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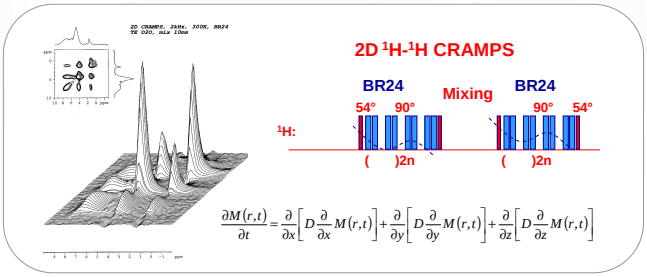
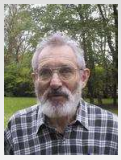
2D NMR spektroskopie v pevné fázi - spinová difuze a separace lokálních polí



Objev více-rozměrné NMR spektroskopie (1971)

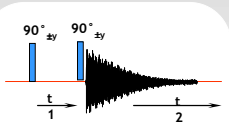


Jean Luis Charles Jeener
*1931

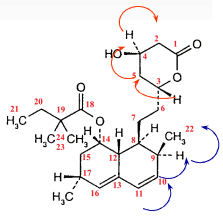
Přenos magnetizace přes vazebné elektrony (konektivita řetězce)

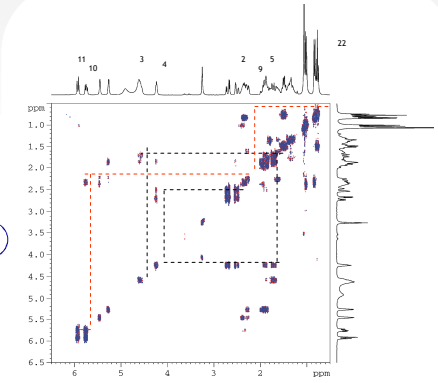
Přednáška na letní škole v Basko Polje, Jugoslávie, 1971
Dvoudimenzionální NMR, COSY

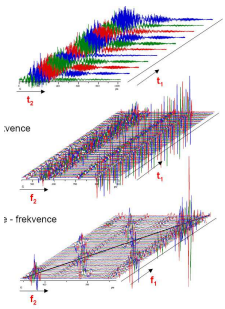
Aue W.P., Bartholdi E., Ernst R.R.
2D Spectroscopy. Application to NMR, *J. Chem. Phys.* (1976); *64*: 229.



2D COSY NMR





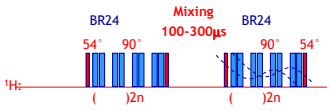


2D korelační NMR v pevné fázi – 1985

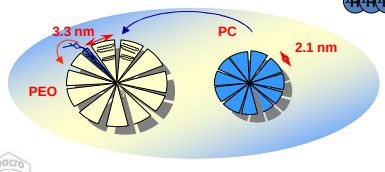
Morfologie polymerních směsí

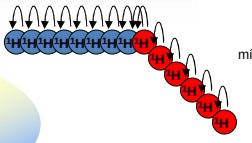
Caravatti P., Neuenschwander P., Ernst R.R.
Characterization of Heterogeneous Polymer Blends by 2D 1H Spin Diffusion Spectroscopy,
***Macromolecules*. (1985); *18*: 119.**

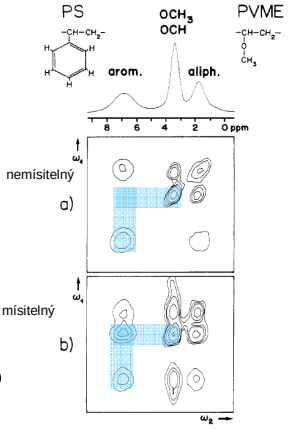
2D ^{1}H MAS NMR pulse sequence



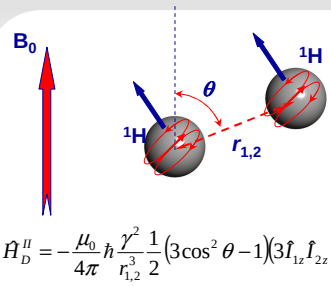
Štafetový přenos polarizace
Korelace ^{1}H-^{1}H chemických posunů





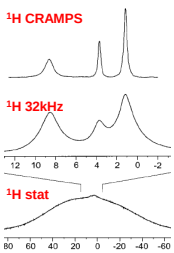


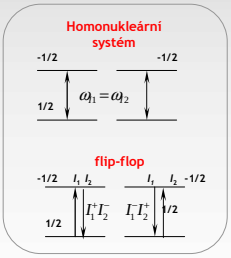
Dipolární interakce v homonukleárním systému

