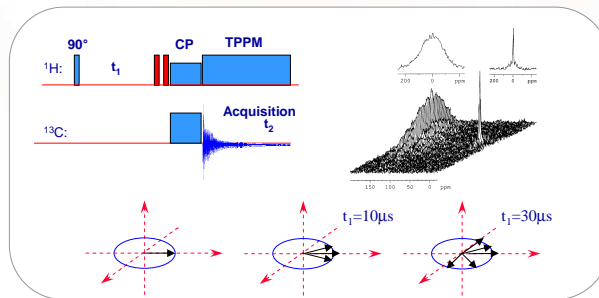


Separace dipolárních spekter struktura vs. dynamika

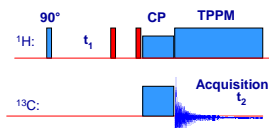


Dipolární separační experimenty (1987 - 1995)

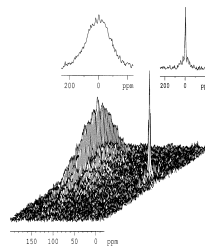


Hans W. Spiess
*1933

2D ¹H-¹³C WISE

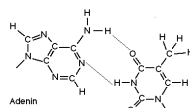


Schmidt-Rohr K., Clauss J., Spiess H.W.
Correlation of Structure and Mobility and Morphology by 2D Wideline-
Separation NMR, *Macromolecules*, (1992); 25: 3273.

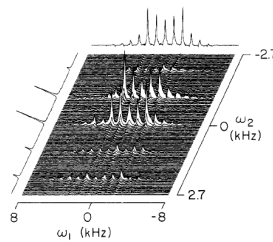


RG Griffin

2D ¹H-¹⁵N SLF NMR

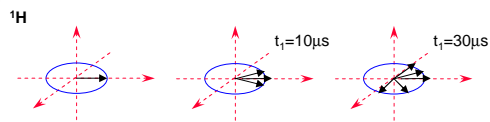


Griffin R.G.
Measurement of Heteronuclear Bond Distances in Polycrystalline
Solids by Solid-State NMR, *J. Am. Chem. Soc.* (1987); 109: 4163.



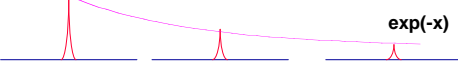
Princip 2D separace ^1H - ^1H dipolárních spekter

Silná dipolární interakce ^1H - ^1H (30-50 kHz)
 ^1H chemický posun nevýznamný (2 kHz)
 Snímají se pouze „cosinová“ data



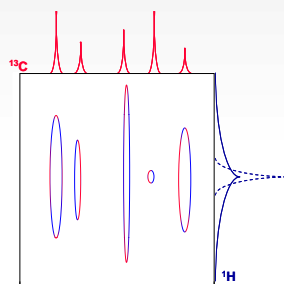
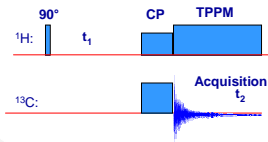
1. FT

$^1\text{H} \rightarrow \text{CP} \rightarrow ^{13}\text{C}$



2. FT

2D ^1H - ^{13}C WISE

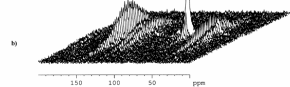
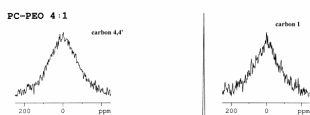
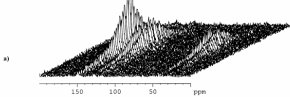
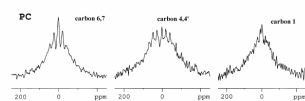


Schmidt-Rohr K., Clauss J., Spiess H.W.
 Correlation of Structure and Mobility and Morphology by 2D Wideline-Separation NMR, *Macromolecules*. (1992); 25: 3273.

