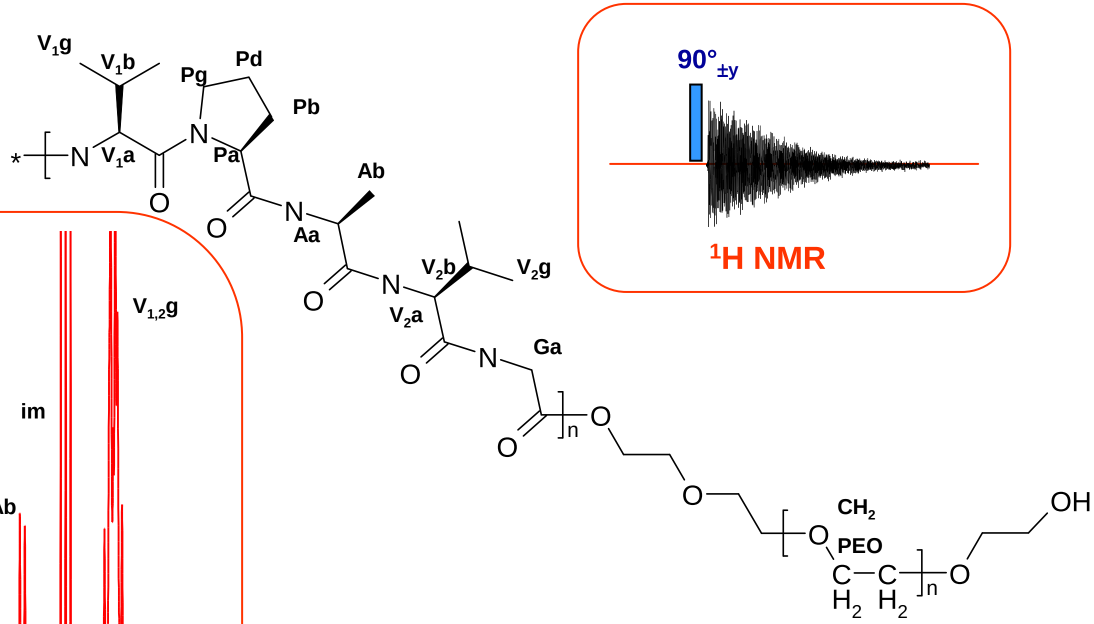
Methyl is perturbed by three possible combinations of spin states in the neighboring methylene.

^{1}H NMR spectra and polymers

1. Multiplicity rapidly disappears.
2. Signals are broadened with increasing molecular weight.
3. Determination of primary structure, composition and purity.

Chemical shift of the signals is specific for every structure unit.





(VPAVG)4-PEO-OH

Primary structure

^{1}H NMR spectra and polymers

1. **Determination of secondary structure.**

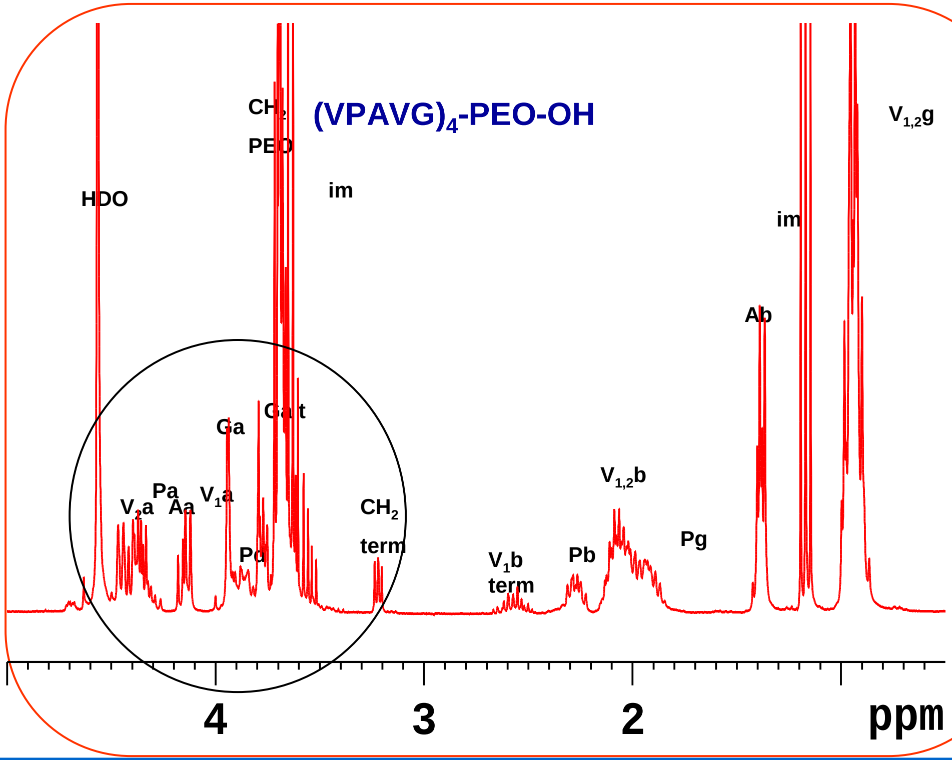
Chemical Shift Index (CSI)

