Polarised Nucleon Targets for Europe, 1st meeting, Bochum 2004

Advanced Nuclear Magnetic Resonance

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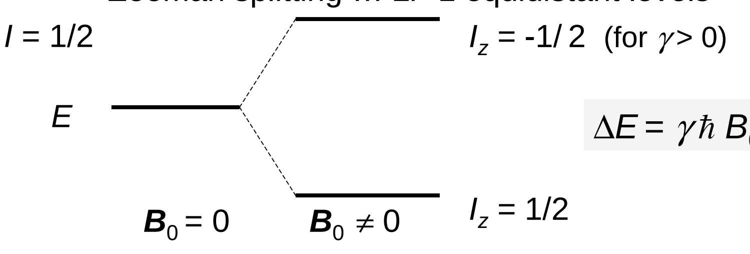
- ❖ NMR at Charles University Prague
- ❖ Experimental techniques, spectra and relaxations
- ❖ Outlook

Introduction

Nuclear magnetic resonance (NMR)

Nucleus with nonzero total angular momentum **(spin)** $\boldsymbol{I}$
nonzero magnetic dipolar momentum $\boldsymbol{\mu} = \gamma \hbar \boldsymbol{I}$
($\gamma \ldots$gyromagnetic ratio)

In a static magnetic field $B_0 \parallel z$ energy depends on μ_z
Zeeman splitting … $2I+1$ equidistant levels



$\Delta E = \gamma \hbar B_0$

Radiofrequency field induces transitions if $\omega_{rf} = \gamma B_0$
(Larmor frequency)

Resonating nucleus = probe sensitive to the local static field B_0

NMR at Charles University Prague

2 laboratories:

High resolution NMR (since 1999)

narrow spectral ranges, narrow spectral lines,T ~ T_{room}

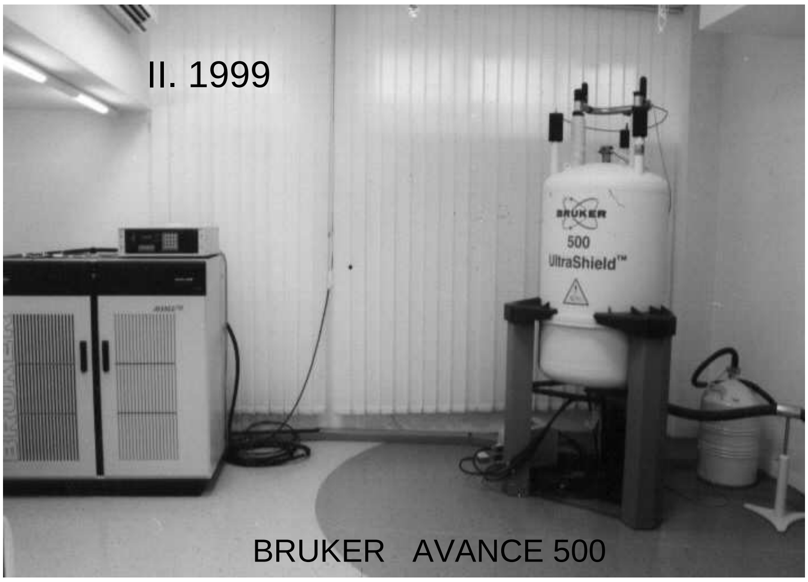
(liquids, solutions of organic molecules, biomolecules and polymers, solids - MAS)

$B_{external}$ = 11.7 T (500 MHz for ^{1}H, 125 MHz for ^{13}C)

NMR of broad spectral lines (since ~ 1965)