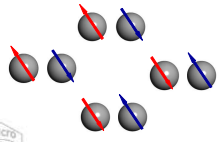


$$\hat{H}_D^{II} = -\frac{\mu_0}{4\pi}\hbar\frac{\gamma^2}{r_{1,2}^3}\frac{1}{2}\left(3\cos^2\theta - 1\right)\left(3\hat{I}_{1z}\hat{I}_{2z} - \hat{\mathbf{I}}_1\hat{\mathbf{I}}_2\right)$$

Flip-flop přechody





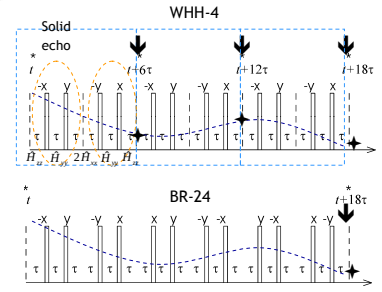


$$\hat{\mathbf{I}}_1\hat{\mathbf{I}}_2 = \left(I_{1x}I_{2x} + I_{1y}I_{2y} + I_{1z}I_{2z}\right)$$

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

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

Multipulsní homodekaplink – 1968



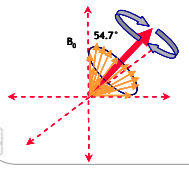
$$\hat{H}_D^{II} = \hat{H}_{xx} + \hat{H}_{yy} + \hat{H}_{zz}$$

$$\left.\begin{aligned} \hat{H}_{xx} &= \ldots\ldots\left(3\hat{I}_{1x}\hat{I}_{2x} - \hat{\mathbf{I}}_1\hat{\mathbf{I}}_2\right) \\ \hat{H}_{yy} &= \ldots\ldots\left(3\hat{I}_{1y}\hat{I}_{2y} - \hat{\mathbf{I}}_1\hat{\mathbf{I}}_2\right) \\ \hat{H}_{zz} &= \ldots\ldots\left(3\hat{I}_{1z}\hat{I}_{2z} - \hat{\mathbf{I}}_1\hat{\mathbf{I}}_2\right) \end{aligned}\right\} = 0$$

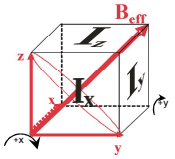
$$\hat{H}_{CS} \approx \hat{I}_z$$

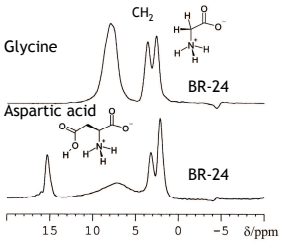
$$\hat{H}_{CS} \approx \left(\hat{I}_x + \hat{I}_y + \hat{I}_z\right)/3$$

Efektivní precese pod magickým úhlem



"Magická krychle"





Kontinuální homodekaplink

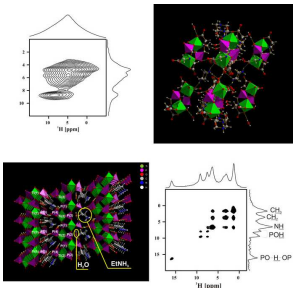
FSLG dekaplink

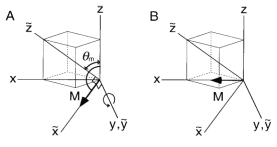
Mimorezonanční podmínka $\Delta\mathrm{LG}(O2) = \omega_1/\sqrt{2}$

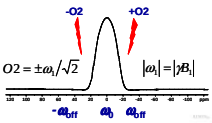
Doba trvání jednoho pulsu $\tau = \left(\frac{2\pi}{\omega_1}\right)\sqrt{\frac{2}{3}}$

Pak následuje změna fáze a offsetu $\Delta\mathrm{LG}(O2) = -\omega_1/\sqrt{2}$

τ odpovídá 2π rotaci kolem efektivního pole.







van Rossum BJ.; Foerster H.; De Groot HJM.
High-Field and High-Speed CP-MAS ^{13}C NMR Heteronuclear Dipolar-Correlation Spectroscopy of Solids with Frequency-Switched Lee-Goldburg Homonuclear Decoupling, *J. Magn. Reson.* 124, 516, (1997).