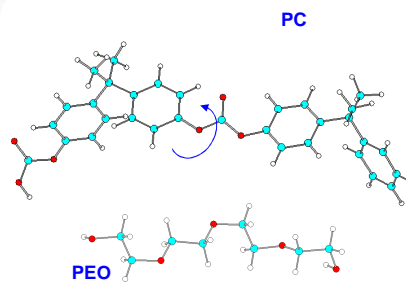
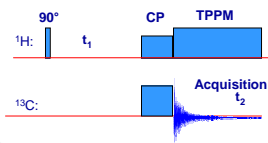


Princip 2D separace ^1H - ^1H dipolárních spekter

Polykarbonát-Polyethylenoxid

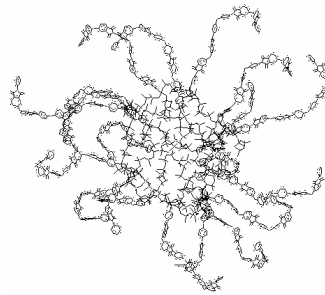
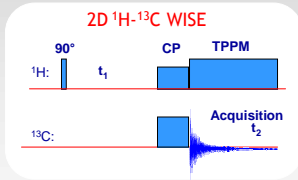
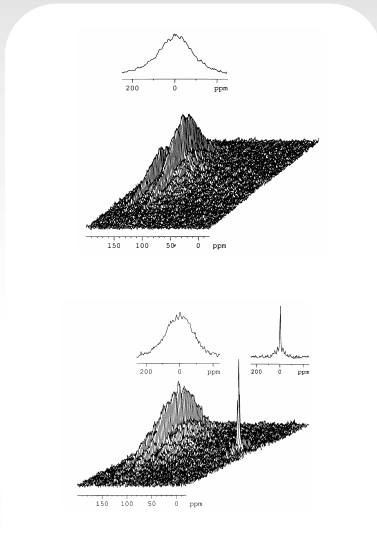


2D ^1H - ^{13}C WISE

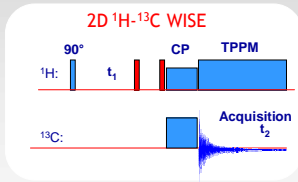
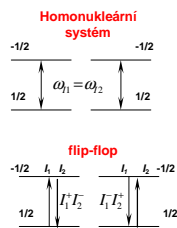


Princip 2D separace ^1H - ^1H dipolárních spekter

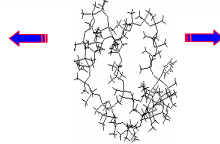
Polyimid-Polydimethylsiloxan



2D separace ^1H - ^1H spekter a spinová difuze



Selektivní excitace

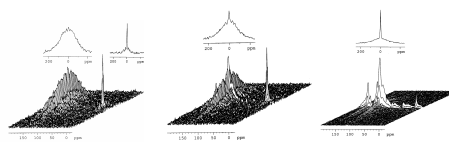


Polyimid-Polydimethylsiloxan

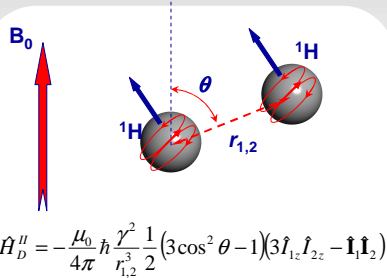
Žádná SD

Krátká doba SD
0,5 ms

Dlouhá doba SD
40,5 ms

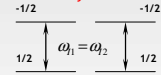


Přenos polarizace v homonukleárním systému

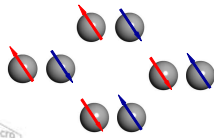
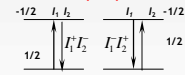


Flip-flop přechody

Homonukleární systém



flip-flop



$$\hat{\mathbf{I}}_1\hat{\mathbf{I}}_2 = (I_{1x}I_{2x} + I_{1y}I_{2y} + I_{1z}I_{2z})$$

$$I^+ = I_x + iI_y; I^- = I_x - iI_y$$

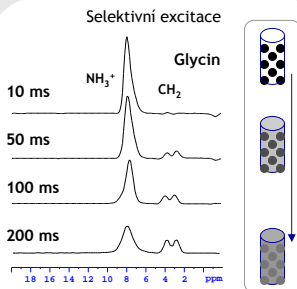
$$\hat{H}_D'' = -\frac{\mu_0}{4\pi} \hbar \frac{\gamma^2}{r_{1,2}^3} \frac{1}{2} (3\cos^2\theta - 1) (2\hat{I}_{1z}\hat{I}_{2z} - 1/2(I_1^+I_2^- + I_1^-I_2^+))$$



