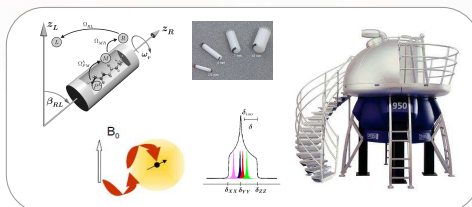


Anizotropní interakce v pevných látkách (CSA, DC, MAS, dipolární dekaplink)



Anizotropie chemického posunu a MAR - 1958

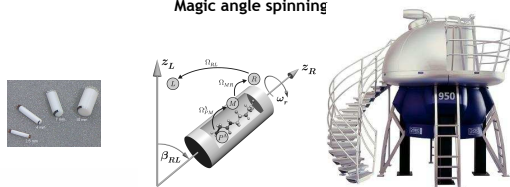


I.J. Lowe

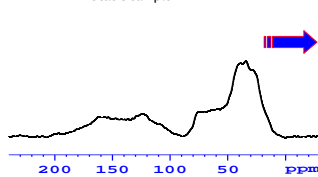
Lowe, I.J.
Free Induction Decays in Rotating Solids, *Phys. Rev. Lett.* (1959); 2: 285.

Andrew E.R., Bradbury A., Eadges R.G.
NMR spectra from a Crystal Rotated at High Speed, *Nature* (1958); 182: 1659.

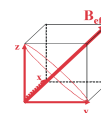
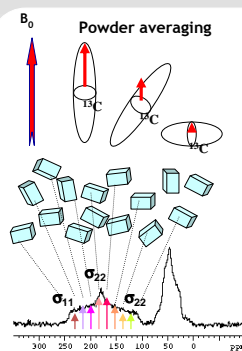
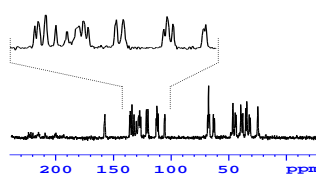
Magic angle spinning



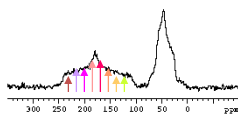
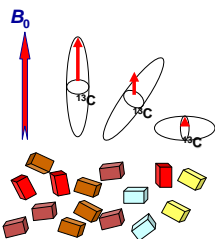
Static sample



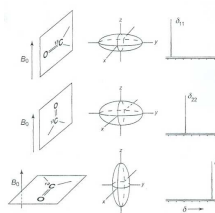
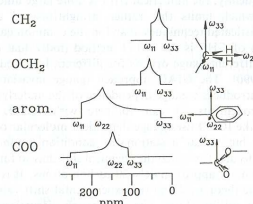
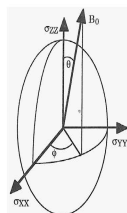
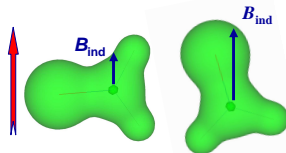
Rotating sample. 12 kHz



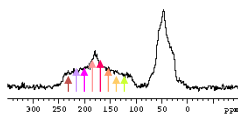
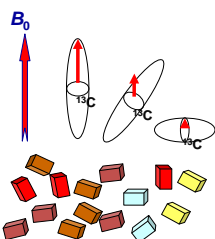
Anizotropie chemického posunu



Každý spin individuálně přispívá svou vlastní frekvencí k výslednému spektru překryv mnoha signálů



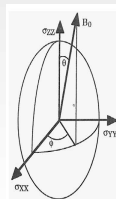
Anizotropie chemického posunu



Každý spin individuálně přispívá svou vlastní frekvencí k výslednému spektru překryv mnoha signálů

Hamiltonián chemického posunu

$$\hat{H}_{CS} = \left\{ \sigma_{iso} + \frac{1}{2} \delta_{CS} [3 \cos^2 \theta - 1 - \eta_{CS} \sin^2 \theta \cos(2\phi)] \right\} \gamma B_0 \hat{I}_z$$



