Joint Laboratory of Solid-State NMR
IMC AS CZ and JHIPC AS CZ

Institute of Macromolecular
Chemistry AS CR
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162 06 Praha 6
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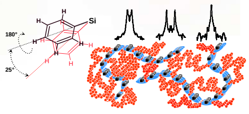
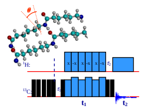
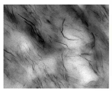
(1)

NMR spectroscopy in characterization of organic solids - overview

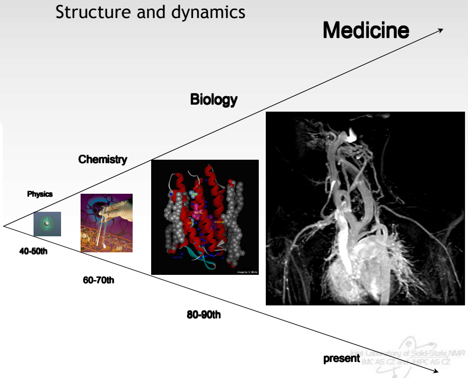
Schedule

- **Lecture 1. NMR spectroscopy in characterization of organic solids - overview**
  - Basic principles
  - First NMR signals
  - Sample rotation
  - Cross-polarization
  - 2D spectroscopy
  - NMR crystallography and polymer systems
- **Lecture 2. Dynamics of multicomponent polymer systems**
  - Principles of 1H-1H wide-line separation experiments
  - Determination of size of domains: motional averaging and spin diffusion
  - Location of external water molecules
  - Measurements of 1H-13C dipolar spectra
  - Models of segmental motions – motional amplitudes
  - Domain-selective experiments for polymer nanocomposites
- **Lecture 3. Structure of multicomponent polymer systems**
  - 2D spectroscopy
  - Spin-diffusion and multiple-pulse decoupling
  - Morphology of polymer blends and networks
  - Measurements of interatomic distances
  - NMR crystallography – refinement of 3D structure
- **Lecture 4. Structure of aluminosilicate materials**
  - Amorphous aluminosilicate inorganic polymers (AIP) – synthesis
  - Primary structural data about Al/Si materials – ^{29}Si a ^{27}Al MAS NMR
  - Amorphous-crystalline phase transition of AIPs
  - How to get structural parameters
  - Multiple-quantum experiments
  - Location of water molecules

NMR spectroscopy in chemistry, biology and medicine

Structure and dynamics

NMR spectroscopy



Dawn of the Universe and NMR

"Epoch of Nucleosynthesis" – 3 min – 400 000 years: 10^9-3000 K – formation of heavier nuclei

"Lepton Epoch" – 1s – 3 min: 10^{10}-10^9K – formation of protons

"Hadron Epoch" – 10^{-6}-1s: 10^{13}-10^{10}K – quarks combine to form protons and neutrons

"Electroweak Epoch" – 10^{-12}-10^{-6} s: 10^{15}-10^{13}K – formation of electrons and pozitrons

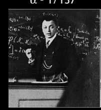
"Grand Unification Epoch" – 10^{-35}-10^{-12} s: 10^{27}-10^{15}K – formation of quarks

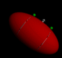
"Planck Epoch" – 10^{-43}-10^{-345}s: 10^{32}-10^{27}K

The Big Bang -time 0 s

time

α - 1/137



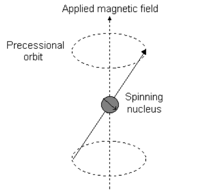


Spin predicted by W. Pauli in 1924 as the 4-th quantum number

1945 - Nobel Prize

Basic principles – spin precession

Rotating gyroscope in gravity field



Spin precession in magnetic field

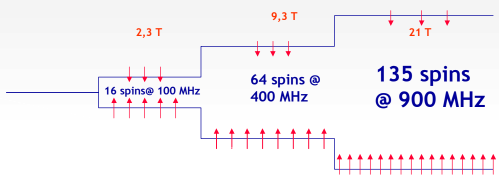
$\Delta E = h\nu = \omega_0/2\pi$

Spin precession in magnetic field 11.9T
1H: 500 MHz
13C:125 MHz
15N: 50 MHz

Energy levels – sensitivity

Increasing difference at energy levels with increasing intensity of magnetic field