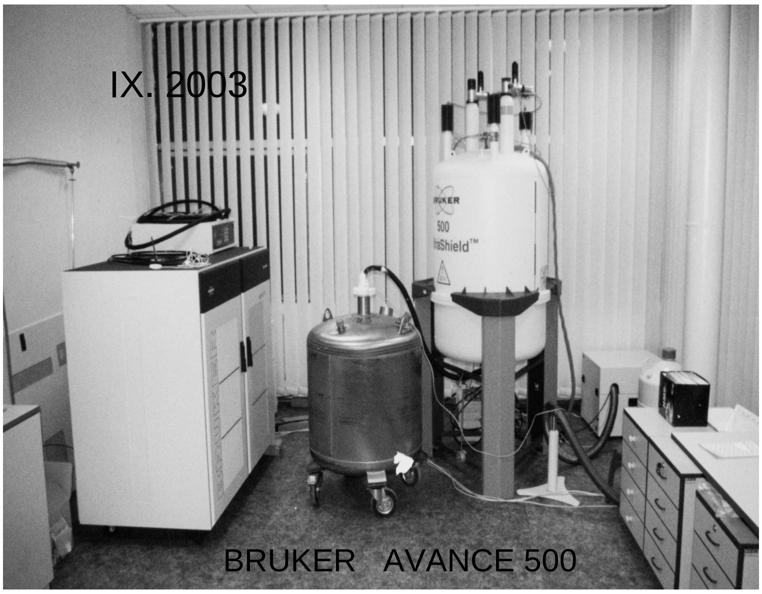
NMR at Charles University Prague

High resolution NMR (since 1999)



NMR at Charles University Prague

High resolution NMR (since 1999)



NMR at Charles University Prague

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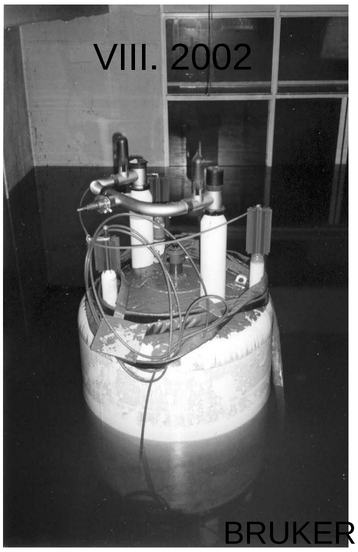

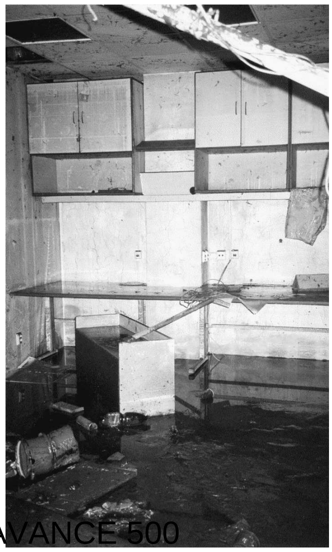

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NMR at Charles University Prague

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$B_{external}$ = 11.7 T (500 MHz for ^{1}H, 125 MHz for ^{13}C)

NMR of broad spectral lines (since ~ 1965)

broad band spectrometer, spectral range 6 –700 MHz,

T~ 4.2 – 500 K

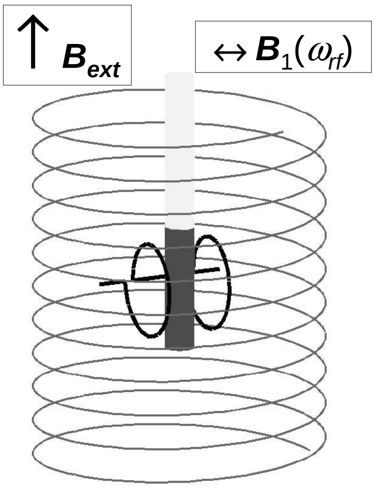
(solids, mainly magnetic materials; also NQR;

spectra mostly measured without external static magnetic field)

NMR at Charles University Prague

NMR of broad spectral lines (since ~ 1965)