Isotropní složka

$$\sigma_{iso}$$



anisotropní složka

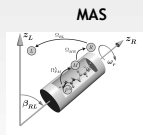
$$+ \frac{\delta}{2} (3 \cos^2 \theta - 1 - \eta \sin^2 \theta \cos 2\phi)$$



Rotace vzorku pod magickým úhlem - MAS

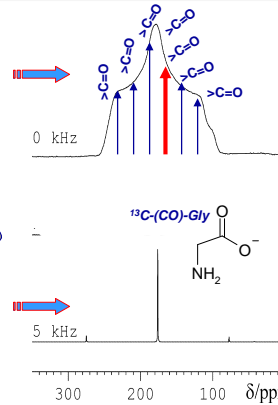
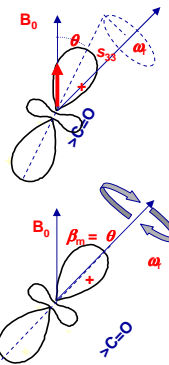
Hamiltonián chemického posunu

$$\hat{H}_{CS} = \left\{ \sigma_{iso} + \frac{1}{2} \delta_{CS} [3 \cos^2 \theta - 1 - \eta_{CS} \sin^2 \theta \cos(2\phi)] \right\} \gamma B_0 \hat{I}_z$$



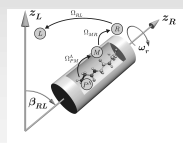
MAS

$$\hat{H}_{CS} = \left\{ \sigma_{iso} + \frac{1}{2} \delta_{CS} [0 - 0] \right\} \gamma B_0 \hat{I}_z = \sigma_{iso} \gamma B_0$$

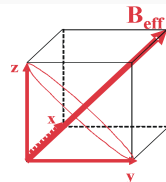


Joint Laboratory of Solid-State NMR
IMC AS CZ and JHPC AS CZ

Rotace vzorku pod magickým úhlem - MAS



Pohybová implementace
kubické symetrie
měřenému systému



ZrO₂ rotory

- 1.2 mm (<60kHz)
- 2.5 mm (<35kHz)
- 4mm (<20kHz)
- 7mm (<7kHz)



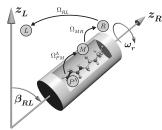
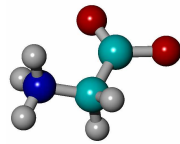
$$\delta_{eff} = (\delta_{xx} + \delta_{yy} + \delta_{zz}) / 3 = (\delta_{11} + \delta_{22} + \delta_{33}) / 3 = \delta_{iso}$$



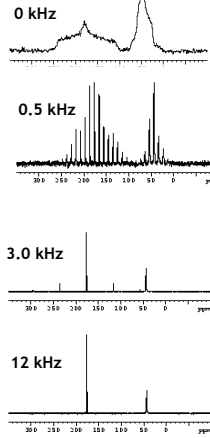
Joint Laboratory of Solid-State NMR
IMC AS CZ and JHPC AS CZ

Provedení NMR experimentu (1)

MAS a CSA



¹³C CP/MAS NMR



Rotace vzorku pod magickým úhlem (1970)



NARROWING OF PROTON NMR LINES BY MAGIC ANGLE ROTATION

D. DOSKOČILOVÁ and B. SCHNEIDER
 Institute of Macromolecular Chemistry,
 Czechoslovak Academy of Sciences, Prague, Czechoslovakia

Received 16 June 1970

Narrowing of NMR signals of protons by "magic angle" rotation has been achieved in some solid polymers, and in liquids sorbed on, or dispersed in solid lattices; in these, resolution equal to that of pure liquids is obtained.