Joint Laboratory of Solid-State NMR
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¹H-¹H Spinová výměna (difuze)

Výběr a přenos magnetizace



Rychlost spinové výměny: $\frac{\partial M(r,t)}{\partial t} = \frac{\partial}{\partial x} \left[D \frac{\partial M(r,t)}{\partial x} \right] + \frac{\partial}{\partial y} \left[D \frac{\partial M(r,t)}{\partial y} \right] + \frac{\partial}{\partial z} \left[D \frac{\partial M(r,t)}{\partial z} \right]$

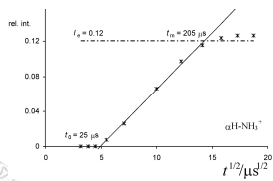
Velikost domény dispergované složky A :

$$d_A = 2 \frac{\epsilon}{f_B} \left(\frac{1}{\pi} D r_m^s \right)^{1/2}$$

Stanovení spin-difusního koeficientu z pološířky:

$$D_{rig} = \frac{1}{12} \sqrt{\frac{\pi}{2 \ln 2}} \langle r^2 \rangle \Delta \nu_{1/2} \quad D_{mob} = \frac{1}{6} \langle r^2 \rangle [\alpha \Delta \nu_{1/2}]^{1/2}$$

$$D_{mob} = 8.2 \times 10^{-6} T_2^{-1} + 0.007 \quad D_{mob} = 4.4 \times 10^{-5} T_2^{-1} + 0.26$$

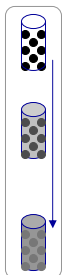
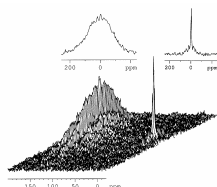


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^1H - ^1H Spinová výměna (difuze)

Výběr a přenos magnetizace

Frekvenční kódování



Rychlost spinové výměny: $\frac{\partial M(r,t)}{\partial t} = \frac{\partial}{\partial x} \left[D \frac{\partial}{\partial x} M(r,t) \right] + \frac{\partial}{\partial y} \left[D \frac{\partial}{\partial y} M(r,t) \right] + \frac{\partial}{\partial z} \left[D \frac{\partial}{\partial z} M(r,t) \right]$

Velikost domény dispergované složky A :

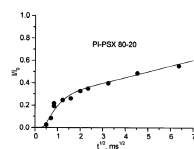
$$d_A = 2 \frac{\epsilon}{f_B} \left(\frac{1}{\pi} D t_m^s \right)^{1/2}$$

Stanovení spin-difusního koeficientu z pološířky:

$$D_{rig} = \frac{1}{12} \sqrt{\frac{\pi}{2 \ln 2}} \langle r^2 \rangle \Delta v_{1/2} \quad D_{mob} = \frac{1}{6} \langle r^2 \rangle [\alpha \Delta v_{1/2}]^{1/2}$$

$$D_{mob} = 8.2 \times 10^{-6} T_2^{-1} + 0.007 \quad D_{mob} = 4.4 \times 10^{-5} T_2^{-1} + 0.26$$

$$D = 0,05 - 0,8 \text{ nm}^2 \text{ ms}^{-1}$$

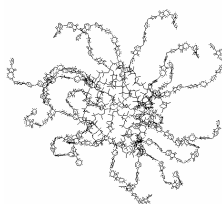
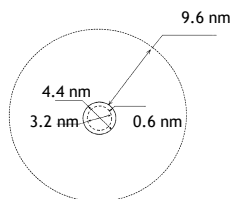
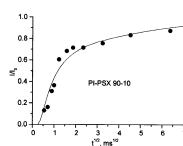


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2D separace ^1H - ^1H spekter a spinová difuze

Polyimid-Polydimethylsiloxan

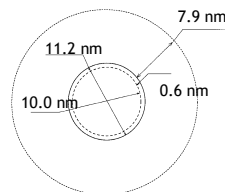
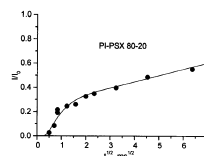
Malé domény