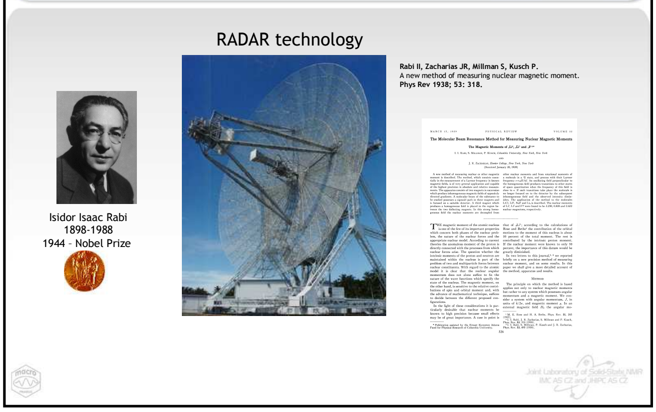
The difference for 1 000 000 spins is:



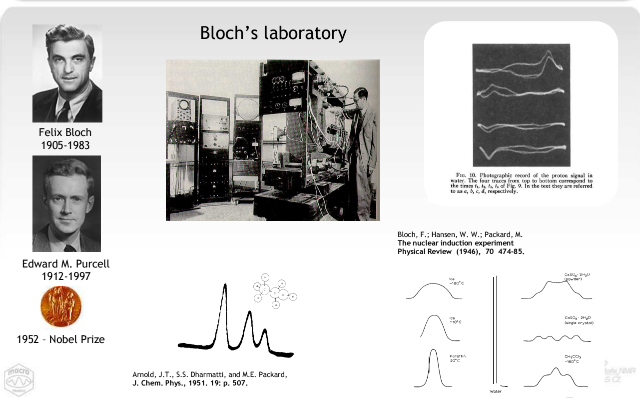
$$N_\alpha / N_\beta = e^{\Delta E/kT} = 1.000064.......(400MHz)$$

How to generate strong magnetic field

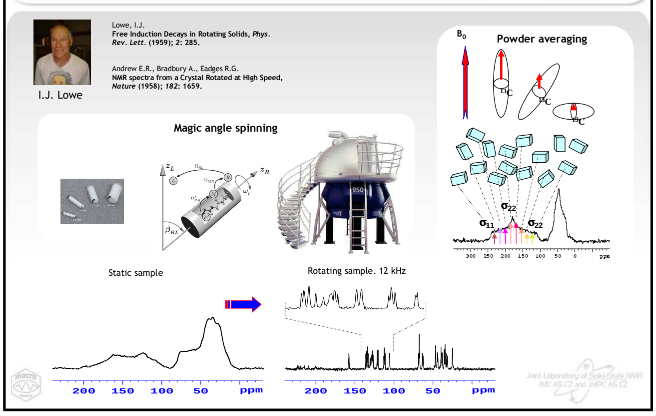
History – measurements of magnetic moment 1938



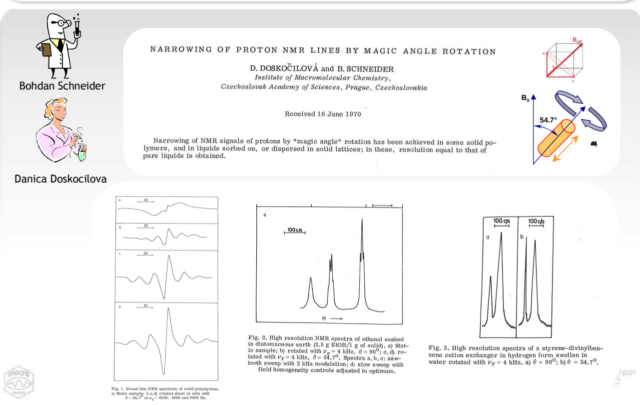
History – first NMR signals 1946-51



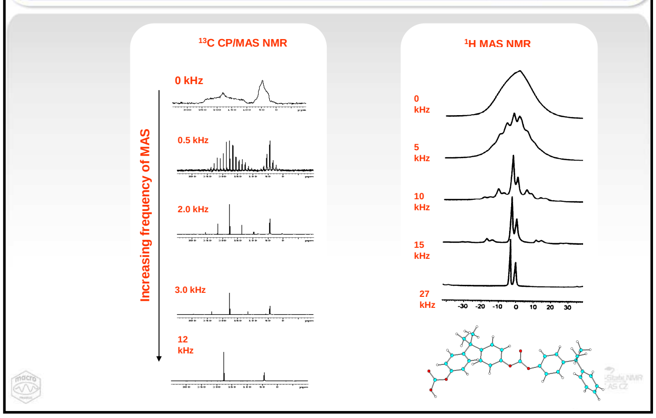
History – magic angle spinning 1958



History – MAS and proton NMR signals (1970)