NMR experiment



Spectrum

relative amount of nuclei resonating at different frequencies

Relaxation times

spin-lattice relaxation T_1

spin-spin relaxation T_2

Nuclear magnetization m

differences in population of energy levels

Rotating reference frame S'

effective field B_{eff}

$(\boldsymbol{B}_{eff})_z = B_0 - \omega_{rf}/\gamma = \Delta\omega/\gamma$

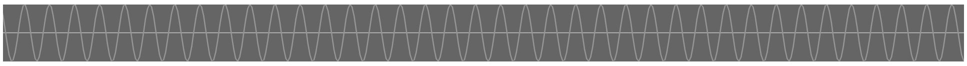
$\Delta\omega$ … offset

$(\boldsymbol{B}_{eff})_\perp = B_1$

$\delta \boldsymbol{m}/\delta t$ …torsion $\boldsymbol{m} \times \boldsymbol{B}_{eff}$

CW NMR experiments

CW… continuous wave



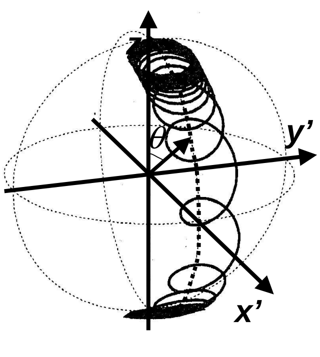
Frequency sweep - various conditions

- stationary passage

(slow with respect to relaxations)

⋮

- adiabatic fast passage



(in a time short compared to relaxations)

sweeping starts and ends at a large offset $\Delta\omega$,

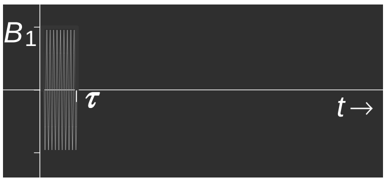
magnetization remains aligned with B_{eff}

if the sweep rate is sufficently slow

(dΘ/dt << γB_{eff}, critical dΘ/dt <<γB_1

Θ… *inclination of* B_{eff} *from z-axis*)

Pulsed NMR experiments



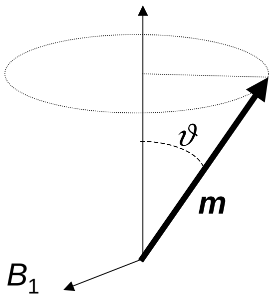
Pulsed rf field

- short pulse $\tau \sim \mu s$
- amplitude B_1
- frequency $\omega_{rf} \sim \omega_0 \equiv \gamma B_0$

In S´ (= noninertial system of coord. rotating around z with ω_{rf} , $x'||\mathbf{B}_1$):

precession of $\boldsymbol{m}$ around

$\mathbf{B}_{eff} = (B_1, 0, B_o - \omega_{rf} / \gamma) \approx (B_1, 0, 0)$

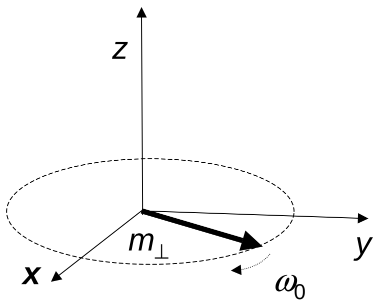


$t = 0$ … $\boldsymbol{m}||z$
$t = \tau$ … $\vartheta = \gamma B_1 \tau$
spec. $\vartheta = \pi/2$ … $\pi/2$ pulz

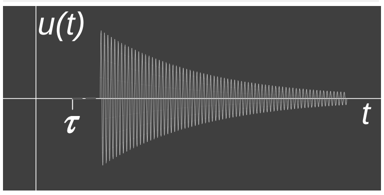
Pulsed NMR experiments

FID = free induction decay

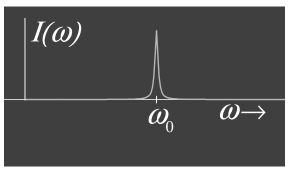
$\mathbf{B}_0||z$, *homogeneous,* $\mathbf{B}_1 \perp z$, $\omega_{rf} \approx \omega_0 = \gamma B_0$