Kontinuální homodekaplink

Fázově modulovaný
Lee-Goldburgův experiment

Fázová modulace

$$\phi(t) = \omega_{PMLG} t$$
$$|\omega_{PMLG}| = \omega_1/\sqrt{2}$$

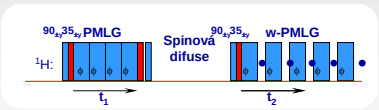
Doba trvání LG cyklu

$$t_{LG} = \sqrt{(2/3)}(2\pi/\omega_1)$$

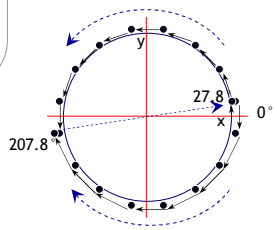
Celková fázová změna během jednoho LG cyklu

$$\alpha_{LG} = |\omega_{PMLG}| t_{LG} = 207.8^\circ$$

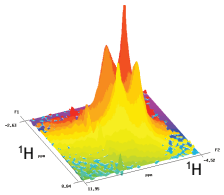
„On-resonance“ experiment



Trajektorie *rf* pole během cyklu PMLG-9

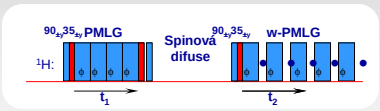


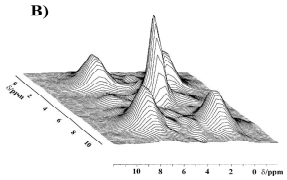
^{1}H-^{1}H PMLG w-PMLG



^{1}H-^{1}H Spinová výměna (difuse)

Výběr a přenos magnetizace

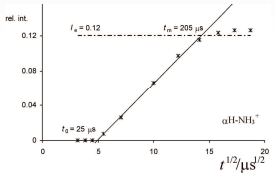




Rychlost spinové výměny: $\frac{\partial M(r,t)}{\partial t} = \frac{\partial}{\partial x}\left[D\frac{\partial}{\partial x}M(r,t)\right] + \frac{\partial}{\partial y}\left[D\frac{\partial}{\partial y}M(r,t)\right] + \frac{\partial}{\partial z}\left[D\frac{\partial}{\partial z}M(r,t)\right]$

Velikost domény dispergované složky A :

$$d_A = 2\frac{\varepsilon}{f_B}\left(\frac{1}{\pi}Dt_m^s\right)^{1/2}$$



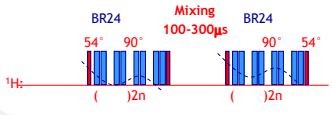
Stanovení spin-difusního koeficientu z položšířky:

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

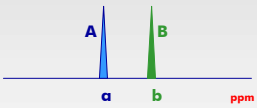
$$D_{mob} = 8.2\times10^{-6}T_2^{-1} + 0.007 \qquad D_{mob} = 4.4\times10^{-5}T_2^{-1} + 0.26$$

2D spin-difuzní ^1H-^1H NMR experimenty

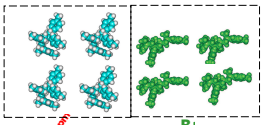
2D ^1H MAS NMR pulse sequence

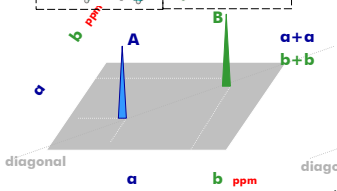


Obecný dvousložkový systém v 1D ^1H NMR spektru



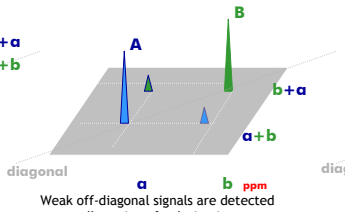
Fázově separované domény A.....B





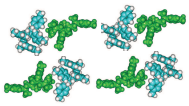
Only diagonal signals are detected - no polarization transfer occurs

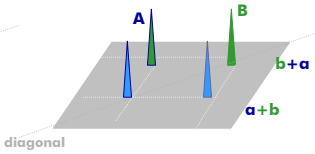
Obecný dvousložkový systém ve 2D spektru



Weak off-diagonal signals are detected - small portion of polarization was transferred from A to B

Molekulární komplex A-B



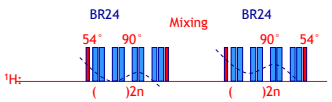


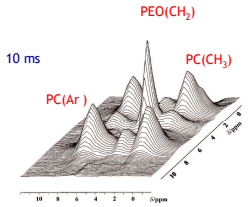
Strong off-diagonal signals are detected -polarization was completely transferred from A to B

