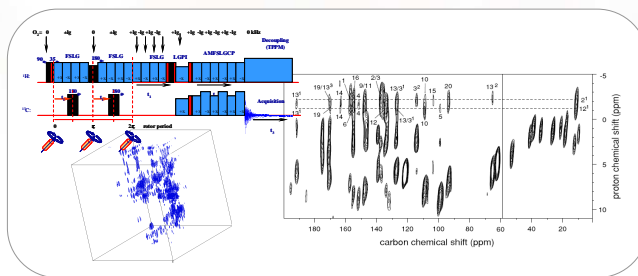
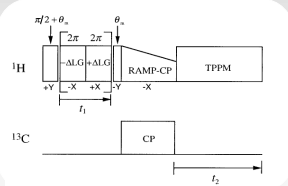


Heteronukleární korelační experimenty



2D korelační NMR v pevné fázi - 1990-2000

FSLG dekaplink

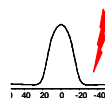
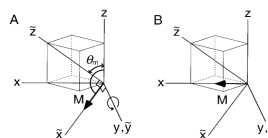
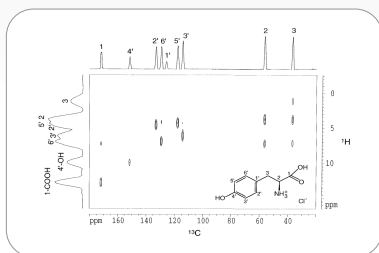


Mimorezonanční podmínka $\Delta LG(O2) = \omega_1/\sqrt{2}$

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

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

τ odpovídá 2π rotaci kolem efektivního pole.

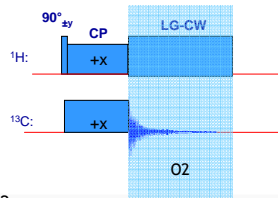
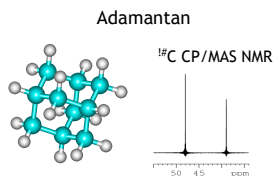


van Rossum BJ.; Foerster H.; De Groot HJM.
High-Field and High-Speed CP-MAS ¹³C NMR Heteronuclear Dipolar-Correlation Spectroscopy of Solids with
Frequency-Switched Lee-Goldburg Homonuclear Decoupling. *J. Magn. Reson.* 124, 516, (1997).



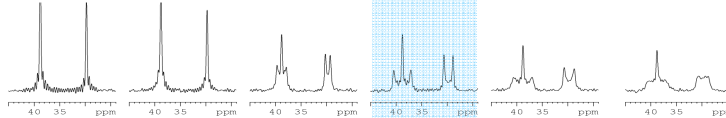
Optimalizace FSLG

Pro výkon dekaplovacího pole ^{13}C hledáme optimální offset O2.



Optimalizace offsetu O2.

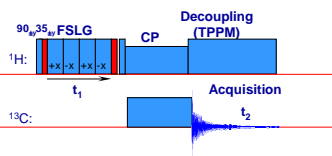
Offset = 9.8 kHz 18.8 kHz 38.0 kHz 64.0 kHz 84.0 kHz 94.0 kHz



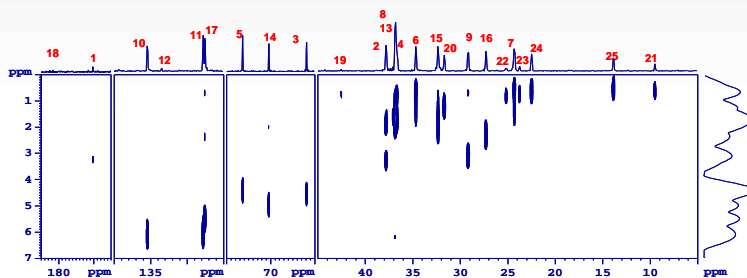
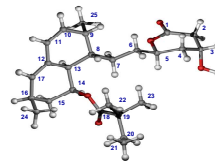
Joint Laboratory of Solid-State NMR
IMCAS CZ and JHPCAS CZ

2D ^1H - ^{13}C FSLG HETCOR

Jednovazebné korelace



Velmi krátká doba přenosu polarizace CP kontaktní doba 50-100 μs .