Velikost domény dispergované složky A :

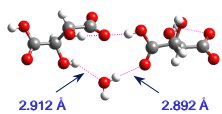
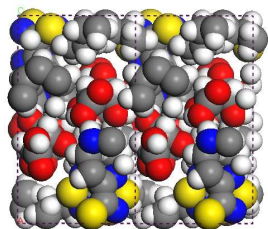
$$d_A = 2 \frac{\epsilon}{f_B} \left(\frac{1}{\pi} D t_m^s \right)^{1/2}$$

Velké domény

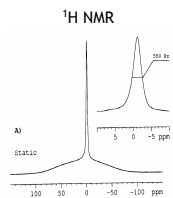


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2D separace ^1H - ^1H spekter a mimorezonanční efekt



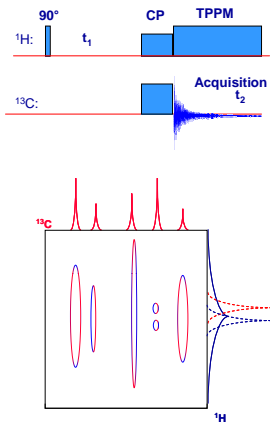
Lokalizace externích
pohyblivých molekul vody



Slabá dipolární interakce ^1H - ^1H (1-2 kHz)
Superponovaný úzký signál

^1H chemický posun se projeví
(2-5 kHz)
Offset je mimo rezonanci -
bez kvadraturní detekce =
vznik dubletu

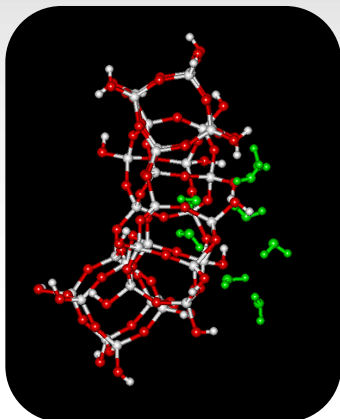
2D ^1H - ^{13}C WISE



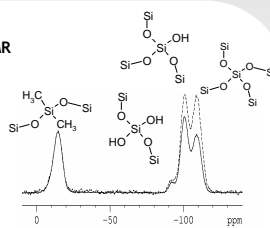
Joint Laboratory of Solid-State NMR
IMC AS CZ and JHPCAS CZ

Lokalizace externích molekul vody

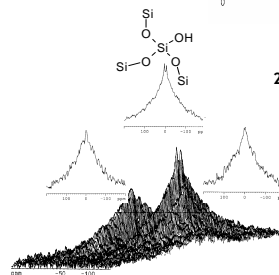
Polysiloxanová síť



^{29}Si CP/MAS NMR



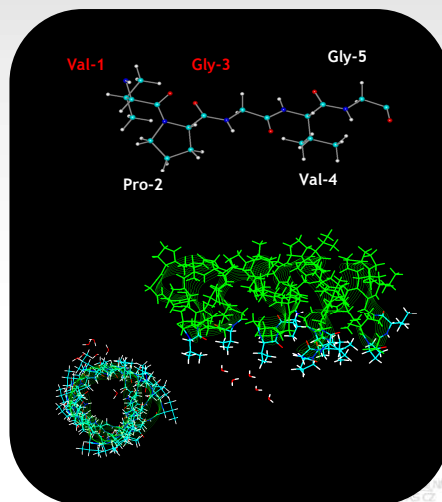
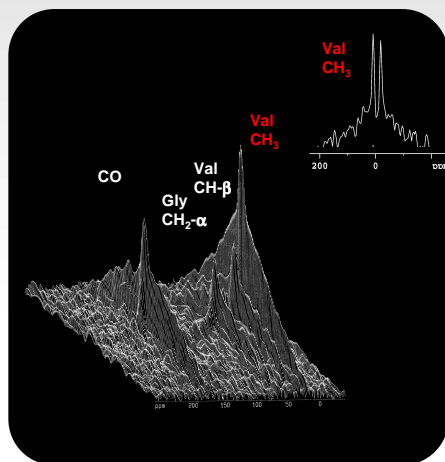
2D ^1H - ^{29}Si WISE