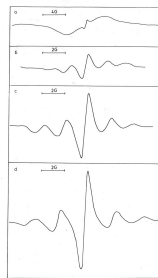
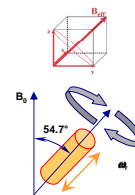


Fig. 1. Solid line NMR spectrum of solid polystyrene. a) Static sample; b, c, d) rotated about an axis with $\theta = 54.7^\circ$ at $\nu_r = 1000, 5000$ and 10000 Hz.

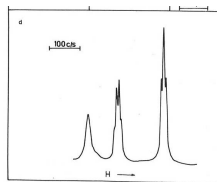


Fig. 2. High resolution NMR spectra of ethanol soaked in histonaceous earth (2.5 g 500/1) of solid: a) Static sample; b) rotated with $\nu_r = 4$ kHz, $\theta = 90^\circ$; c, d) rotated with $\nu_r = 4$ kHz, $\theta = 54.7^\circ$. Spectra a, b, c) saw-tooth sweep with 2 kHz modulation; d) slow sweep with field homogeneity controls adjusted to optimum.

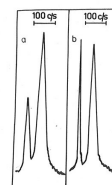
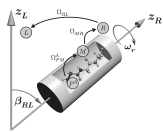
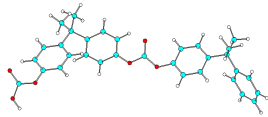


Fig. 3. High resolution spectra of a styrene-allylbenzene cation exchanger in hydrogen form swollen in water rotated with $\nu_r = 4$ kHz. a) $\theta = 90^\circ$; b) $\theta = 54.7^\circ$.

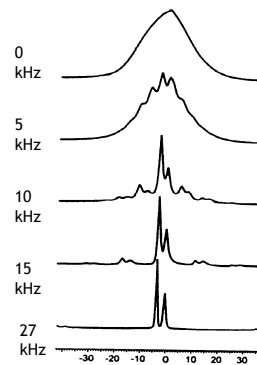


Provedení NMR experimentu (2)

MAS a dipolární interakce

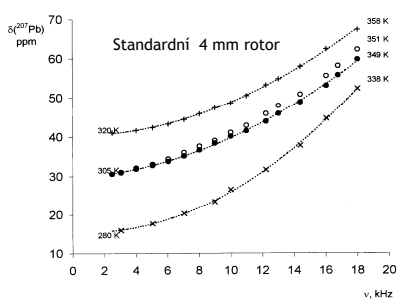


¹H MAS NMR



Zahřívání vzorku při MAS

²⁰⁷Pb NMR chemický posun vs. MAS frekvence

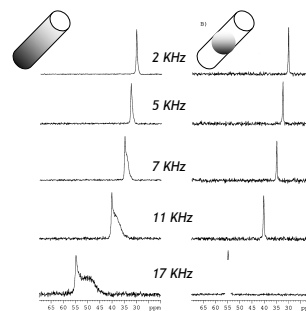


Při MAS 18 kHz se vzorek zahřeje až o 45 K.