Resolution of α-helix and β-sheet:

Chemical shift signals is specific for every structure unit and may reflects conformation of polypetide chain.

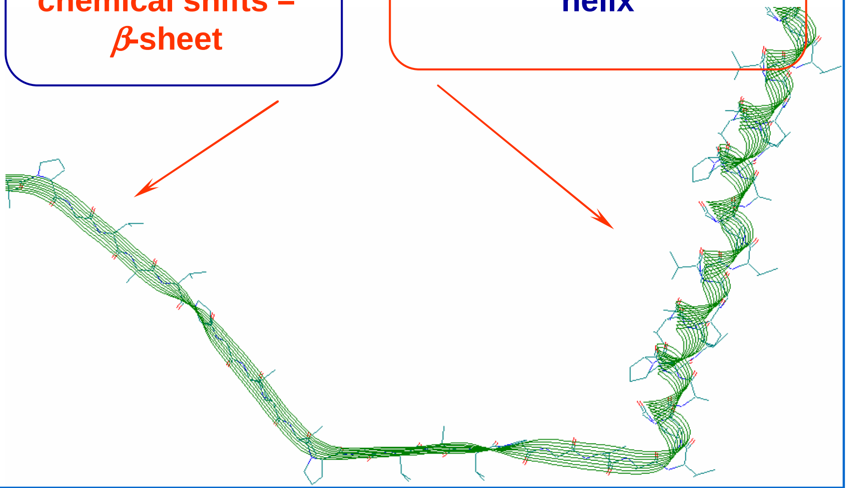
r.c. values of ^{1}H NMR Chemical shift:

Val1α – 4.44 ± 0.1 ppm
Proα – 4.42 ± 0.1 ppm
Alaα – 4.33 ± 0.1 ppm
Val2α – 3.95 ± 0.1 ppm
Glyα – 3.97 ± 0.1 ppm



Out of range toward higher values of chemical shifts – β-sheet

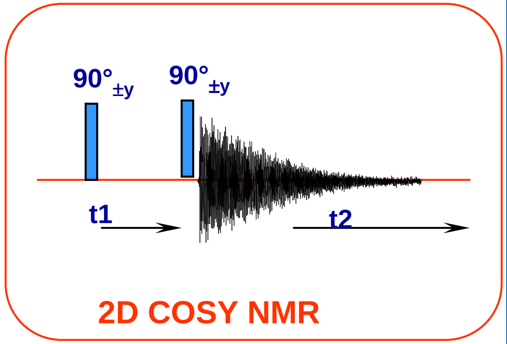
Out of range toward smaller values – α-helix