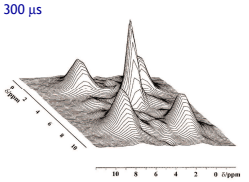
ss NMR – 2D spin-difuzní experimenty

Polymer blend
Polycarbonate – Polyethyleneoxide (PC-PEO)

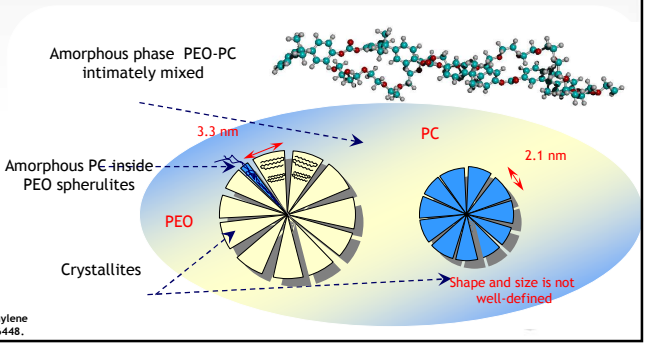
2D ^1H MAS NMR pulse sequence





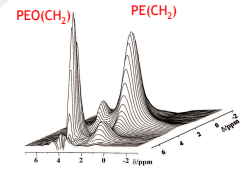


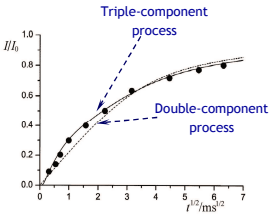
Brus J. et al.,
Order and mobility in polycarbonate-poly(ethylene oxide) blends, *Macromolecules* (2000); *33*: 6448.



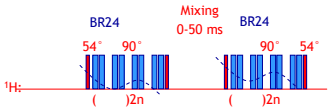
ss NMR – 2D spin-difuzní experimenty

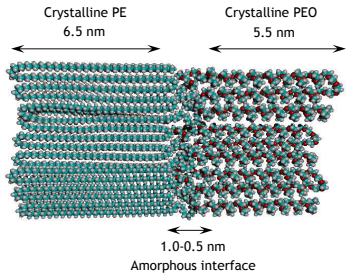
Blokový kopolymer
Polyethyleneoxide-Polyethylene
PEO-PE





2D ^{1}H MAS NMR pulse sequence

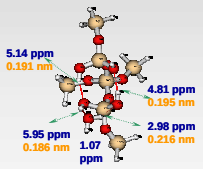


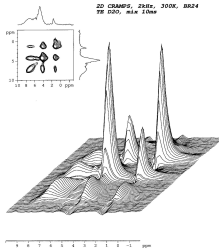


Brus J. et al.,
Potential and limitations of 2D H-1-H-1 spin-exchange CRAMPS experiments to characterize structures of organic solids, *MONATSHEFTE FUR CHEMIE* (2002); *133*: 1587.

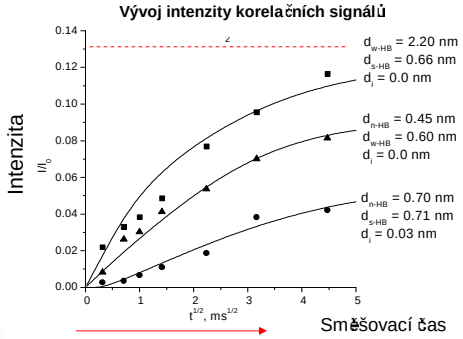
ss NMR – 2D spin-difuzní experimenty

Siloxanová síť

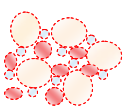




Vývoj intenzity korelačních signálů



Směšovací čas

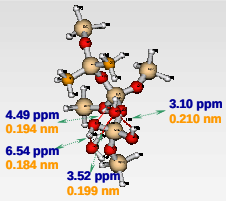


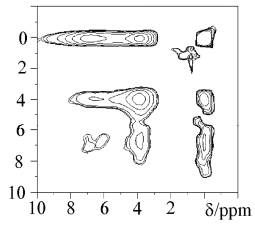
Velikost klastrů:

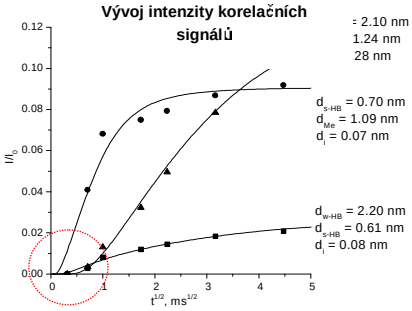
w-HB OH 1.5-2.0 nm
s-HB OH < 1.0 nm
n-HB OH 0.5 -0.4 nm

ss NMR – 2D spin-difuzní experimenty

Modifikovaná siloxanová síť

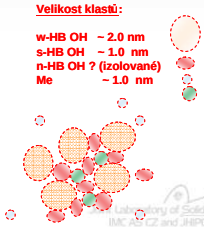




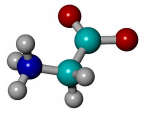


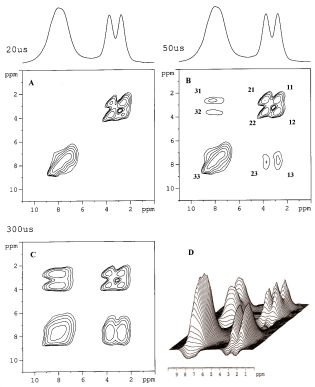
Velikost klastů:

w-HB OH ~ 2.0 nm
s-HB OH ~ 1.0 nm
n-HB OH ? (izolované)
Me ~ 1.0 nm



Měření meziatomových vzdáleností

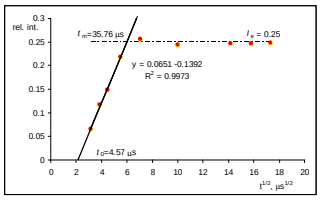


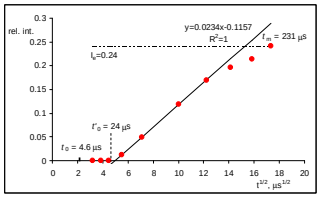


$\langle r^2 \rangle = 3\, D_{eff}\, t_m$

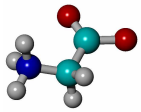
$r_{12} = 0.178$ nm

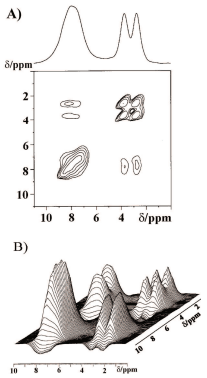
$r_{12} = 0.247$ nm

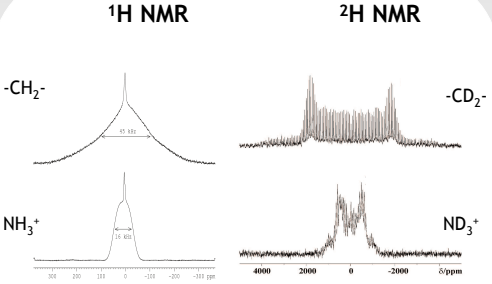




Měření meziatomových vzdáleností



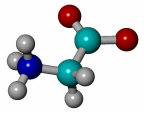


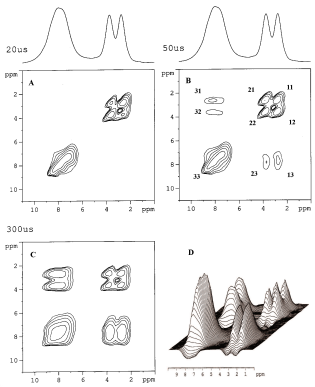


$$\frac{D_{eff}^{*}}{D_{eff}} \cong \frac{\Delta\nu_{1/2}\left(NH_3^+\right)}{\Delta\nu_{1/2}\left(CH_2\right)} \cong \frac{\delta_Q\left(NH_3^+\right)}{\delta_Q\left(CH_2\right)} \cong \frac{1}{3}$$

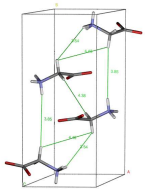
Spinová výměna je ovlivněna segmentálním pohybem, rozsah ovlivnění lze odhadnout z kvadrupolových interakčncích konstant.

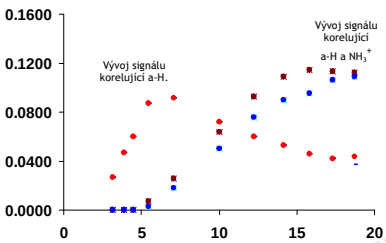
Měření meziatomových vzdáleností





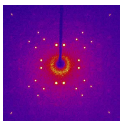
Mezimolekulární vzdálenosti mohou být teoreticky získány z vývoje spinové difuse.