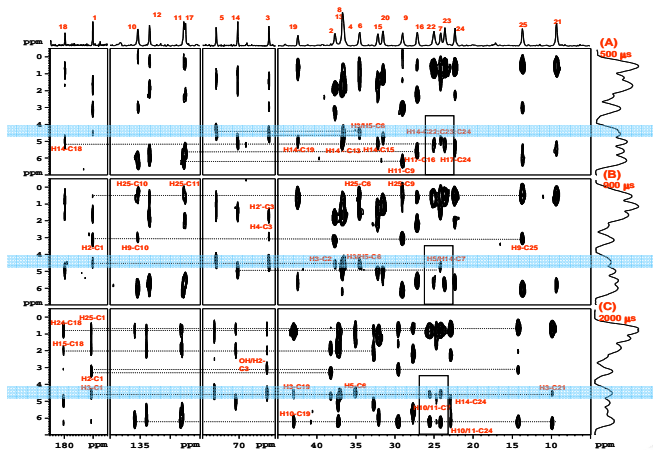


Joint Laboratory of Solid-State NMR
IMCAS CZ and JHPCAS CZ

2D ^1H - ^{13}C FSLG HETCOR

Vzdálené korelace

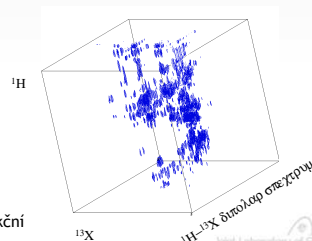
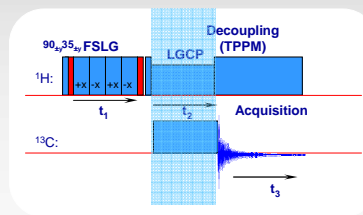
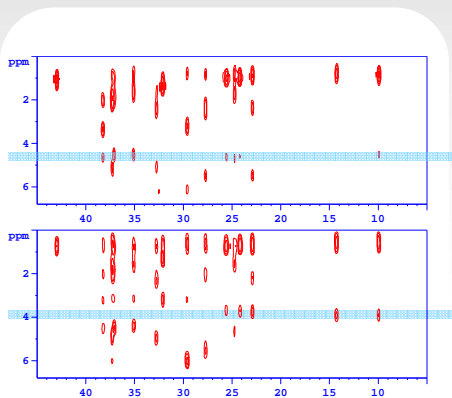
Prodlužující se doba přenosu polarizace až na 5 ms.



Laboratory of Solid-State NMR
JMC AS CZ and JHPC AS CZ

3D ^1H - ^{13}C FSLG HETCOR

Vzdálené korelace



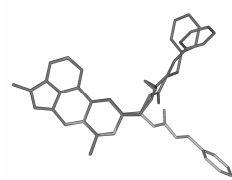
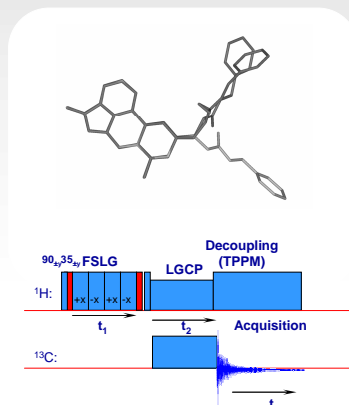
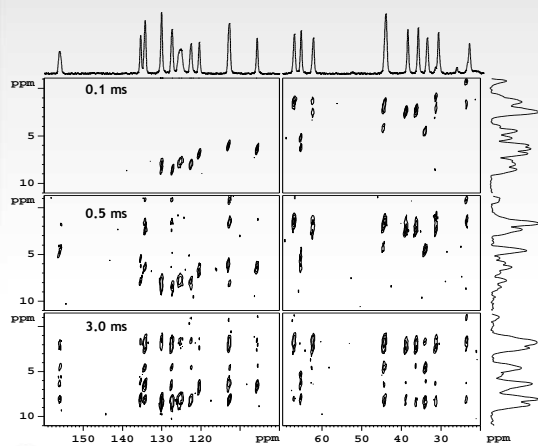
Pro každý rozlišený spinový pár ^1H - ^{13}C lze naměřit dipolární interakční konstantu a odhadnout meziatomovou vzdálenost.