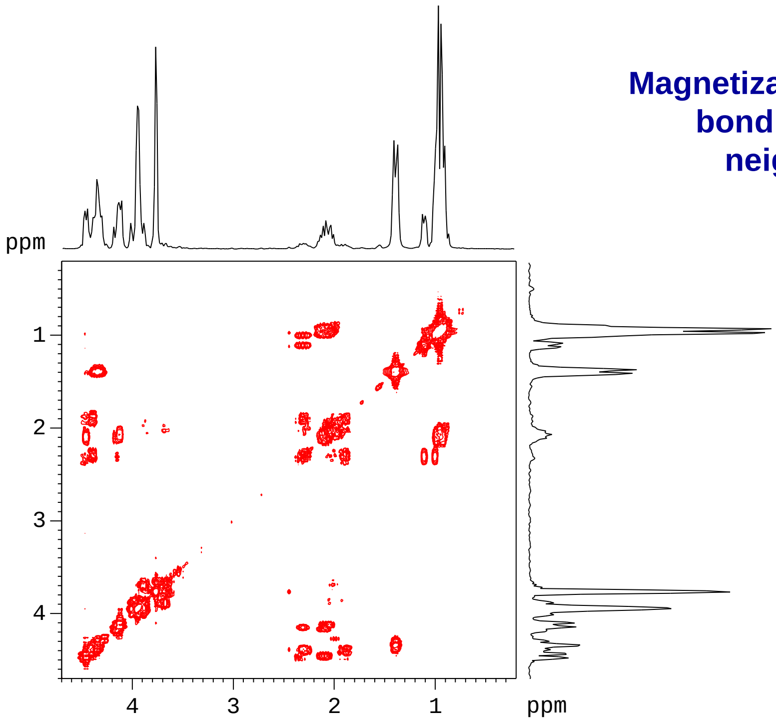


Two dimensional NMR spectra

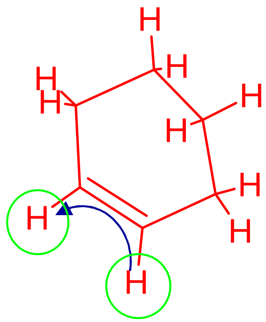
Basic principles of correlation spectroscopy

1. Enhancement of spectral resolution.
2. Two Fourier transformations.
3. At least two pulses.
4. Two detection periods.
5. Series of 1D NMR spectra recorded at gradually modified conditions.
6. Determination of connectivity of ^{1}H-^{1}H atoms in molecule.