$u(t) \sim N e^{-t/T_2} \cos(\omega_0 t + \beta)$



FOURIER TRANSFORM



FID

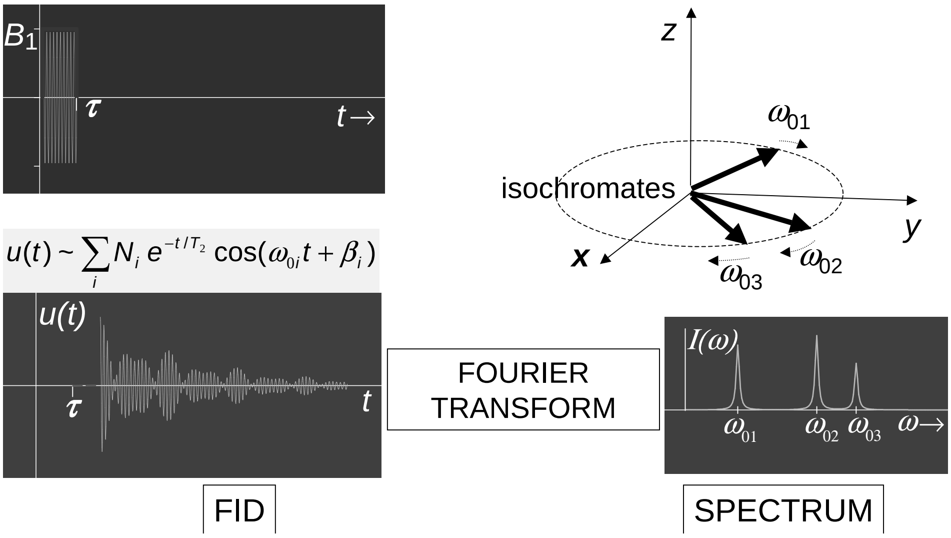
SPECTRUM

Pulsed NMR experiments

FID = free induction decay

Distribution of Larmor frequencies,

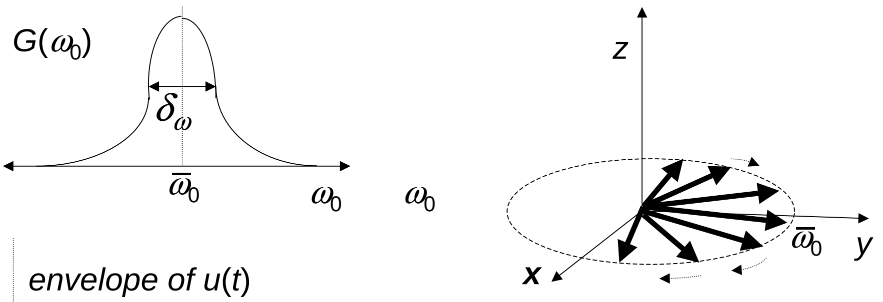
inequivalent sites of resonating nuclei $\omega_{01} < \omega_{02} < \omega_{03}$