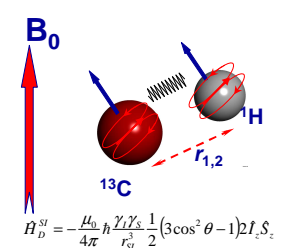
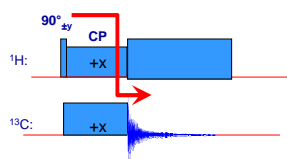
Joint Laboratory of Solid-State NMR
IMC AS CZ and JHPCAS CZ

Lokalizace externích molekul vody

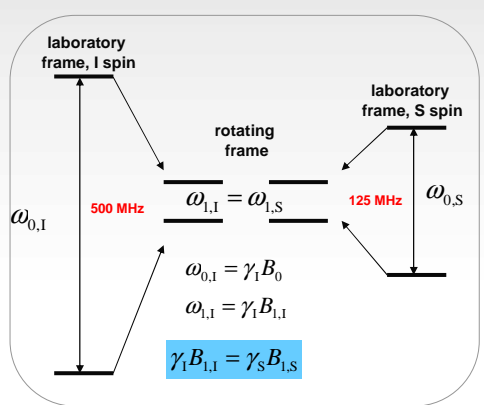
Polyptapeptid elastinového typu



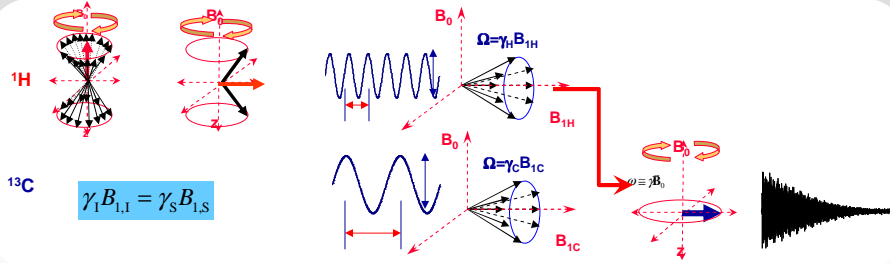
Separace heteronukleárních ¹H-X spekter



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

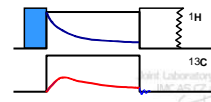
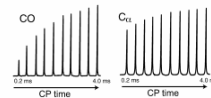


Přenos polarizace - experimentální uspořádání



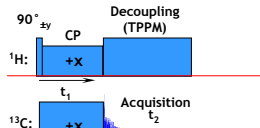
Během spin-locku jsou aktivní nejen heteronukleární I - S dipolární interakce, ale i homonukleární I - I dipolární interakce

$$\begin{aligned} \langle \hat{H}_{II}^u \rangle &= \sum_k \sum_j \omega_{kj} \int_0^{n \cdot 2\pi} \frac{d\alpha}{n \cdot 2\pi} \\ &\times \frac{1}{2} \{ 3(I_x^k \cos \alpha + I_y^k \sin \alpha)(I_x^j \cos \alpha + I_y^j \sin \alpha) - \mathbf{I}^k \cdot \mathbf{I}^j \} = \\ &= \sum_k \sum_j \omega_{kj} \frac{1}{2} \left(3 \frac{1}{2} I_x^k I_x^j + 3 \frac{1}{2} I_y^k I_y^j - \mathbf{I}^k \cdot \mathbf{I}^j \right) = \\ &= \frac{1}{2} (\hat{H}_x^u + \hat{H}_y^u) = -\frac{1}{2} \hat{H}_z^u \end{aligned}$$



Vývoj ^1H - ^{13}C dipolární interakce během CP

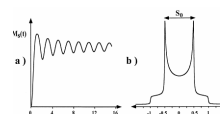
Vzorek nerotuje, izolovaný spinový pár I - S , žádné dipolární I - I interakce



$$(\Delta = \omega_{I1} - \omega_{IS} = 0)$$

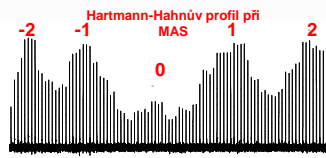
$$r_{CH} = a \left(\frac{S_0}{2\pi} \right)^{\frac{1}{3}}$$

$$S_0 = D_{IS} \approx \frac{1}{r^3}$$



Štěpení mezi singularitami S_0 , které je rovno D_{IS} může být použito k měření mezijaderné vzdálenosti.