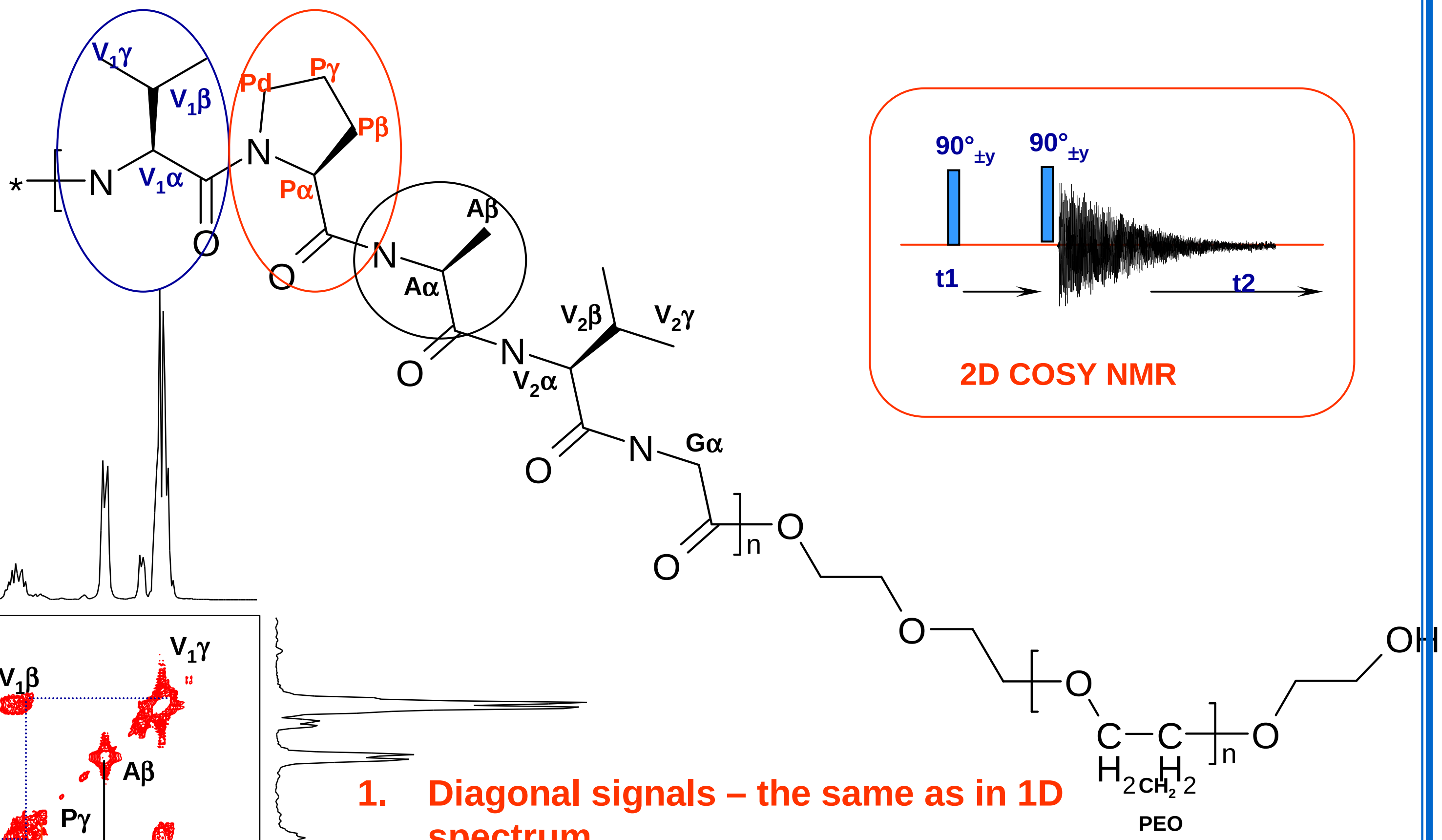


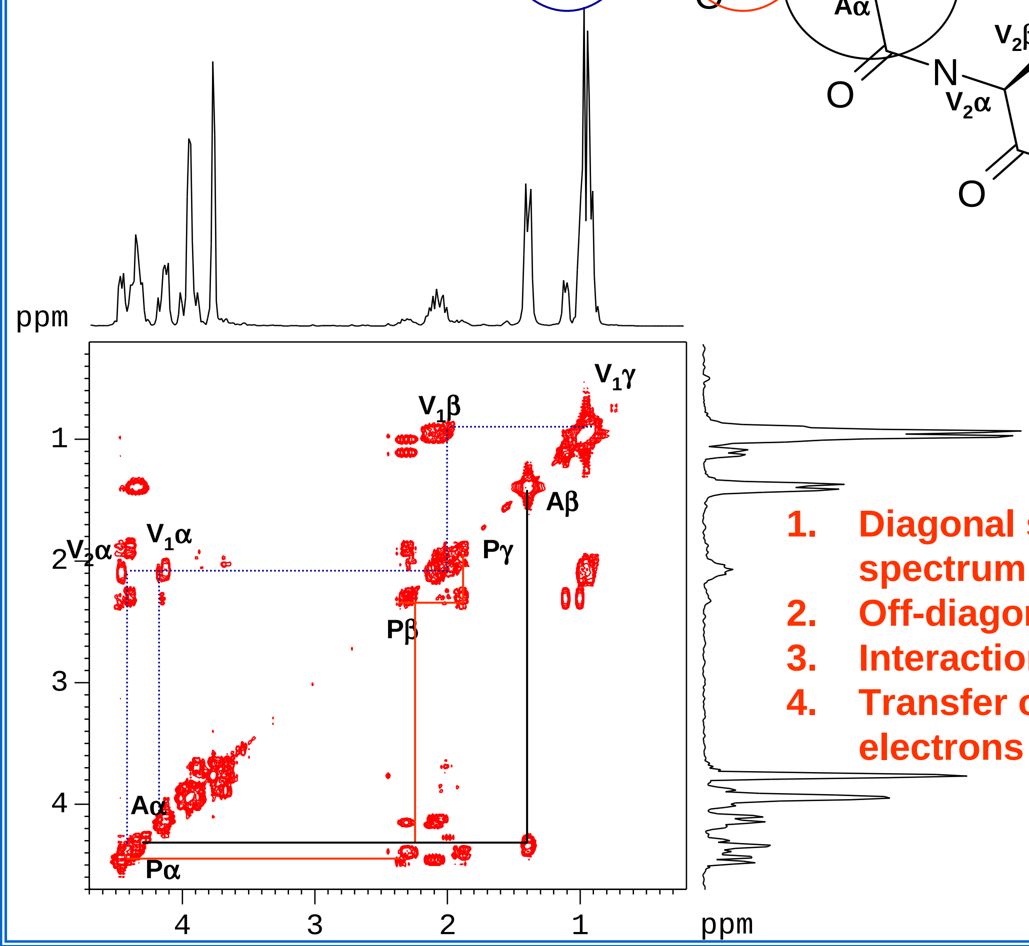


Magnetization is transferred via bonding electrons into neighboring nuclei

