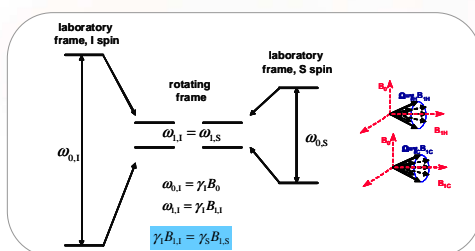




Techniky přenosu polarizace - „cross“-polarizace a spinová difuze



Zvýšení citlivosti NMR experimentu

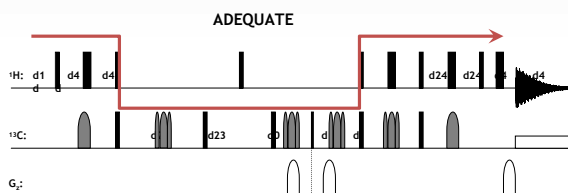
Problém relaxace

- 1) Absorpce *rf* záření není doprovázena spontánní emisí.
- 2) Disipace je vynucena fluktuacemi lokálních magnetických polí.
- 3) Vnitřní molekulární pohyb je u krystalických systémů velmi omezený.
- 4) Relaxační časy izotopicky řídkých jader v řádech minut a hodin.

Problém malé polarizovatelnosti

$$\frac{\gamma_I}{\gamma_S}$$

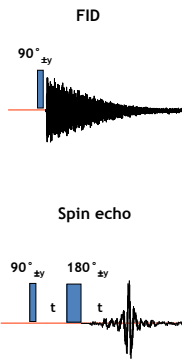
nucleus	natural abundance	max. enhancement factor
¹³ C	1.11 %	4
¹⁵ N	0.37 %	10
²⁹ Si	4.70 %	5
³¹ P	100 %	2.5



Historie - Hahnovi experimenty (1950-1962)



Erwin L. Hahn
*1921

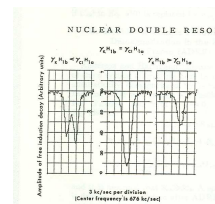
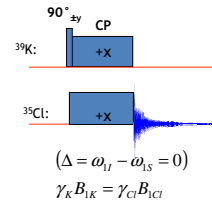


Hahn, E. L.,
Spin echoes, *Phys. Rev.*, **80**, 580-594 (1950).

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

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

Cross polarization



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Křížová-polarizace - 1972

Zvýšení citlivosti NMR experimentu

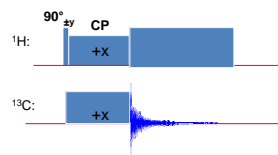


Alex Pines
*1945

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

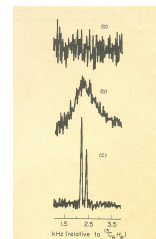
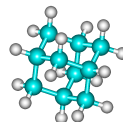
Zvýšení citlivosti až 1000-krát

- 1) Polarizace izotopicky hojných jader *I*.
- 2) Snížení spinové teploty jader *I* v rotující soustavě souřadné.
- 3) Ustavení kontaktu mezi *I* a *S* - spin-lock a HH kontakt.
- 4) Detekce magnetizace *S* při současném dekaplinku *I*.