Laboratory of Solid-State NMR
JMC AS CZ and JHPC AS CZ

^1H - ^{13}C kontakty: dipolární spektroskopie

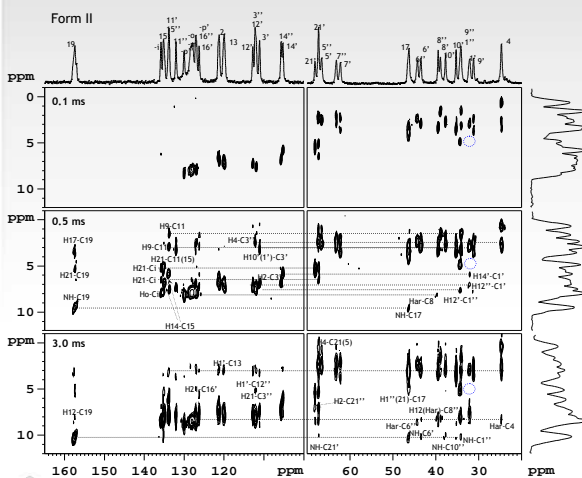
Rozšířený 3D experiment



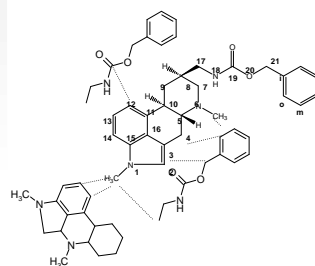
Joint Laboratory of Solid-State NMR
IMC AS CZ and JHPC AS CZ

Strukturní fragmenty

3D ^1H - ^{13}C FSLG-LGCP HETCOR



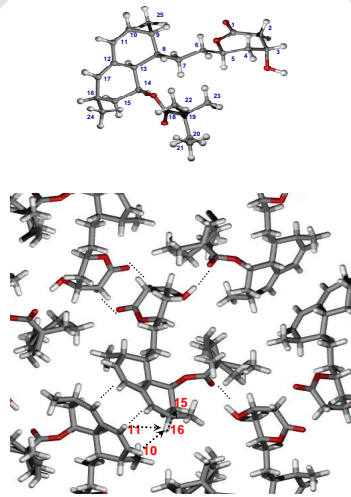
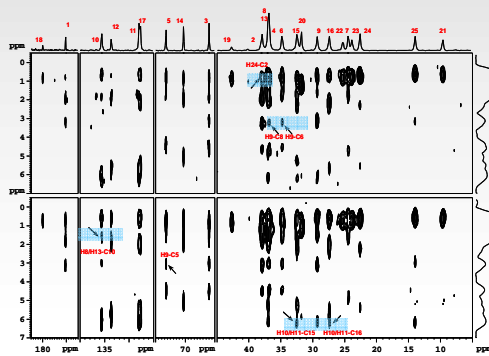
Structural fragments determined from ssNMR spectra



Joint Laboratory of Solid-State NMR
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2D ^1H - ^{13}C FSLG HETCOR - $^1\text{H}\dots^1\text{H}\dots^{13}\text{C}$

Štafetový přenos polarizace

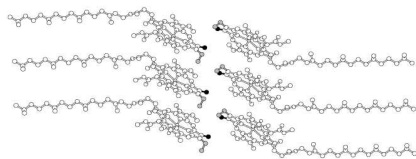
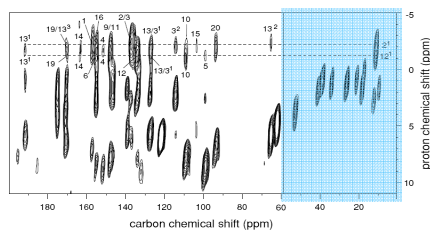


HH-CP - Během delší doby CP se velká část ^1H magnetizace rozfázuje, ale také nastává spinová difuze a magnetizace se šíří mezi vodíky a teprve po jisté době se přeneše do vzdálenějších ^{13}C .

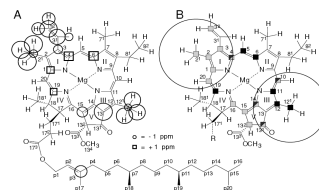
Korelační signály reflektují $^1\text{H}\dots^1\text{H}\dots^{13}\text{C}$ transfer. To je výhodné pro detekci intermolekulárních kontaktů.



2D ^1H - ^{13}C HETCOR - krystalový disorder



Chlorofyl $a/\text{H}_2\text{O}$



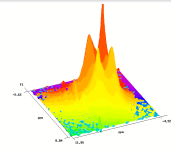
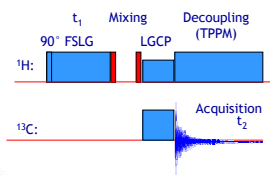
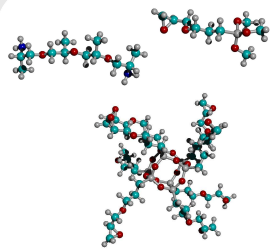
Alifatické řetězce - Korelační signály jsou trochu skloněny - disperze ^1H a ^{13}C posunů je korelovaná - malé nehomogenní rozšíření: nepatrné změny v konformaci alifatických ocásků.