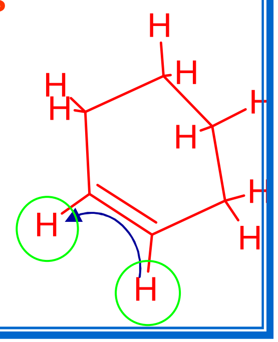


Two dimensional NMR spectra

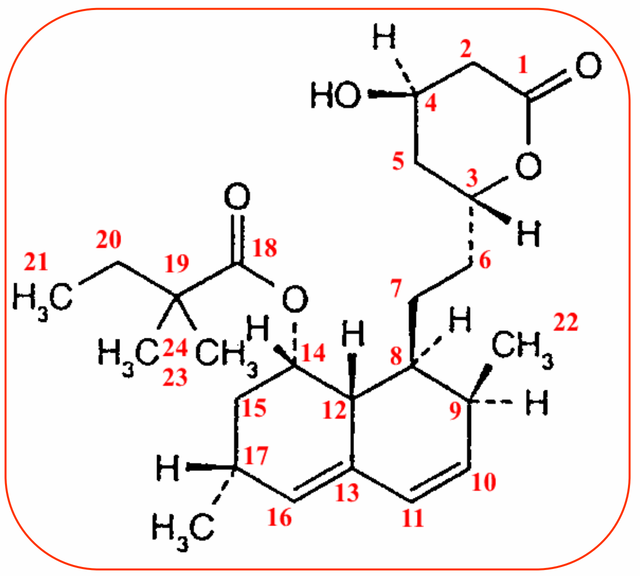


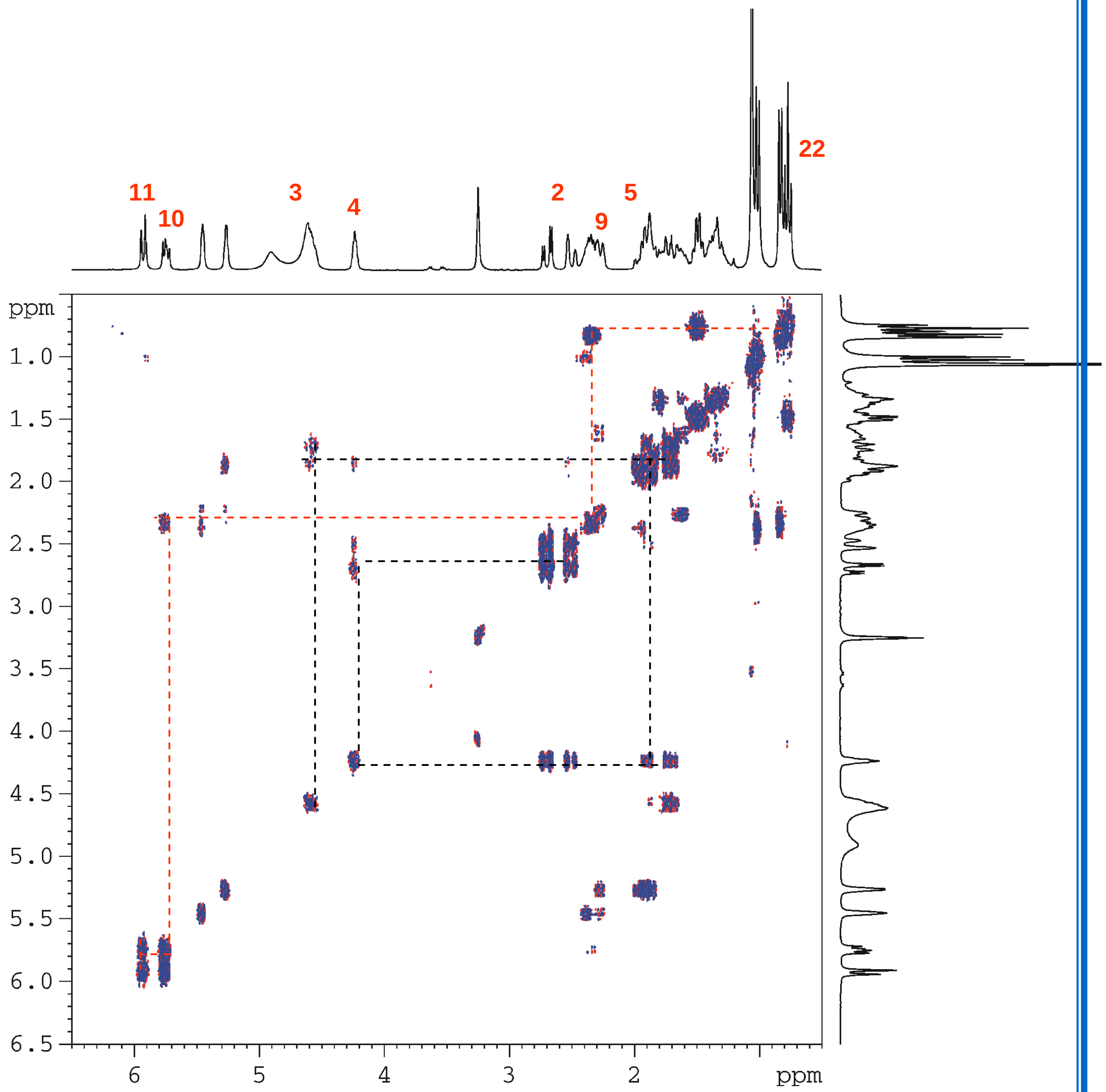


1. Diagonal signals – the same as in 1D spectrum
2. Off-diagonal signals – indicate correlations
3. Interaction of ^{1}H via 3 chemical bonds
4. Transfer of Magnetic energy – bonding electrons