$(\Delta = \omega_{I1} - \omega_{S1} = 0)$
 $\gamma_H B_{1H} = \gamma_C B_{1C}$

Adamantan



NMR
SCZ

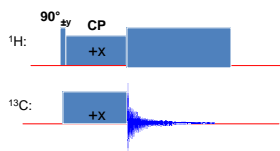
Křížová-polarizace - 1976

Zvýšení citlivosti NMR experimentu

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

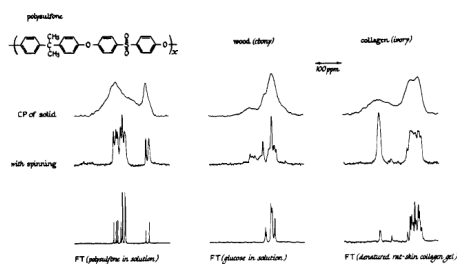


J. Schaefer



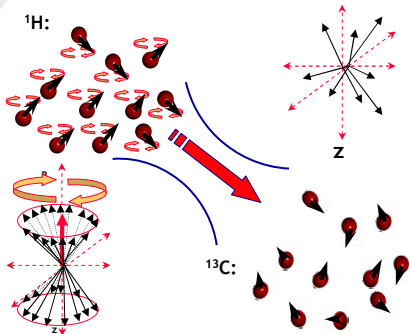
Zvýšení citlivosti až 1000-krát

- 1) Polarizace izotopicky hojných jader I.
- 2) Snížení spinové teploty jader I v rotující soustavě souřadné.
- 3) Ustavení kontaktu mezi I a S - spin-lock a HH kontakt.
- 4) Detekce magnetizace S při současném dekaplínku I.



Dipolární kontakt a přenos polarizace

Dipolární kontakt



Magnetizace proudí z vysoce polarizovaných systémů do systémů málo polarizovaných

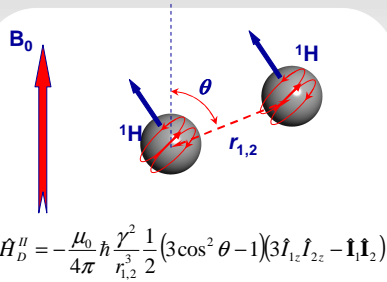
Tepelný kontakt



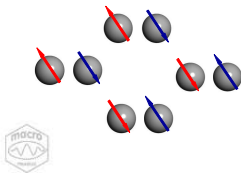
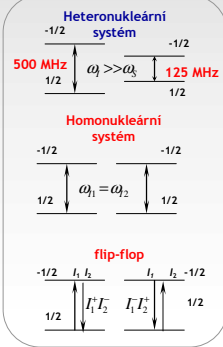
Teplo teče z horkého objektu do objektu s nízkou teplotou



Přenos polarizace v homonukleárním systému



Flip-flop přechody



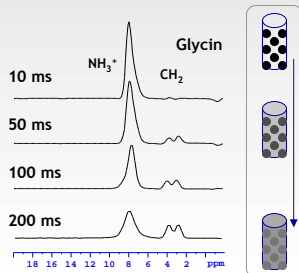
$$\hat{\mathbf{I}}_1 \hat{\mathbf{I}}_2 = (I_{1x} I_{2x} + I_{1y} I_{2y} + I_{1z} I_{2z})$$

$$I^+ = I_x + i I_y; I^- = I_x - i I_y$$

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

¹H-¹H Spinová výměna (difuze)

Výběr a přenos magnetizace



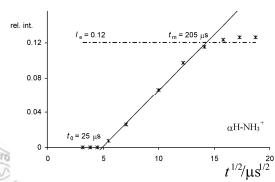
Rychlost spinové výměny: $\frac{\partial M(r,t)}{\partial t} = \frac{\partial}{\partial x} \left[D \frac{\partial M(r,t)}{\partial x} \right] + \frac{\partial}{\partial y} \left[D \frac{\partial M(r,t)}{\partial y} \right] + \frac{\partial}{\partial z} \left[D \frac{\partial M(r,t)}{\partial z} \right]$

Velikost domény dispergované složky A: $d_A = 2 \frac{\mathcal{E}}{f_B} \left(\frac{1}{\pi} D t_m^s \right)^{1/2}$