Teplotní gradient

Standardní rotor
17 K

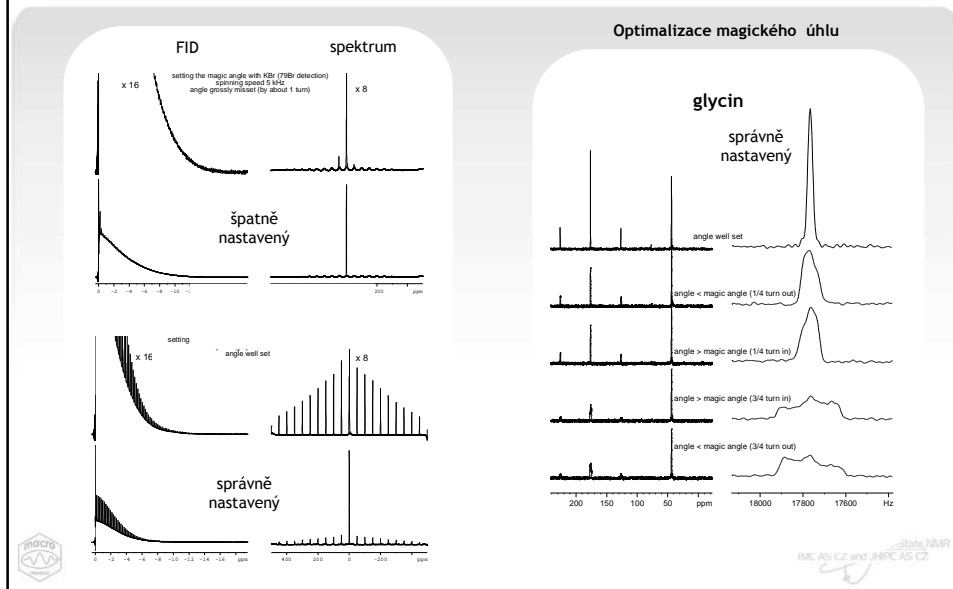
Spacer
0.7 K



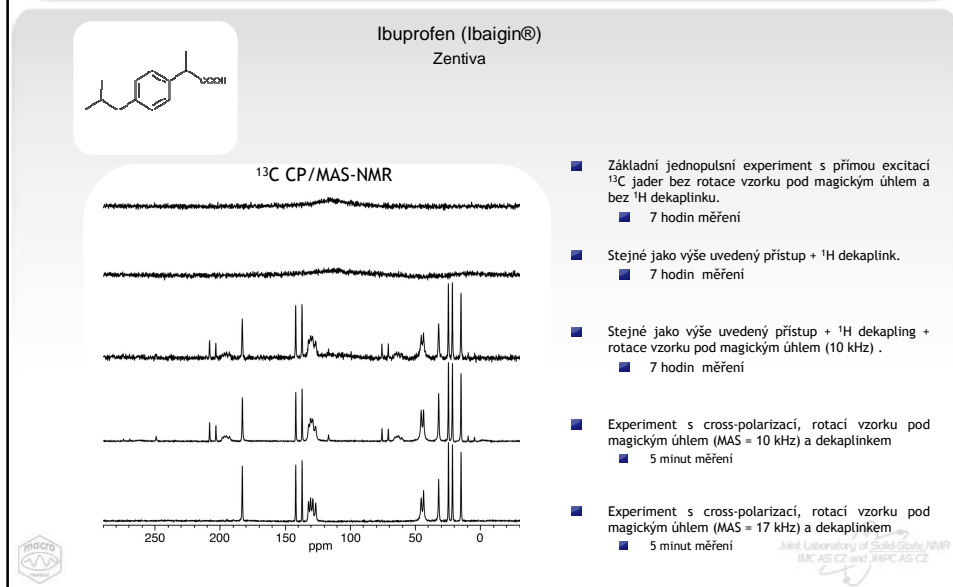
Solid State NMR 16, 151 (2000).



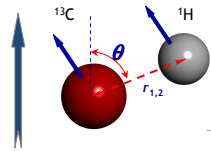
Experimentální optimalizace MAS - KBr, glycin



Provedení NMR experimentu (2)



Heteronukleární dipolární interakce



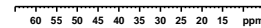
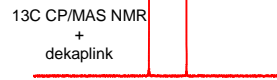
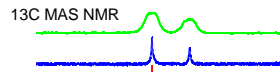
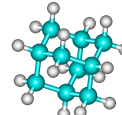
$$H_D^{IS} = -\frac{\mu_0}{4\pi} \frac{\gamma_I \gamma_S}{r_{I,S}^3} (3\cos^2\theta - 1) 2I_z S_z$$

I - jádro izotopicky hojně s vysokým g.
S - jádro izotopicky řídké s nízkým g.

1. Úměrný gyromagnetickým poměrům.
2. Nepřímě úměrný třetí mocnině vzdálenosti - (intramolekulární i intermolekulární působení).
3. Závislý na orientaci mezijaderného vektoru.