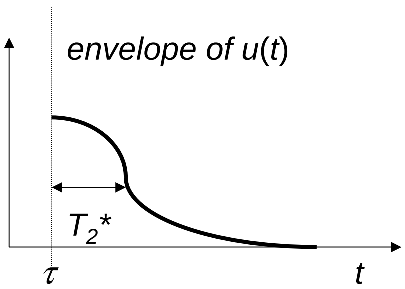


Pulsed NMR experiments

FID = free induction decay

Broad distribution of Larmor frequencies $G(\omega_0)$





Decay of $u(t)$ determined by $T_2^* << T_2$

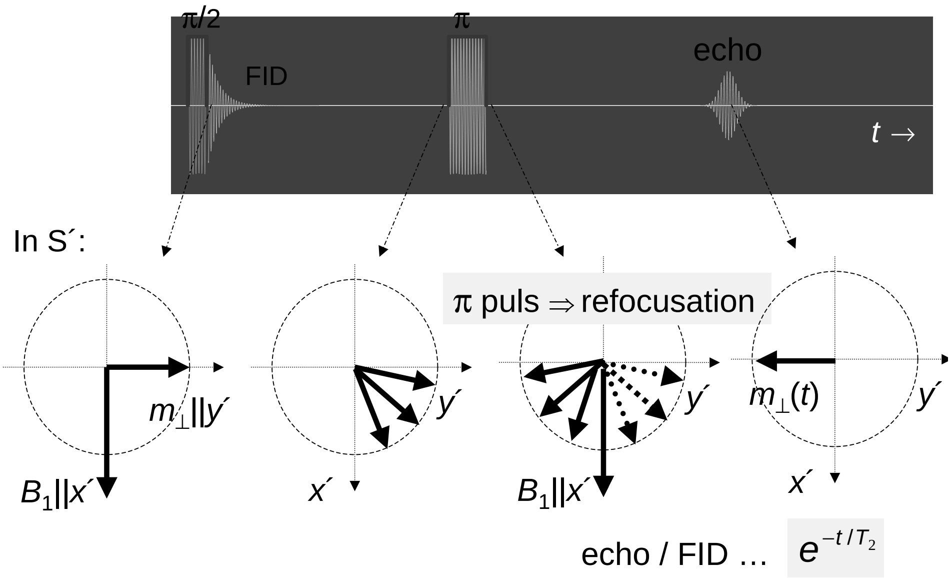
Broader $G(\omega_0) \Rightarrow$ faster FID decay

$T_2^* \sim 1/\delta_\omega$

Pulsed NMR experiments

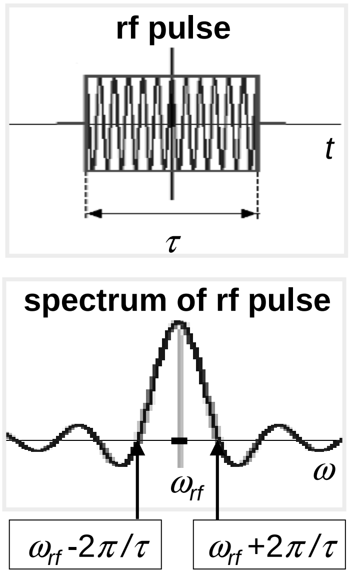
Spin echo

Distribution of Larmor frequencies

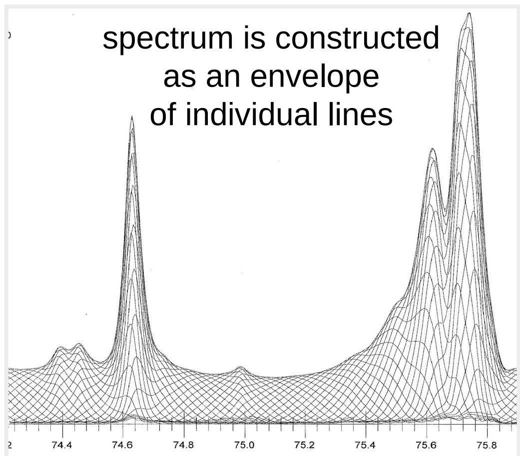


Pulsed NMR experiments

Broad lines – pulse does not excite the whole spectral range



Frequency is changed step by step,



Application of pulsed NMR to the nuclear polarisation measurement

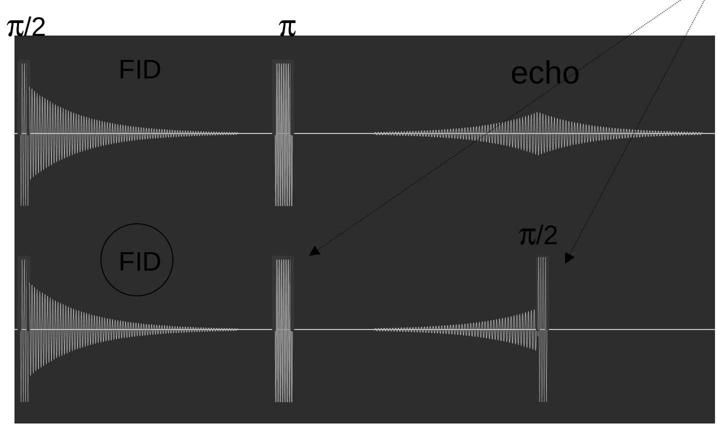
Pulsed rf field destroys polarisation in the $\boldsymbol{B}_{ext}$ direction

How to minimize this effect?