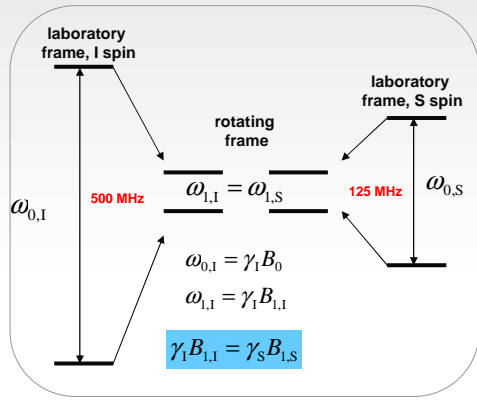
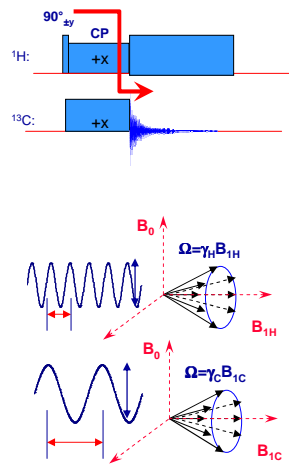
Stanovení spin-difusního koeficientu z pološířky:

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

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

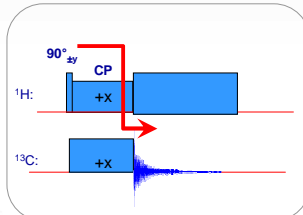
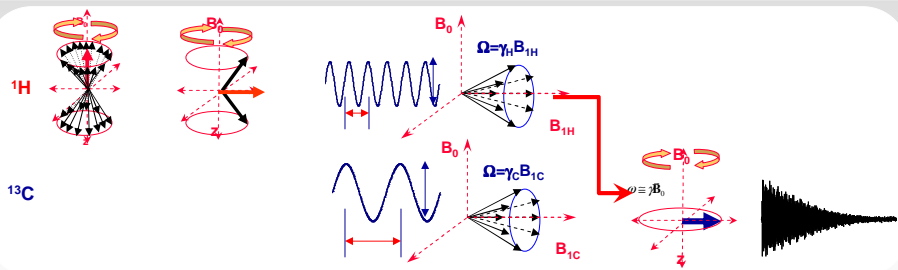


Přenos polarizace v heteronukleárním systému



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Přenos polarizace - experimentální uspořádání



flip-flop

$$\begin{array}{c} -1/2 \quad I_1 S_2 \quad I_1 S_2 \quad -1/2 \\ \hline 1/2 \quad I_1^+ S_2^- \quad I_1^- S_2^+ \quad 1/2 \end{array}$$

$\gamma_1 B_{1,I} = \gamma_S B_{1,S}$

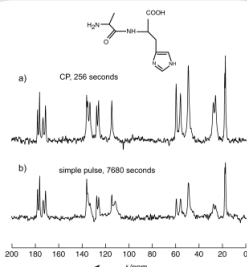
- Polarizace izotopicky hojných jader I.
- Snížení spinové teploty jader I v rotující soustavě souřadné.
- Ustavení kontaktu mezi I a S - spin-lock a HH kontakt.
- Detekce magnetizace S při současném dekaplinku I.



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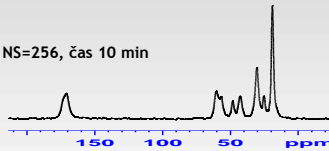
Cross polarizace - zesílení signálů

Porovnání CP a SP/MAS NMR experimentu



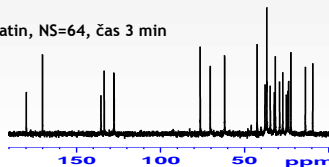
CP - 4 min

Elastin, NS=256, čas 10 min

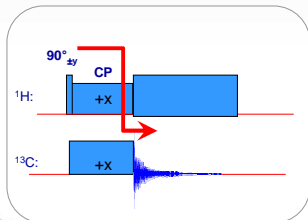
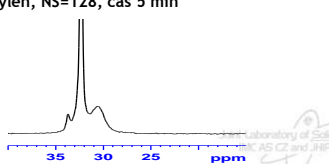