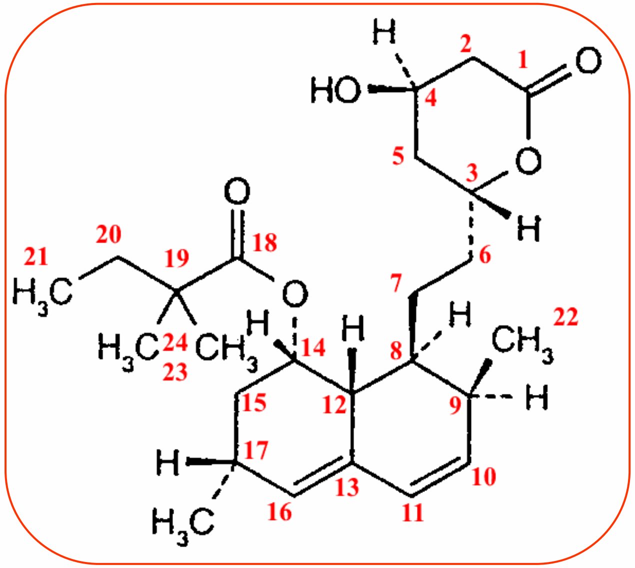
Two dimensional NMR spectra

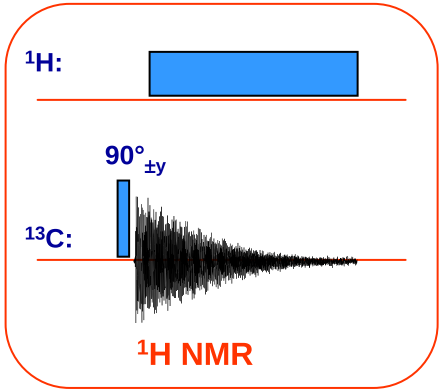




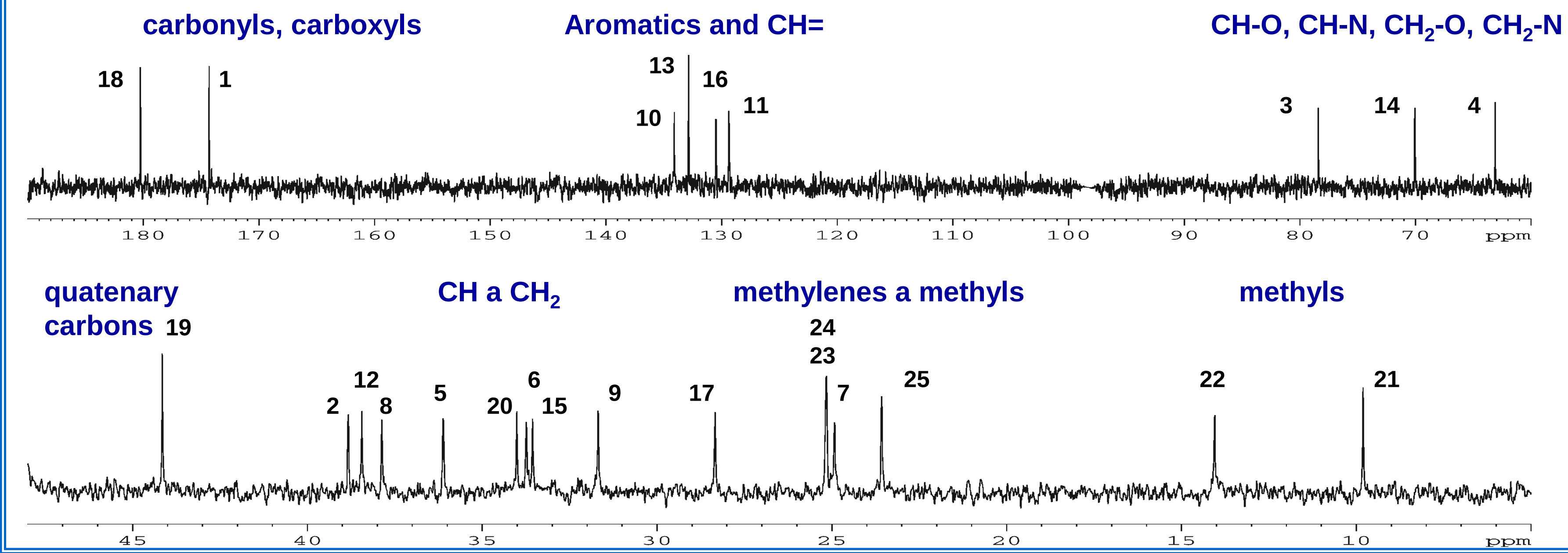
1. Trial and error
2. According to the expected structure we want to assign all signals
3. Sometimes the interaction network is broken
4. ^{1}H spectrum – low resolution
5. Signals are overlapped

One-dimensional ^{13}C NMR spectra



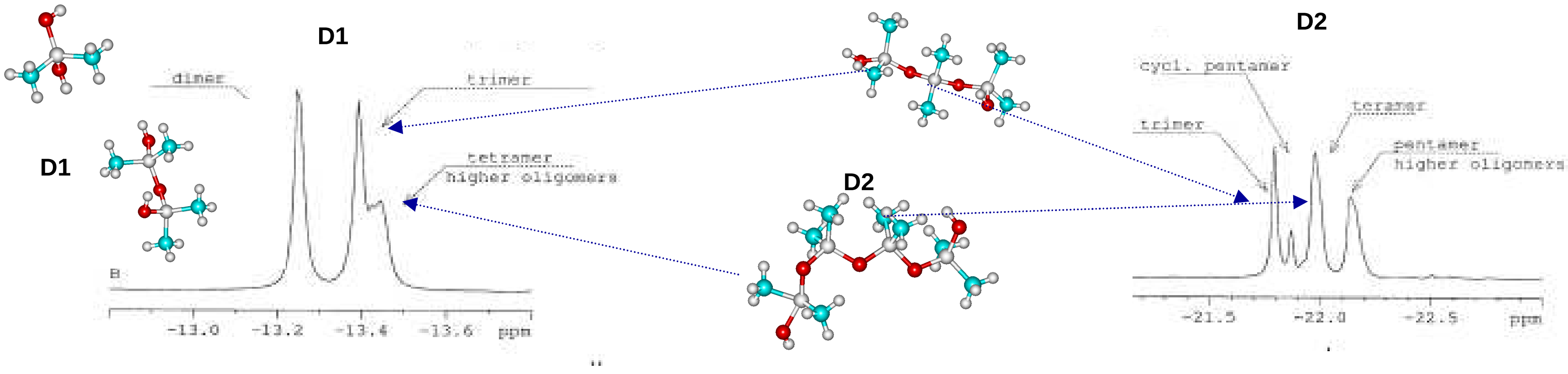


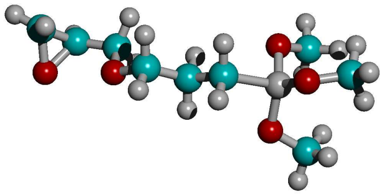
1. Low sensitivity
2. ^{13}C only 1% (^{1}H - 100%)
3. Enhanced spectral resolution
4. No fine multiplet structure
5. Spin decoupling