- turning angles smaller than $\pi/2$, π
- return of magnetization to z by additional pulses

Application of pulsed NMR to the nuclear polarisation measurement

Measured FID, magnetization returned to z by additional pulses

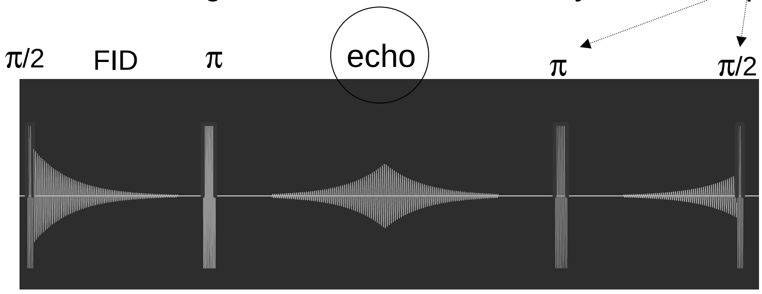


Decrease of magnetization during the sequence duration depends (in addition to T_1 relaxation) on T_2 relaxation

? relation between T_1 and T_2 ?

Application of pulsed NMR to the nuclear polarisation measurement

Measured echo, magnetization returned to z by additional pulses



Decrease of magnetization during the sequence duration depends (in addition to T_1 relaxation) on T_2 relaxation

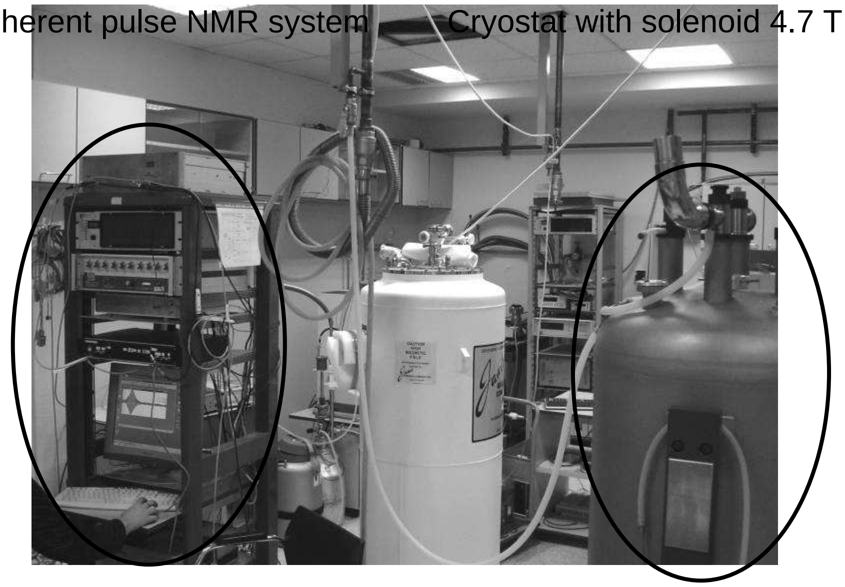
? relation between T_1 and T_2 ?

Building of NMR spectrometer and accessories for the project

- Cryostat with a superconducting solenoid, magnetic field 4.7T (200 MHz for ^{1}H), bore 52 mm
- Pulse NMR system with coherent data summation + subsequent FFT, broad band
- Dewar insert for liquid N_2
- Continuous flow cryostat
- NMR probes

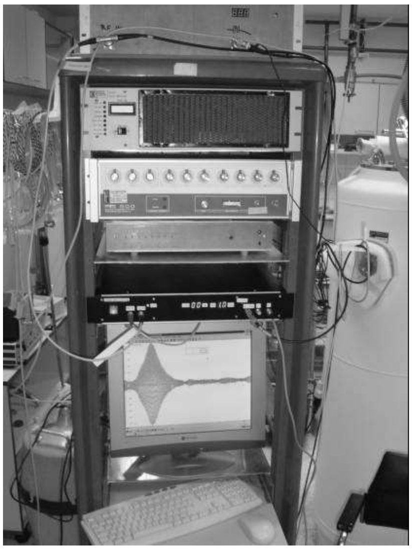
Building of NMR spectrometer and accessories for the project