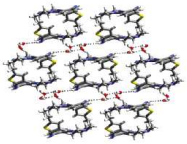




NMR krystalografie – 2006…

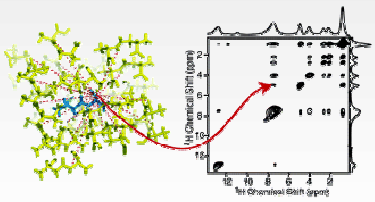
XRD





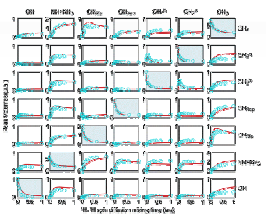
Reutzel-Edens S. et al. ***Crystal Growth & Design 3, 897 (2003)***

ss-NMR



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

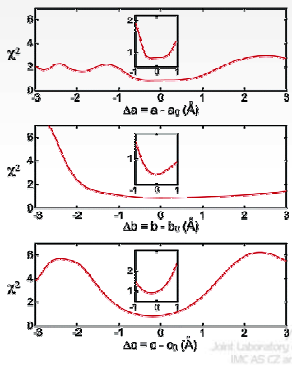
NMR krystalografie - parametry krystalové buňky



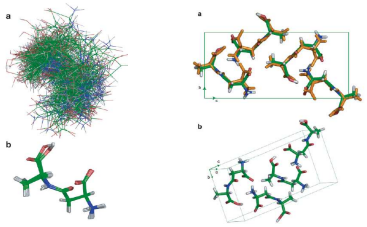
$$\frac{d\mathbf{M}}{dt} = -\mathbf{K}(\mathbf{M}-\mathbf{M}_0) \quad k_{ij} = \sum_{\lambda}\left(\frac{\mu_0\gamma^2\hbar}{4\pi}\right)^2 \frac{A}{(r_{ij}^n)_{\lambda}} \quad k_{ii} = -\sum_{i} k_a$$

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

n … *Functional dependence on internuclear distance*

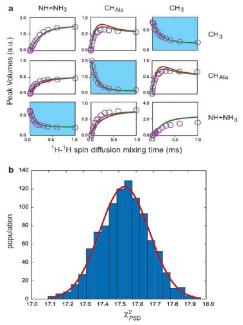


NMR krystalografie



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*.



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

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

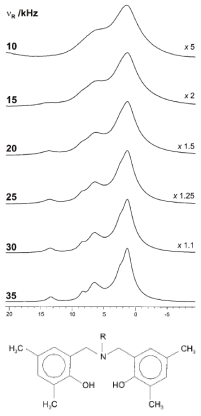
n ... *Functional dependence on internuclear distance*

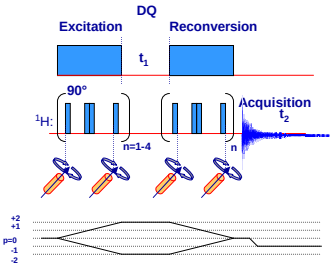
$$\chi^2 = \sum \frac{(calc_i - t_i)^2}{\sigma_i^2}$$

2D dvoukvantové ^{1}H-^{1}H korelační techniky

Steven P. Brown and Hans Wolfgang Spiess.
Advanced Solid-State NMR Methods for the Elucidation of Structure and Dynamics of Molecular, Macromolecular, and Supramolecular Systems, *Chem. Rev.* 2001, *101*, 4125-4155

Steven P. Brown
1972

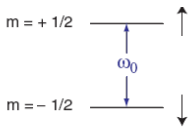




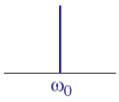
* Zúžení signálů - pouze rotace vzorku 30 kHz.
* Teplotně stabilní látka.
* Řídká ^{1}H-^{1}H interakční síť.
* **Neuplatňuje se spinová difuze.**
* Existence dvou dipolárně interagujících H atomů.
* Meziatomová vzdálenost nepřesáhne 3-4 A.