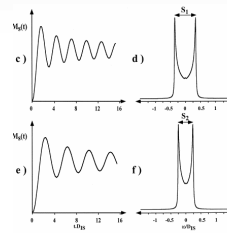
Vzorek rotuje, izolovaný spinový pár I - S , žádné dipolární I - I interakce



Podobné chování je sledováno i při rotaci vzorku, ale HH podmínka musí být přesně nastavena do rotační resonance $n = \pm 1$ nebo ± 2 .

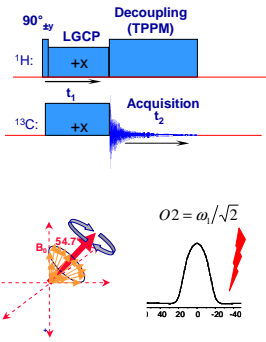
$$S_1 = \frac{D_{IS}}{\sqrt{2}}$$

$$S_2 = \frac{D_{IS}}{2}$$

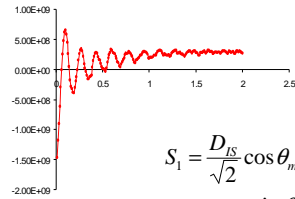


Separace heteronukleárních ^1H -X spekter

Lee-Goldburg CP -
mimorezonanční spin-lock



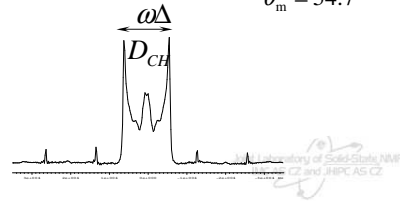
Dipolární oscilace ^{13}C signálů
během LGCP



$$S_1 = \frac{D_{IS}}{\sqrt{2}} \cos \theta_m = 12.5 \text{ kHz}$$

$$\sin \theta_m = 0.816$$

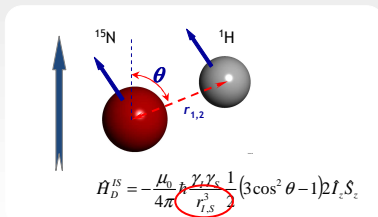
$$\theta_m = 54.7^\circ$$



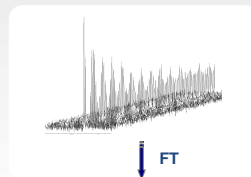
Měření meziatomových vzdáleností

Dipolární interakce a meziatomová vzdálenost

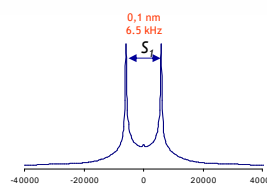
Dipolární oscilace ^{15}N NMR signálu pro
typickou N-H skupinu



■ D - dipolární interakční konstanta závisí na $1/r_{CH}^3$.



Dipolární spektrum



Škátování D

$$r_{CH} = a \left(\frac{S_1}{2\pi} \right)^{\frac{1}{3}}$$

$$S_1 = \sin \theta_m \frac{D_{IS}}{\sqrt{2}}$$

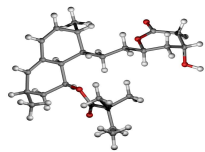
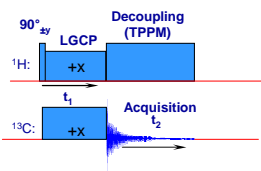
$$\sin \theta_m = 0.816$$

$$\theta_m = 54.7^\circ$$

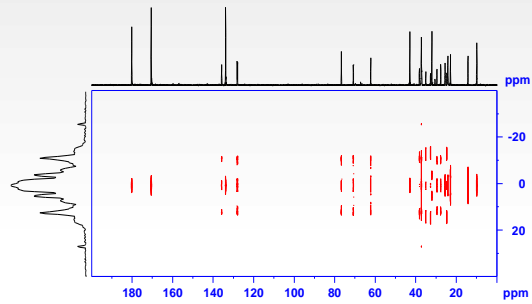


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Separace heteronukleárních ^1H -X spekter