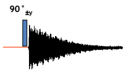
Line narrowing under MAS: ^{13}C vs. ^{1}H



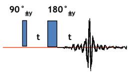
History – Hahn's experiments (1950-1962)

Erwin. L. Hahn
*1921

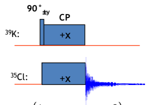
FID



Spin echo

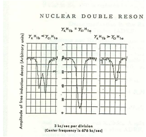


Cross polarization



$(\Delta = \omega_{1I} - \omega_{1S} = 0)$

$\gamma_K B_{1K} = \gamma_{Cl} B_{1Cl}$



Hahn, E. L.,
Spin echoes, *Phys. Rev.*, *80*, 580-594 (1950).

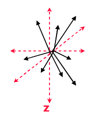
Hahn, E. L.,
Free nuclear induction, *Physics Today*, Nov. (1953), pp. 4-9.

Hartmann S.R., Hahn E.L.
Nuclear Double Resonance in Rotating Frame, *Phys. Rev.* (1962); *128*: 2042.

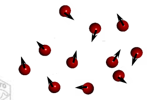
What happens in magnetic field

Spins out of magnetic field

No macroscopic magnetization

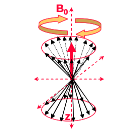


No phase coherence in the precession of spins

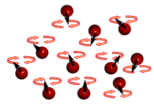


Spins in magnetic field

Longitudinal magnetization

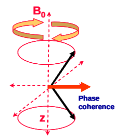


No phase coherence in the precession of spins

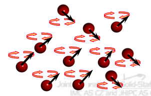


Spins after a pulse

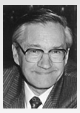
Transverse magnetization



Phase coherence of spin precession is created

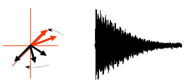


History – Pulsed NMR (1966, 1985 …….1822)

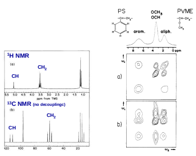


Richard R. Ernst
*1933
1991 – Nobel Prize

Free Induction Decay
FID



1D Spectra　　2D Spectra

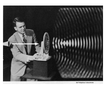


Ernst R.R., Anderson W.A.
Application of FT Spectroscopy to Magnetic resonance, *Rev.Sci.Instr. (1966); 37: 93*.

Caravatti P., Neuenschwander P., Ernst R.R.
Characterization of Heterogeneous Polymer Blends by 2D 1H Spin Diffusion Spectroscopy, *Macromolecules* (1985); 18: 119.

Jean Baptiste Joseph Fourier
1768-1830

Noise waves



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

Sheet of music

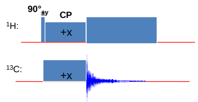
Fourier J.B.J.
Theorie analytique da la chaleur, *Firmin Didot, pere et fils, Paris. (1822).*

History – cross-polarization (1972)

Sensitivity enhancement

Alex Pines
*1945

Pines A., Gibby M.G., Waugh J.S.
Proton-Enhanced Nuclear Induction Spectroscopy. A Method for High Resolution NMR of Dilute Spins in Solids, *J. Chem. Phys.* (1972); *56*: 1776.

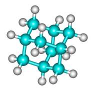


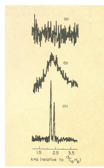
$(\Delta = \omega_{1I} - \omega_{1S} = 0)$

$\gamma_H B_{1H} = \gamma_C B_{1C}$

1) Transverse magnetization is created in ^{1}H spin system.
2) Then ^{1}H magnetization is spin-locked.
3) Hartmann-Hahn matching condition is established.
4) ^{13}C transverse magnetization is created.
5) Repetition period depends on the relaxation of ^{1}H spins (short).