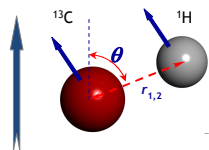


Adamantan



IOOC NMR
AV ČR

Heteronukleární dipolární interakce



$$H_D^{IS} = -\frac{\mu_0}{4\pi} \frac{\gamma_I \gamma_S}{r_{I,S}^3} (3\cos^2\theta - 1) 2I_z S_z$$

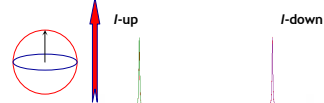
I - jádro izotopicky hojně s vysokým g.
S - jádro izotopicky řídké s nízkým g.

1. Úměrný gyromagnetickým poměrům.
2. Nepřímě úměrný třetí mocnině vzdálenosti - (intramolekulární i intermolekulární působení).
3. Závislý na orientaci mezijaderného vektoru.



B_0

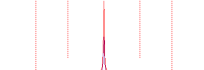
Spinový pár, $q=0^\circ$



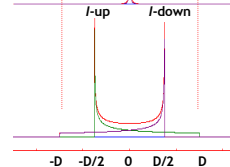
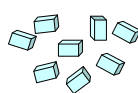
Spinový pár, $q=90^\circ$



Spinový pár, $q=54,7^\circ$

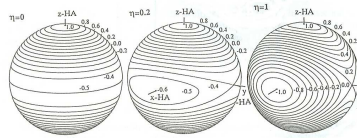
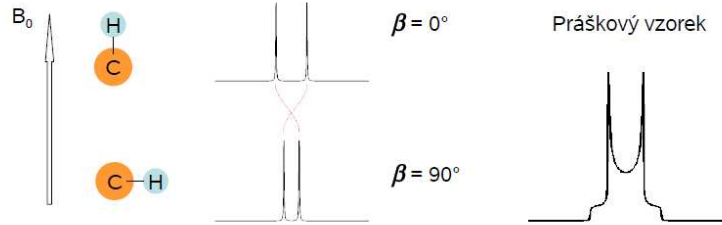


Polykrystalický systém



IOOC NMR
AV ČR

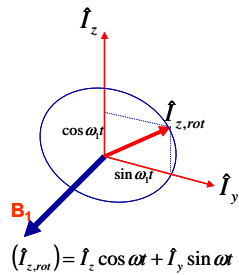
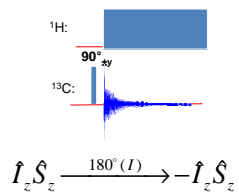
„Powder averaging“, prášková spektra



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

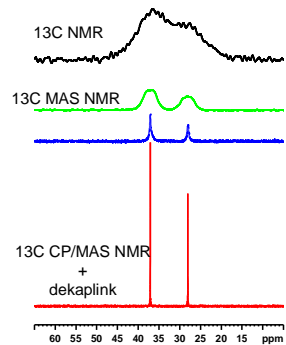
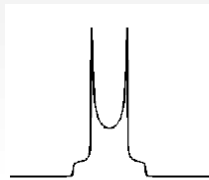
Dipolární dekaplink - rušení dipolárních interakcí

CW dekaplink



$$\langle \hat{I}_{z,rot} \rangle = \hat{I}_z \cos \alpha t + \hat{I}_y \sin \alpha t$$

Polykrystalický systém



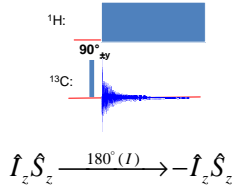
$$\langle \hat{H}_D^{SI} \rangle = \sum \omega_{SI} S_z \int_0^{n \cdot 2\pi} \frac{d\alpha}{n \cdot 2\pi} (\hat{I}_z \cos \alpha t + \hat{I}_y \sin \alpha t)$$



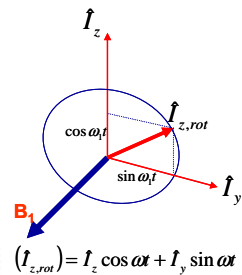
Joint Laboratory of Solid-State NMR
IMC AS CZ and JHPC AS CZ