SP - 2 hod

Simvastatin, NS=64, čas 3 min



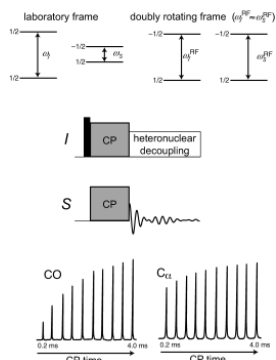
Polyethylen, NS=128, čas 5 min



Dynamika „cross“-polarizace

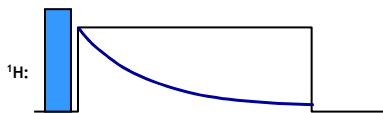
Výstavba NMR signálu

¹³C CP/MAS NMR Glycin, CO a Ca signály

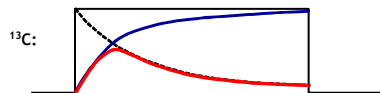


Kombinovaná výstavbová křivka uhlíkové magnetizace

Pokles protonové magnetizace - $T_{1\rho}$



Výstavba cross-polarizace - $T_{1\rho}$



Typické hodnoty CP = 100 ms až 10 ms

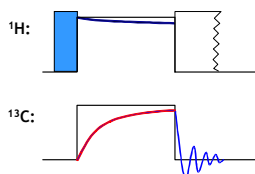
Delší doba CP vyžaduje snížení výkonů obou rf polí - pozor na poškození sondy



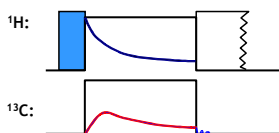
Dynamika „cross“-polarizace

Výstavba NMR signálu

Vhodné okolnosti pro provedení
CP experimentu: $T_{1r} \gg T_{IS}$



Nevhodné okolnosti pro provedení
CP experimentu: $T_{1r} \ll T_{IS}$



Kontaktní doba - praktické aspekty ^{13}C CP/MAS NMR

- Krátká kontaktní doba T_{IS} ($\sim 500 \mu\text{s}$): detekce především jednotek s přímo vázanými protony, ($-\text{CH}_3$, $-\text{CH}_2-$, $>\text{CH}-$)
- Dlouhá kontaktní doba T_{IS} ($> 1 - 2 \text{ ms}$): kvartérní uhlíky ($>\text{C}<$, $-\text{COO}-$, substituované aromáty, ...)
- Dlouhá kontaktní doba T_{IS} ($> 1 - 2 \text{ ms}$): systémy s vysokou vnitřní pohyblivostí
- krátké T_{1r} : systémy s paramagnetickými příměsmi, vysoká pohyblivost

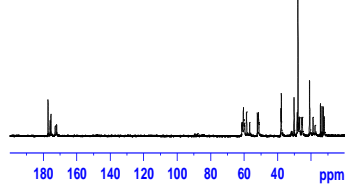


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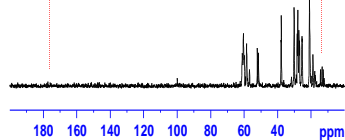
Dynamika „cross“-polarizace