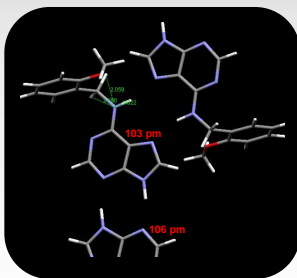


Měření ^1H - ^{13}C dipolárních interakčních konstant



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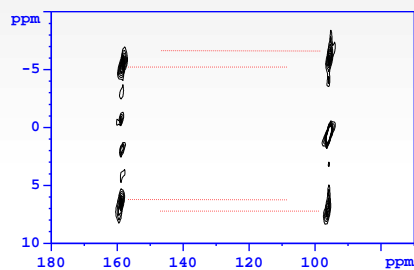
Separace heteronukleárních ^1H -X spekter



$$\omega_d = \frac{\mu_0 \gamma_{1H} \gamma_{15N}}{4\pi (r_{1,2})^3}$$

Měření ^1H - ^{15}N dipolárních interakčních konstant

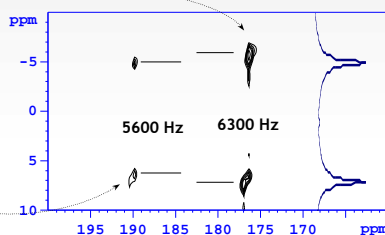
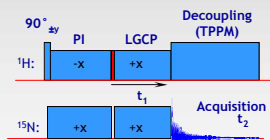
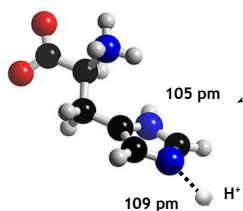
Vhodné k měření N...H vzdáleností ve vodíkových vazbách
(Technika neselektivní pouze nejsilnější dipolární interakce)



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Přesné měření N...H vzdálenosti

Histidin.HCl



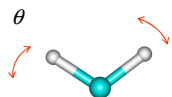
Nízká citlivost experimentu v přirozeném zastoupení.
 Experimentální čas pro získání 2D 1H-15N dipolárního spektra je 4dny až 1 týden pro His.HCl



Pohybové průměrování a segmentová dynamika

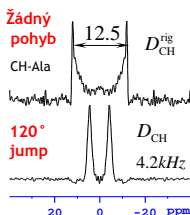
Parametr uspořádání a pohybové modely

Uniaxial rotational diffusion motion



$$S_{CH} = 1 - \frac{3}{2} \langle \theta^2 \rangle$$

Dipolární spektrum



$$S_{CH} = \frac{D_{CH}}{D_{CH}^{rig}} = \frac{D_{CH}}{12.5(\text{kHz})}$$

Fast jumps



$$S_{CH}^2 = \sum_{i,j=1}^N p_i p_j P_2(\cos \theta_{ij})$$



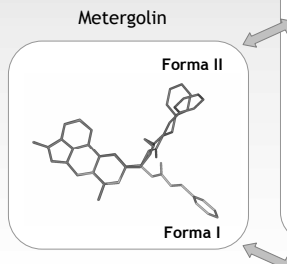
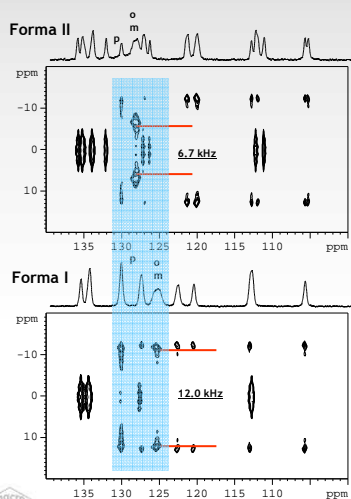
Motion on the cone in parabolic potential

$$S^2 = 1 - 3 \sin^2 \theta \left\{ \cos^2 \theta (1 - \exp[-\sigma_j^2]) + 0.25 \sin^2 \theta (1 - \exp[-4\sigma_j^2]) \right\}$$