Adamantane



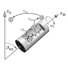


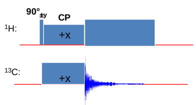
History – cross-polarization & MAS (1976)

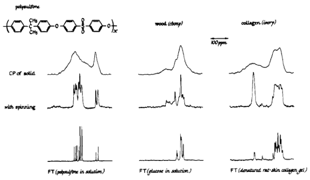
Sensitivity enhancement combined with MAS

J. Schaefer

Schaefer J., Stejskal E.O.J.
^{13}C NMR of Polymers Spinning at Magic Angle, *J. Am. Chem. Soc.* (1976); *98*: 1031.



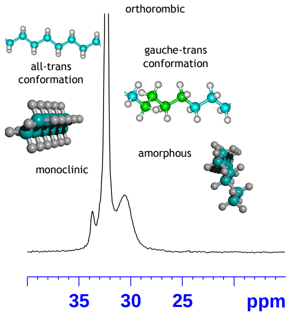




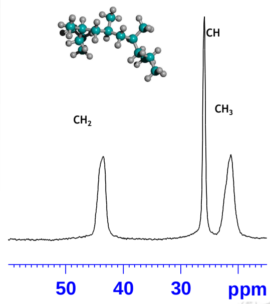
1) **Sample rotates at magic angle to remove chemical shift anisotropy broadening**
2) Transverse magnetization is created in ^{1}H spin system.
3) Then ^{1}H magnetization is spin-locked.
4) Hartmann-Hahn matching condition is established.
5) ^{13}C transverse magnetization is created.
6) Repetition period depends on the relaxation of ^{1}H spins (short).

Typical solid-state NMR spectra of polymers

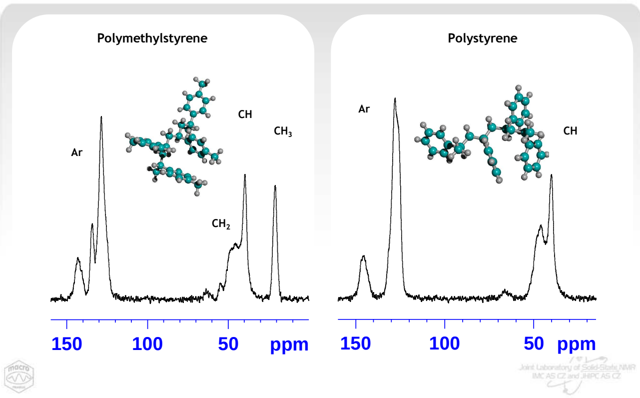
Polyethylene



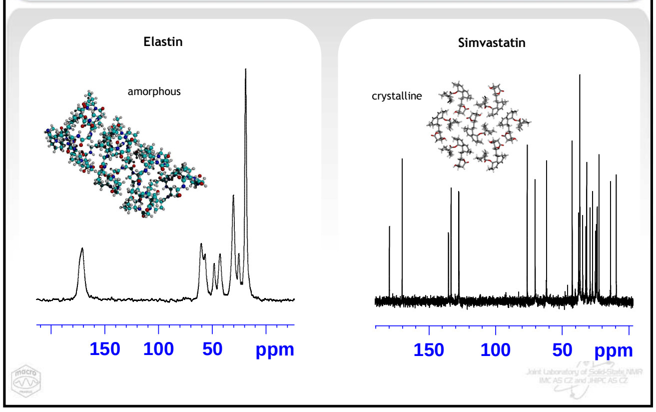
Polypropylene



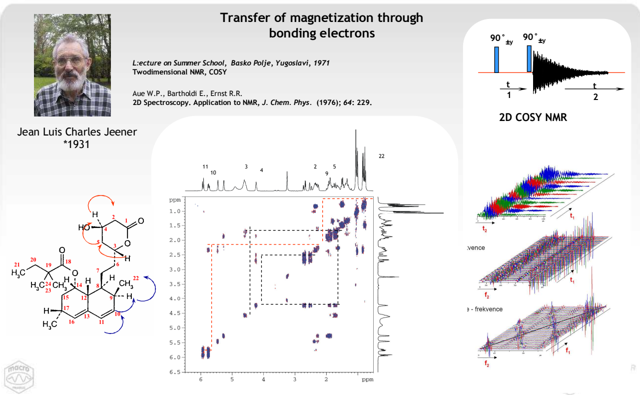
Typical solid-state NMR spectra of polymers