^{13}C CP/MAS NMR

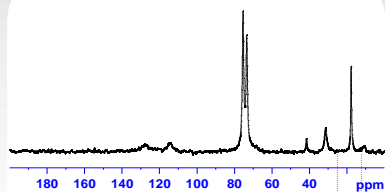
Dlouhá kontaktní doba - 2 ms



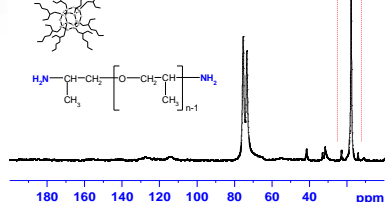
Krátká kontaktní doba - 0,1 ms



^{13}C CP/MAS NMR

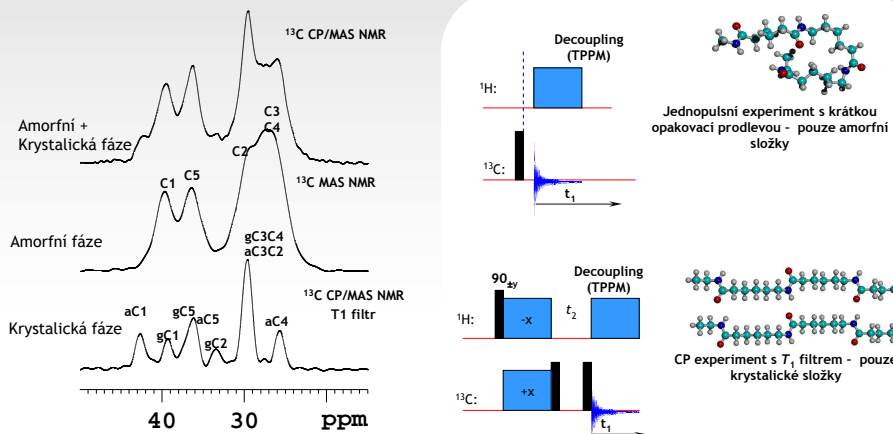


^{13}C MAS NMR

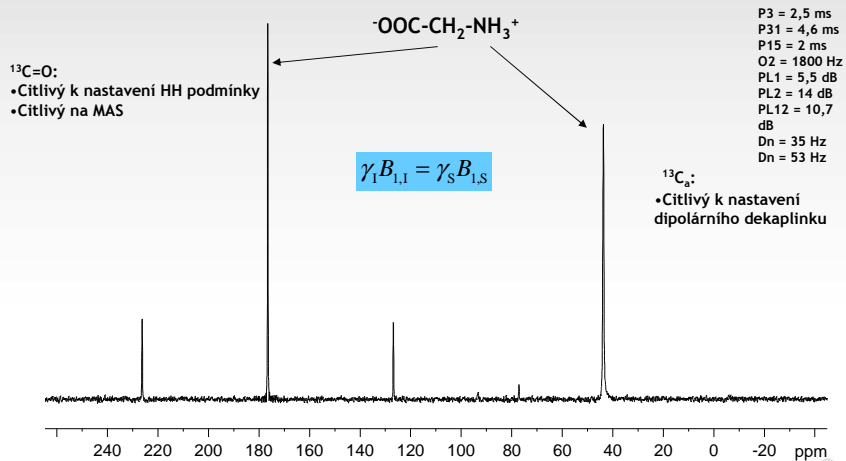


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Dynamika CP a selektivní experimenty

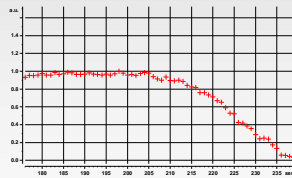


Praktické aspekty: optimalizace CP



Praktické aspekty: optimalizace CP

Glycin- $^{13}\text{C}_\alpha$



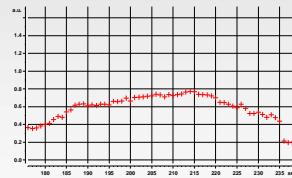
Výkon B_{15} pole

$$\gamma_I B_{1,I} = \gamma_S B_{1,S}$$

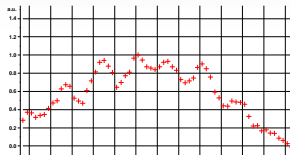
Do frekvence rotace cca. 5-7 kHz

Široké a ploché maximum HH podmínky

Glycin- ^{13}CO



Výkon B_{15} pole

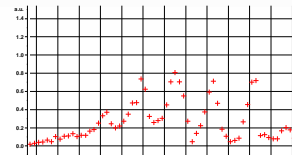


Výkon B_{15} pole

$$\gamma_I B_{1,I} = \gamma_S B_{1,S} \pm n \omega_r$$

Pro MAS frekvence rotace větší jak 8 kHz

Rotační maxima!!!