Jednokvantová vs. dvoukvantová koherence

Izolovaný spin I = 1/2

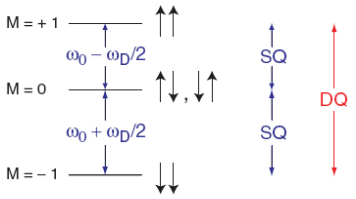


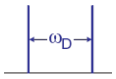
Δm = ±1 Jednokvantová koherence



V NMR spektru pozorujeme singlet

Dipolárně interagující pár spinů I = 1/2





V NMR spektru pozorujeme dubletu

Platí i pro spin-spinové interakce

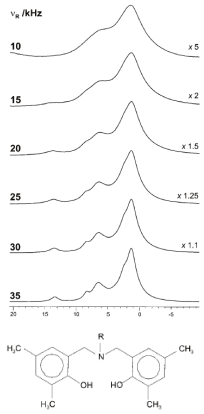
2D dvoukvantové ^{1}H-^{1}H korelační techniky

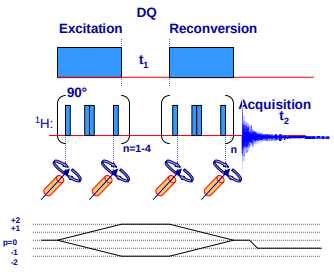
Steven P. Brown and Hans Wolfgang Spiess.
Advanced Solid-State NMR Methods for the Elucidation of Structure and Dynamics of Molecular, Macromolecular, and Supramolecular Systems, *Chem. Rev.* 2001, *101*, 4125-4155

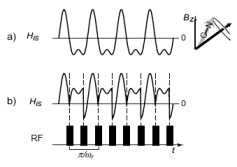
Dvoukvantový Hamiltonián

$$\hat{\mathbf{H}}_{xx} - \hat{\mathbf{H}}_{yy}$$

* DQC - není přímo sledovatelná - 2D experiment.
* Rotor-synchronizovaný experiment.
* Excitace - vývoj - zpětná konverze.
* S klesající sílou dipolárních interakcí - větší počet cyklů.





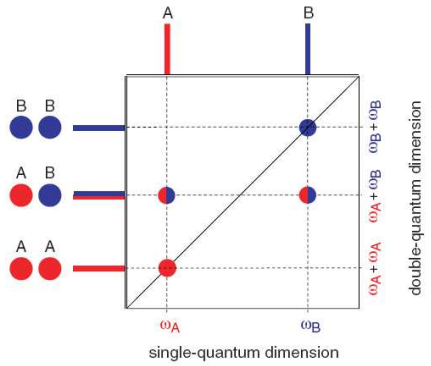


Dvoukvantová koherence

V prvním přiblížení je intenzita signálů druhé mocnině dipolární interakce,

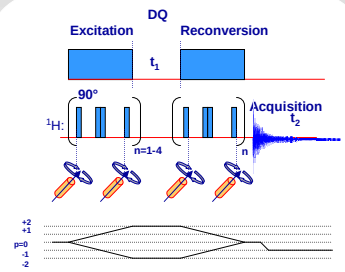
Intenzita signálu je nepřímo úměrná šesté mocnině vzdálenosti

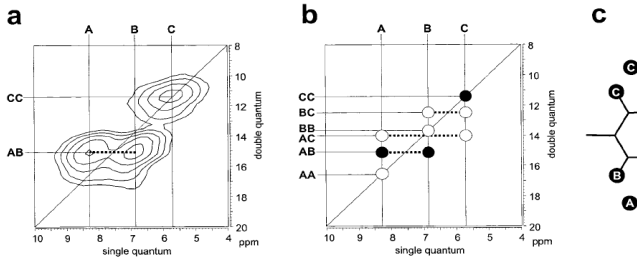
DQC se vyvine pouze tehdy pokud jsou jádra skutečně velmi blízko sebe



Rotor synchronizovaná 2D DQ MAS spektra

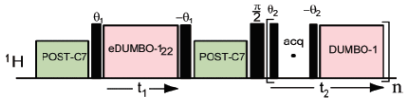
* Inkrement DQC (t_1) = jedna perioda rotace.
* Rotační signály jsou zcela potlačeny.
* Excitace - vývoj - zpětná konverze.
* S klesající silou dipolárních interakcí - větší počet cyklů.



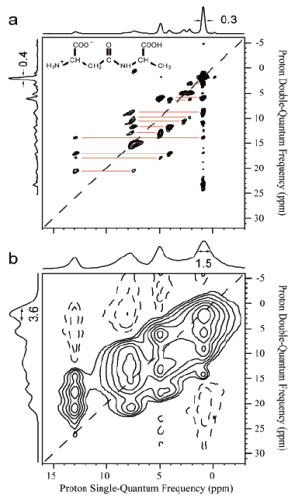


Jak dosáhnout lepšího rozlišení

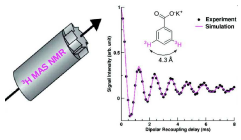
Zavední homodekaplovacích sekvencí do obou detekčních period

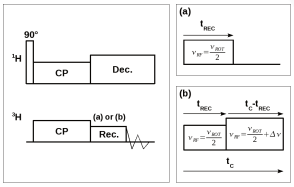


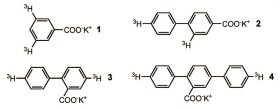
Steven P. Brown Anne Lesage, Be´ne´ dicte Elena, and Lyndon Emsley Probing Proton-Proton Proximities in the Solid State: High-ResolutionTwo-Dimensional 1H-1H Double-Quantum CRAMPS NMR Spectroscopy, *J. Am. Chem. Soc.* 2004, 126, 13230-13231.