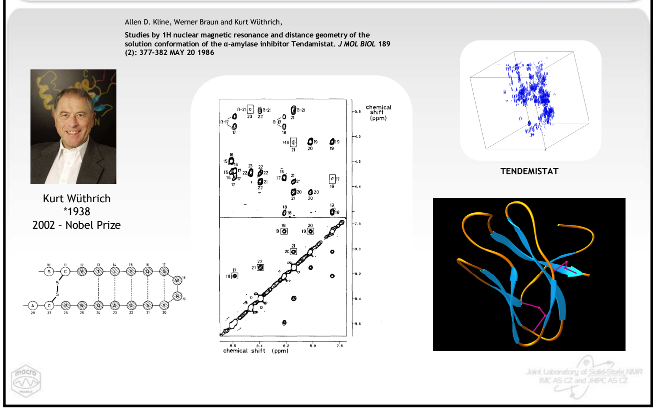
Typical ss NMR spectra amorphs and crystals



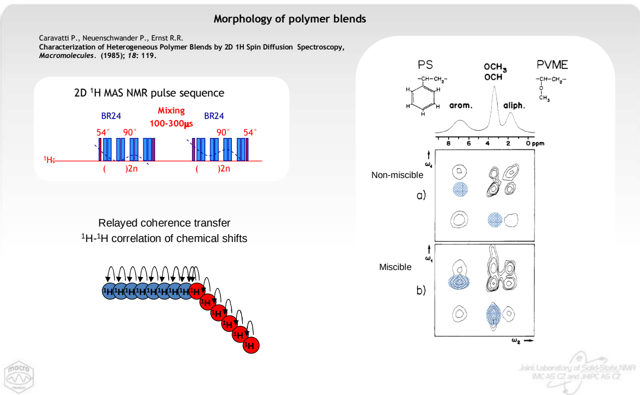
Two-dimensional NMR spectroscopy(1971)



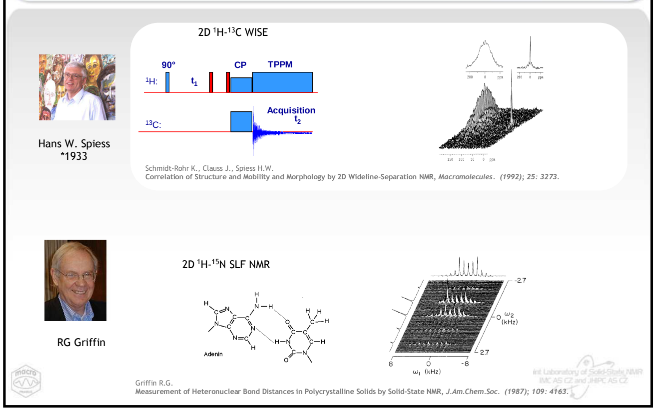
3D structure of proteins (1986)



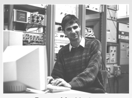
2D correlation experiments in solid state – 1985



Separation experiments (1987 …….1995)

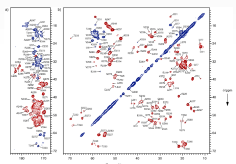


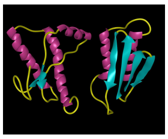
3D structure of prion proteins (2005)

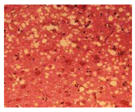


Meier B.H. et al.,
Correlation of Structural Elements and Infectivity of the HET-s prion, *Nature* (2005); *435(9)*: 844.

2D ^{13}C-^{13}C DREAM NMR

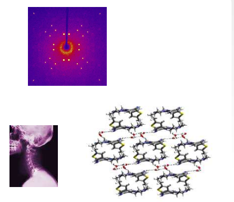






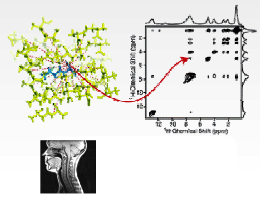
NMR crystallography

XRD



Reutzel-Edens S. et al. *Crystal Growth & Design 3, 897 (2003)*

ss-NMR

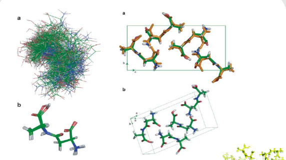


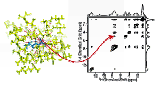
Elena B. et al. *J. Am. Chem. Soc.* (2006); *128, 9555.*

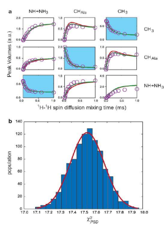
Crystal structure refinement – ^{1}H spin diffusion

Elena B. et al.
Solid-state 1H NMR crystallography, *J. Am. Chem. Soc.* (2005); *127(25)*, 9140.