Dipolární cw dekaplink - výkon a offset

CW dekaplink



$$\hat{I}_z \hat{S}_z \xrightarrow{180^\circ (I)} -\hat{I}_z \hat{S}_z$$



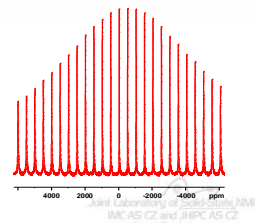
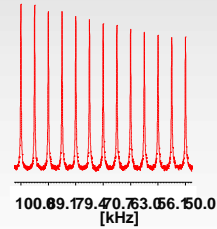
$$(I_{z,rot}) = I_z \cos \omega t + I_y \sin \omega t$$

Výkon

ω_{RF} [kHz]	linewidth [Hz]
100.0	87.2
89.1	92.1
79.4	94.8
70.7	96.8
63.0	100.1
56.1	103.4
50.0	106.2

offset

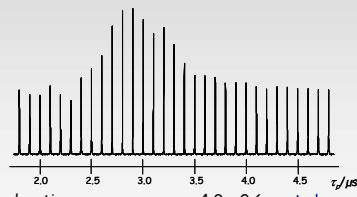
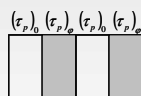
offset [Hz]	linewidth [Hz]
6000	91.0
4000	67.1
2000	54.2
0	50.5
-2000	60.7
-4000	79.4
-6000	108.1



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

Jiné typy dipolárního dekaplinku

Two Pulse Phase Modulated Dekaplink

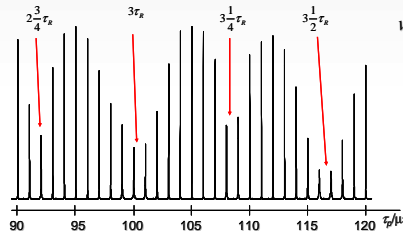
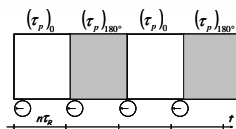


$\nu_{dec} = 150 \text{ kHz}$

$\tau_p = 2.9 \mu\text{s}, (\tau_r = 3.2 \mu\text{s})$

Pulse duration: $\tau_p \approx \tau_r - \varepsilon$, $\varepsilon \approx 4.0 - 0.6 \mu\text{s}$, to be optimised!
phase step: $\varphi \approx 15^\circ$, optimise, if needed!

XiX Dekaplink



$\nu_{dec} = 150 \text{ kHz}$

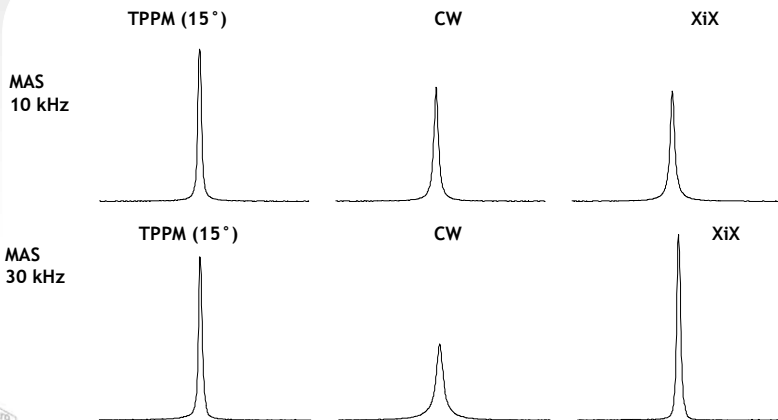
pulse length: $\tau_p = x \cdot \tau_r$, $x = n$, but $x \neq n, \dots$
(recoupling at $(n/4)\tau_r$) to be optimised!