Výkon B_{15} pole

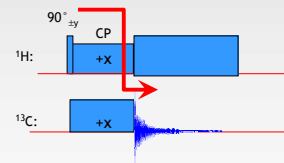
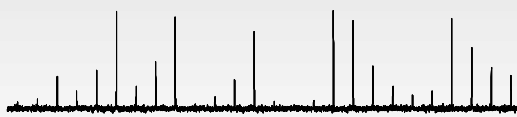


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Praktické aspekty: optimalizace CP

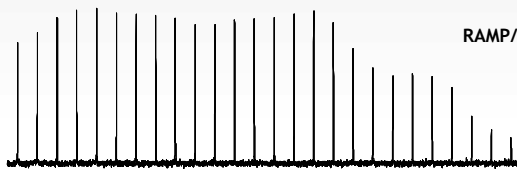
HH/CP/MAS NMR

13 kHz

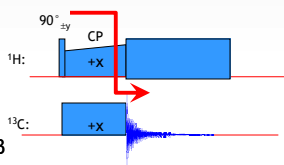


RAMP/CP/MAS NMR

13 kHz



10 11 12 13 14 15 16 17 18 19 p12 in dB



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IMC AS CZ and JHPC AS CZ

Křížová-polarizace - 1972



Alex Pines
*1945

This Week's Citation Classic

Pines A, Gibby M G & Waugh J S. Proton-enhanced NMR of dilute spins in solids. *J Chem Phys* 56:56-69, 1972. Department of Chemistry and Research Laboratory of Electronics, Massachusetts Institute of Technology, Cambridge, MA.

The NMR signals of isotopically or chemically dilute nuclear spins "S" can be enhanced by repeated cross-polarization under the Hartmann-Hahn condition from a more abundant species "I" (usually hydrogen). High-frequency modulation is obtained by decoupling of the spins during observation of the S spin free induction decay. The theory and experimental requirements are discussed, and illustrative applications to carbon-13 NMR in organic solids are demonstrated. (The SC# indicates that this paper has been cited in more than 1,000 publications.)

Carbon-13 NMR in Solids

Alexander Pines
Lawrence Berkeley Laboratory and
Department of Chemistry
University of California
Berkeley, CA 94720

As a small boy, I often wondered about the chemical shift anisotropy of benzene. After my application for graduate school was rejected at Berkeley, I settled for the Massachusetts Institute of Technology (MIT), Cambridge.

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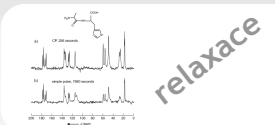
A model sample to try the experiment. Henry A. Resing (known affectionately as Mr. Adamantane because of his work on plastic crystals) was visiting, and I asked him what would be a cheap compound with at least two inequivalent carbon sites, solid at room temperature but with the molecules reorienting roughly isotropically, and with T1 and T1 rho relaxation times of about one second. He suggested adamantane. Indeed, after we vaporized a number of samples in the probe with high radiofrequency power, the first successful experiments showed two resolved carbon-13 peaks with good signal/noise in solid adamantane. We

a model sample to try the experiment. Henry A. Resing (known affectionately as Mr. Adamantane because of his work on plastic crystals) was visiting, and I asked him what would be a cheap compound with at least two inequivalent carbon sites, solid at room temperature but with the molecules reorienting roughly isotropically, and with T1 and T1 rho relaxation times of about one second. He suggested adamantane. Indeed, after we vaporized a number of samples in the probe with high radiofrequency power, the first successful experiments showed two resolved carbon-13 peaks with good signal/noise in solid adamantane. We subsequently obtained



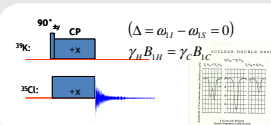
Souhrn

Nizká citlivost ss-NMR experimentů

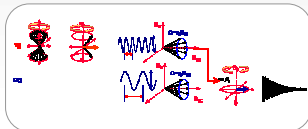


relaxace

Hartman-Hahnova podmínka

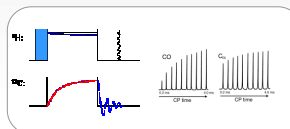


Dipolární kontakt a flip-flop přechody

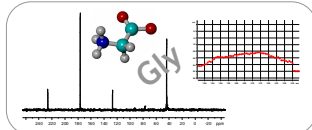


Solid-state NMR and

Dynamika CP



Optimalizace CP experimentů



CP při vysokých frekvencích MAS a B0 polích