Elena B. et al.
Molecular Structure Determination in Powders by NMR Crystallography from Proton Spin Diffusion, *J. Am. Chem. Soc.* (2006); *128, 9555*.







$$\frac{d\mathbf{M}}{dt} = -\mathbf{K}(\mathbf{M}-\mathbf{M}_0) \quad k_{ij} = \sum_{\lambda}\left(\frac{\mu_0\gamma^2\hbar}{4\pi}\right)^2 \frac{A}{(r_{ij}^n)_\lambda} \quad k_{ii} = -\sum_j k_{ij}$$

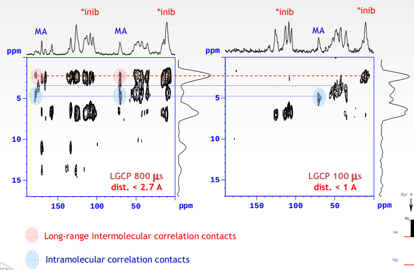
$$\mathbf{M}(t,\tau_{SD}) = \exp(-\mathbf{K}\tau_{SD})\mathbf{M}_z(t,0) \quad \mathbf{P}(\tau_{SD}) = \exp(-\mathbf{K}\tau_{SD})\mathbf{M}_z^e$$

n … Functional dependence on internuclear distance

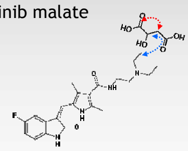
$$\chi^2 = \sum \frac{(calc_i - t_i)^2}{\sigma_i^2}$$

Crystal structure … – intermolecular contacts

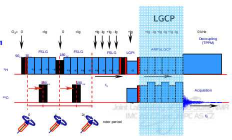
^{13}C-^{1}H HETCOR NMR



*inib malate



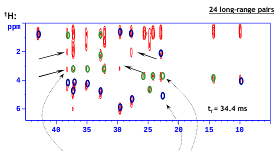
^{13}C-^{1}H HETCOR NMR

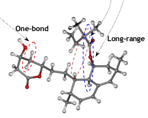


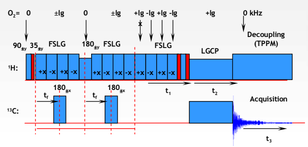
Crystal structure … – interatomic distances

Dipolar couplings and interatomic distances
Basic experimental approach

Extended 3D experiment
REDOR dephased ^{1}H-^{13}C FSLG-LGCP-HETCOR







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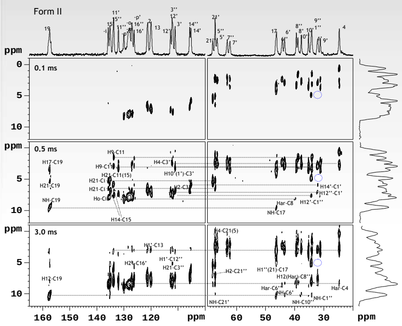
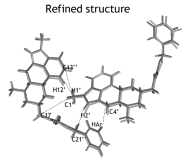
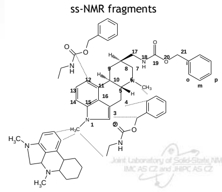
Structural fragments of Metergoline II



Refined structure



ss-NMR fragments



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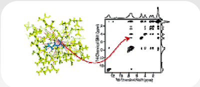
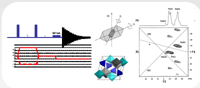
Summary

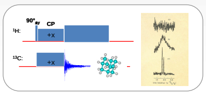
NMR crystallography



MQ/MAS NMR – inorganic systems

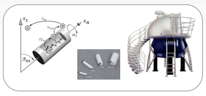


Cross-polarization

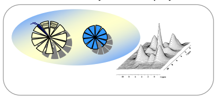


Solid-state NMR and ....

MAS – magic angle spinning



Structure and dynamics of polymers



Structure of proteins