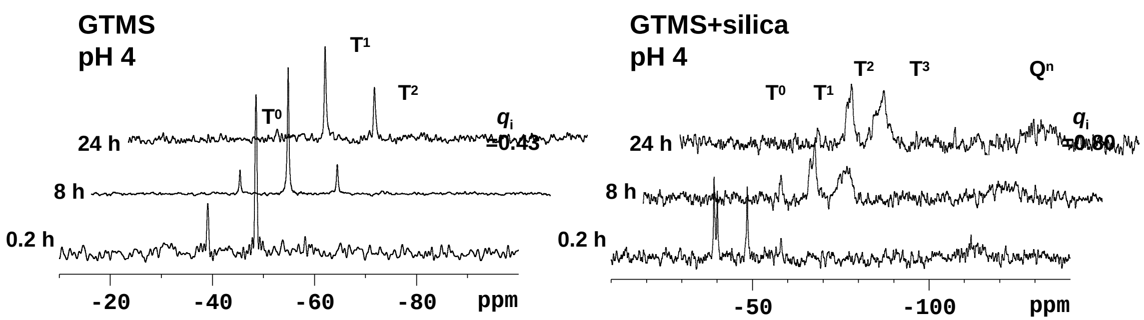


Distribution of polymerization degree

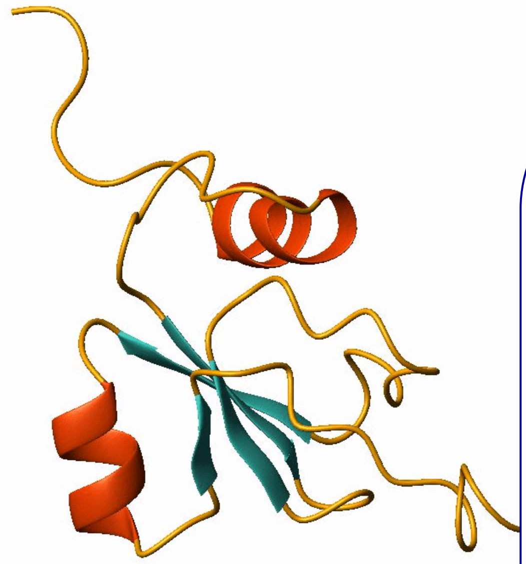
Alkoxysilane Polycondensation ^{29}Si NMR

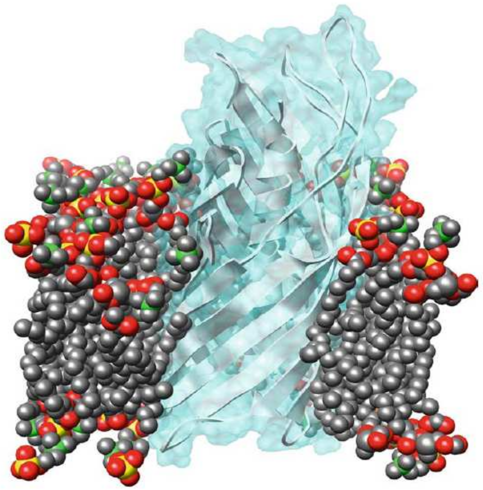




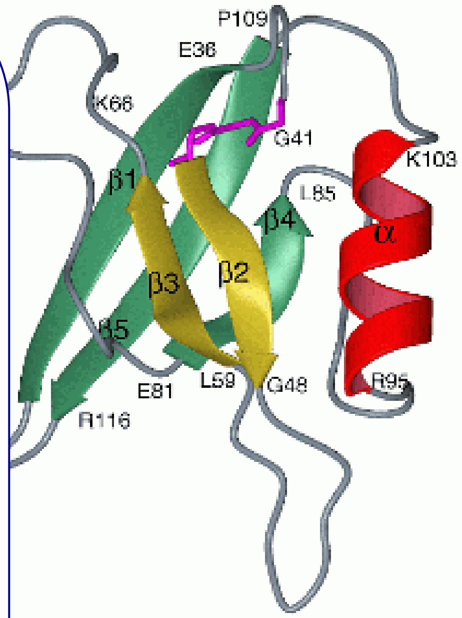


Structure of proteins in solution





Kurt Wüthrich
***1938**
2002 – Nobel Prize



UNESCO/IUPAC Postgraduate Course in Polymer Science

NMR spectroscopy of polymers in solution

- Institute of Macromolecular Chemistry ASCR, Heyrovsky sq. 2, Prague -162 06
- http://www.imc.cas.cz/unesco/index.html
- unesco.course@imc.cas.cz