Coherent pulse NMR system Cryostat with solenoid 4.7 T



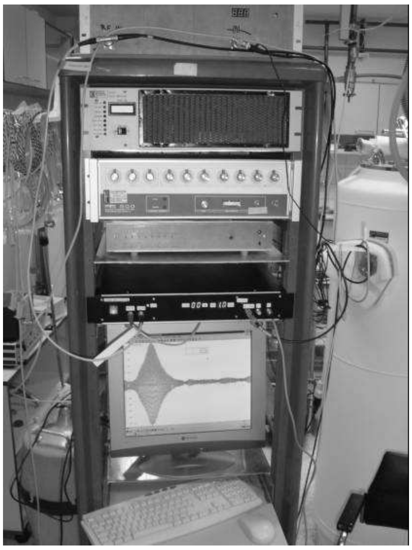
Building of NMR spectrometer and accessories for the project

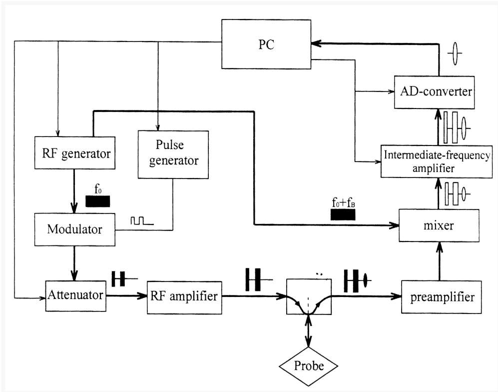
Coherent pulse NMR system Cryostat with solenoid 4.7 T



Building of NMR spectrometer and accessories for the project

Coherent pulse NMR system





Block scheme

Applicability of NMR to characterization of condensed materials

Study of defects / impurities

- the local magnetic field at the resonating nucleus is modified when an impurity is present in its vicinity

- a characteristic shift of NMR frequency is induced

- <u>satellite lines</u> appear in the spectrum

- satellite intensities are proportional to the defect concentration

Applicability:

- single crystals, polycrystalline samples

Sensitivity:

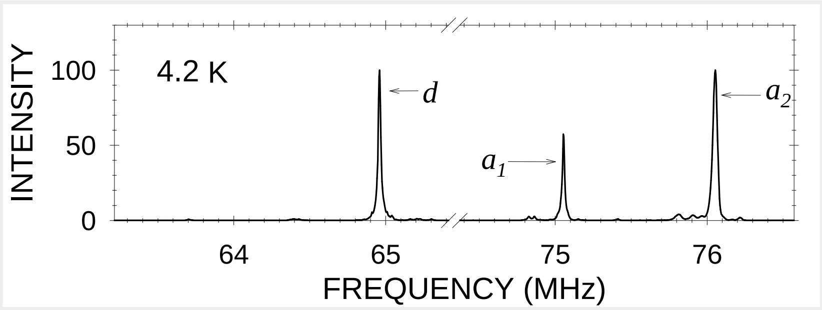
- ~0.01% of defect concentration

Applicability of NMR in characterization of condensed materials

Study of defects / impurities

Example: $Y_3Fe_5O_{12}$ (yttrium iron garnet), ^{57}Fe NMR

3 magnetically inequivalent iron sites
3 lines in a spectrum of nominally pure sample