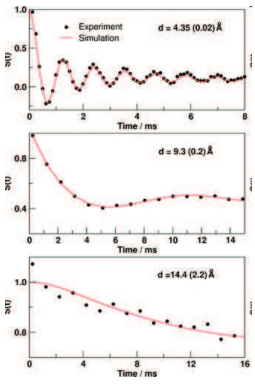


2D ^{3}H-^{3}H korelace – dosah až 13 A



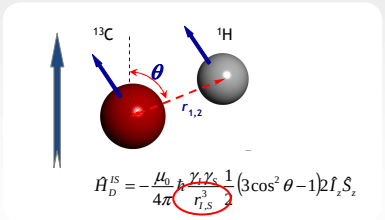






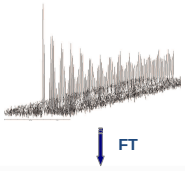
Dipol-dipolové interakce a meziatomová vzdálenost

Dipolární oscilace a Fourierova transformace

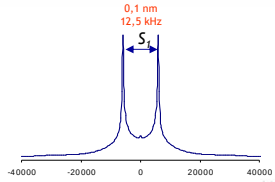


$$\hat{H}_D^{IS} = -\frac{\mu_0}{4\pi}\hbar\frac{\gamma_I\gamma_S}{r_{I,S}^3}\frac{1}{2}(3\cos^2\theta - 1)2\hat{I}_z\hat{S}_z$$

Dipolar oscillation of ^{13}C NMR signal in a typical C-H group



Dipolar spectrum of C-H group



Scaling of *D*

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

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

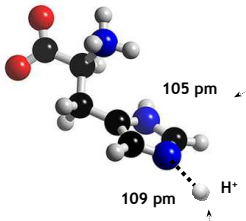
$$\sin\theta_m = 0.816$$

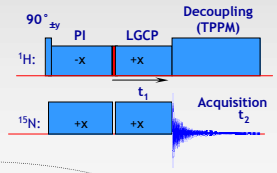
$$\theta_m = 54.7^\circ$$

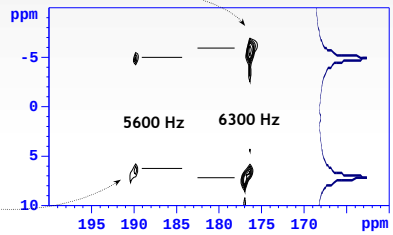
- *D* - dipolar coupling constant depends on $1/r_{CH}^3$.
- *D* - dipolar coupling constant should be constant for all C-H pairs in CH or CH_2 groups as bond length is always ca. 0.11 nm

Přesné měření N...H vzdálenosti

Histidin.HCl





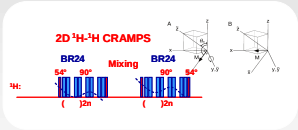


Nízká citlivost experimentu v přirozeném zastoupení.

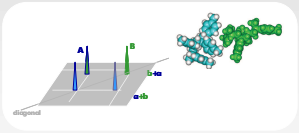
Experimentální čas pro získání 2D 1H-15N dipolárního spektra je **cca. 2-5 dnů**

Souhrn

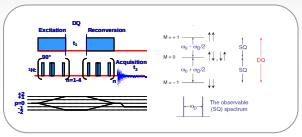
Homodekaplink: BR24, FSLG, PMLG



2D spinová difuse

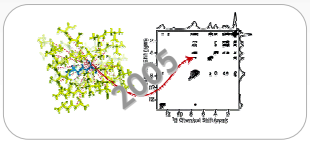


DQ koherence: BABA

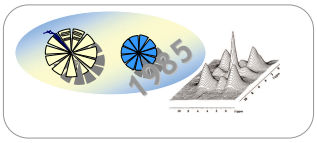


Solid-state NMR and .....

NMR krystalografie



Spinová difuse a morfologie polymerů



CRAMPS-DQ/MAS