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

Jiné typy dipolárního dekaplinku - porovnání

C_α -signal of glycine-2- ^{13}C , $\nu_{dec} = 150$ kHz

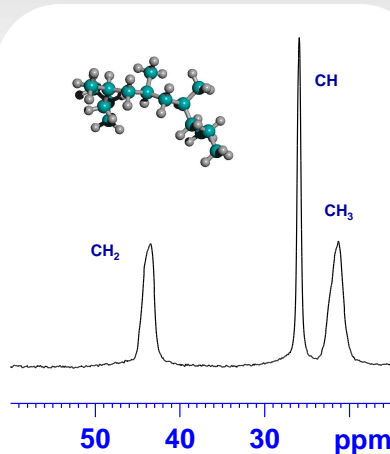
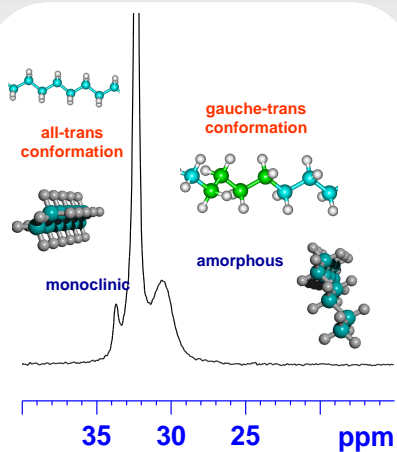


Typická ss-NMR spektra

orthorhombic

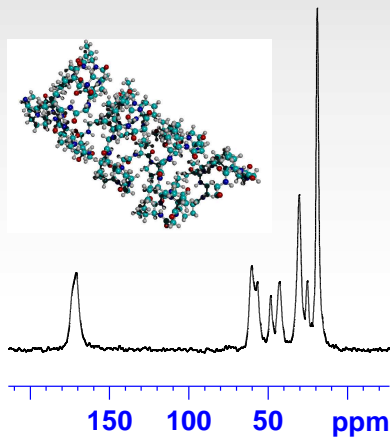
PE

iPP

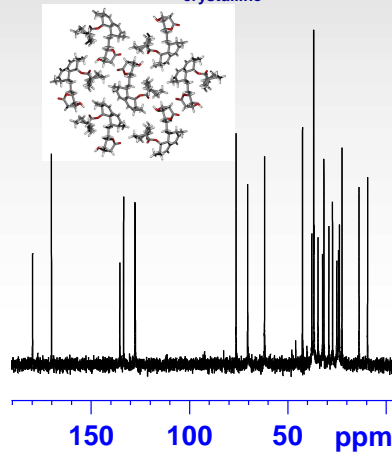


Typická ss-NMR spektra

Elastin
amorphous



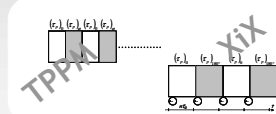
Simvastatin
crystalline



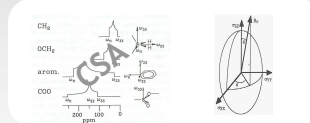
Joint Laboratory of Solid-State NMR
IMC AS CZ and JHPC AS CZ

Souhrn

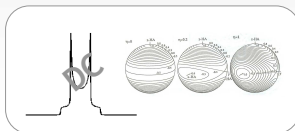
Typy dipolárního dekaplinku



anizotropie chemického posunu

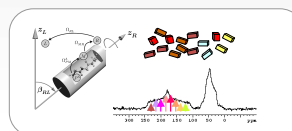


Dipolární interakce

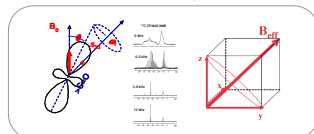


Solid-state NMR
and

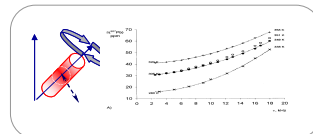
CSA - prášková spektra



MAS - kubická symetrie



MAS - zahřívání vzorku



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