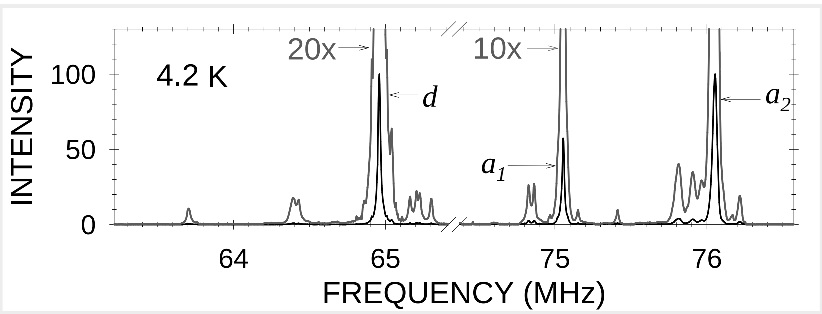


Applicability of NMR to characterization of condensed materials

Study of defects / impurities

Example: $Y_3Fe_5O_{12}$ (yttrium iron garnet), ^{57}Fe NMR

3 magnetically inequivalent iron sites
3 lines in a spectrum of nominally pure sample
satellite pattern coresponding to intrinsic antisite defects
(Y replaces Fe)



Applicability of NMR to characterization of condensed materials

Study of spin dynamics

Relaxation mechanisms due to electron spin:

dipolar interaction

Fermi contact interaction

Diffusion of atoms /molecules (chemical exchange)

Spin diffusion

Fluctuations of magnetic interactions at zero, ω_0, $2\omega_0$ …

models of atomic (molecular) motion

Concentration, temperature, field dependences

Outlook

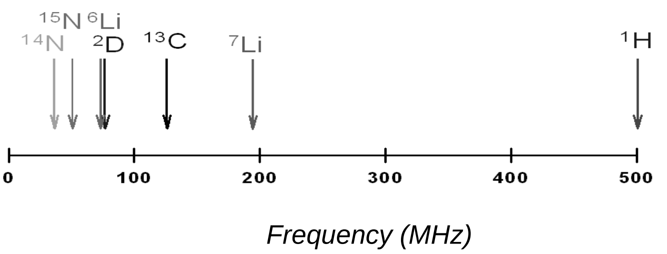
Experimental requirements

NMR, irradiation, sample handling

Spectra and relaxation measurements

alcohols + chemical radicals, NMR in liquid an solid states – relaxations, ESR of free radicals

LiD, LiD irradiated – defects, relaxation



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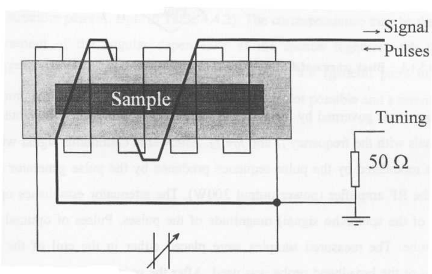
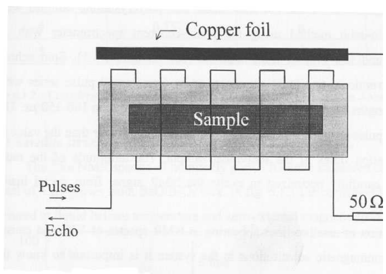
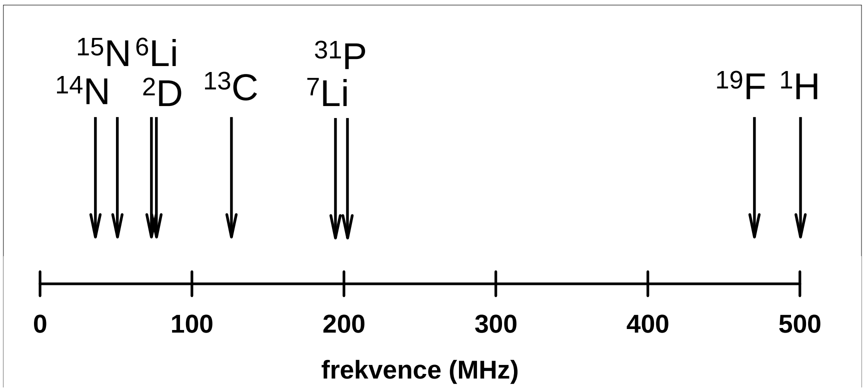


Tuned NMR probe.



Broadband NMR probe.

Rezonanční frekvence vybraných izotopů v poli 11,7 T



NMR at Charles University Prague

NMR in basic laboratory training courses