Pohybové průměrování a segmentová dynamika

Amplituda pohybu - fluktuální úhel



$D = 6.7 \text{ kHz}$

$$S_{CH}^2 = \sum_{i,j=1}^N p_i p_j P_2(\cos \theta_{ij})$$

$\theta_{ij} = 126^\circ$

Přeskoky o 180° kolem osy (1,4)

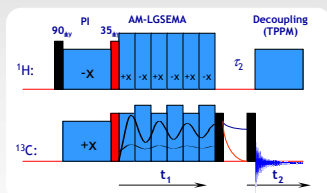
$D = 12.0 \text{ kHz}$

$\sigma = 16^\circ, \theta_0 = 60^\circ$

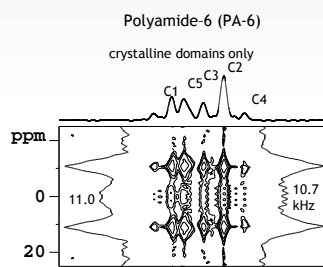
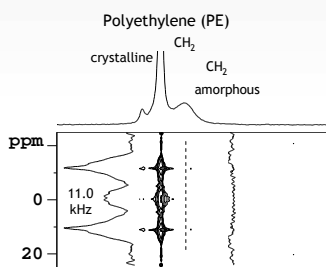
$$S^2 = 1 - 3 \sin^2 \theta [\cos^2 \theta (1 - \exp[-\sigma^2]) + 0.25 \sin^2 \theta (1 - \exp[-4\sigma^2])]$$


Doménově selektivní modifikace: krystalická fáze

T_1 -filtrovaný FSLG-CP experiment



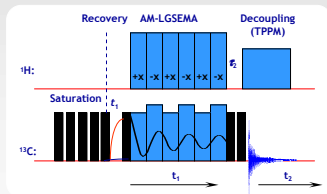
- Experiment snímá data selektivně pouze pro krystalickou frakci
- NMR signály amorfních frakcí relaxují.



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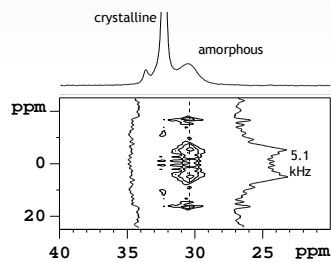
Doménově selektivní modifikace: amorfní fáze

Inverzně- T_1 -filtrovaný FSLG-CP experiment

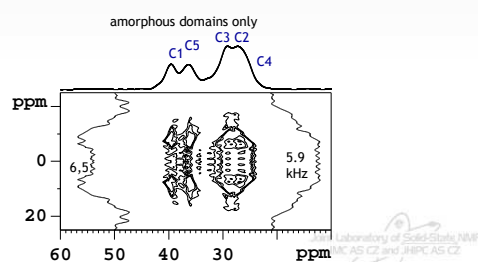


- Experiment snímá data selektivně pouze pro amorfni frakci
- NMR přechody krystalické frakce jsou nasyceny

Polyethylene (PE)

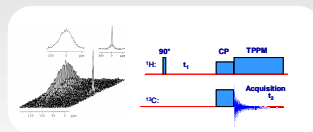


Polyamide - 6 (PA6)

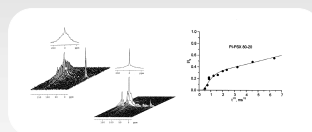


Souhrn

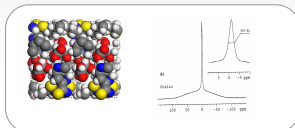
Wide Line Separation - WISE



WISE a spinová difuze - velikost domén

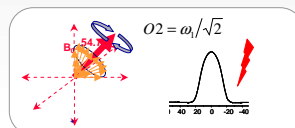


off-resonance wise - loakizace vody

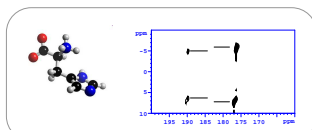


Solid-state NMR and

LGCP - potlačení 1H-1H interakcí



LGCP - měření meziatomových vzdáleností



Parametr uspořádání a segmentová dynamika