Polycyklická část - Korelační signály jsou paralelní s osou ^1H - žádná disperze ^{13}C posunů - zcela krystalické konformačně uniformní: prorotová separace obou částí molekuly.

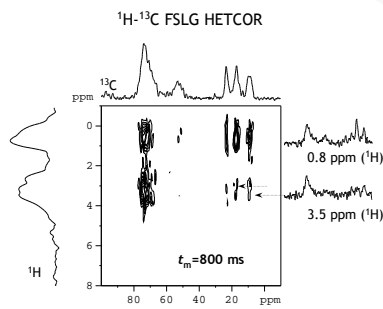


Aplikace: nano-heterogeneous networks

Epoxy-siloxane networks



2D ¹H MAS NMR spectrum

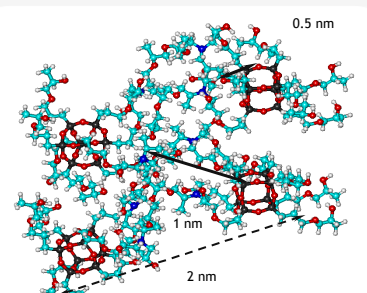
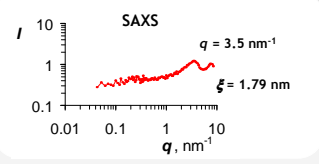
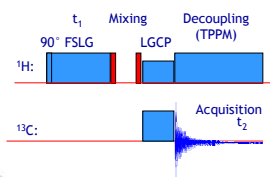
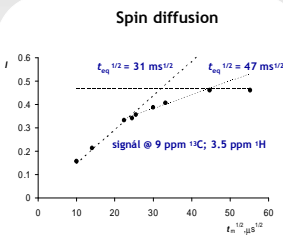


¹H-¹³C FSLG HETCOR



Aplikace: Nano-heterogeneous networks

Epoxy-siloxane networks



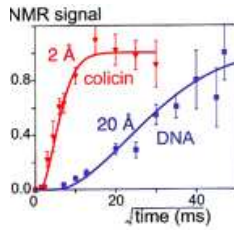
Brus J. et al., Self-organization, structure, dynamic properties, and surface morphology of silica/epoxy films as seen by solid-state NMR, SAXS, and AFM, *Macromolecules* (2004); 37: 1346.



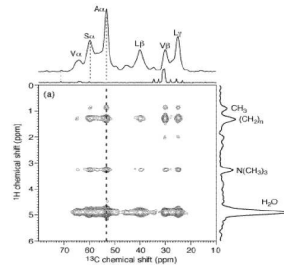
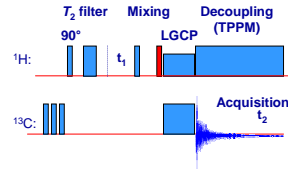
Aplikace: uspořádání v lipidové membráně



Colicin Ia - částečně zabořený do lipidové membrány - rychlá spinová difuze.



DNA - řetězce jsou pouze na povrchu - pomalá spinová difuze.



Daniel Huster, Xiaolan Yao, and Mel Hong.
Membrane Protein Topology Probed by ^1H Spin Diffusion from Lipids Using Solid-State NMR Spectroscopy, *J. Am. Chem. Soc.*, VOL. 124, NO. 5, 2002.



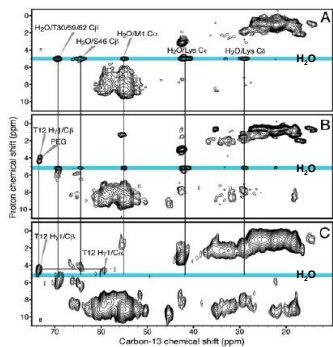
Aplikace: mikrokrytalické proteiny

Lokalizace vody - detekce ^1H NMR signálu

A. Böckmann, M. Juy, E. Bettler, L. Emsley, A. Galinier, F. Penin, A. Lesage, Water-Protein Hydrogen Exchange in the Micro-Crystalline Protein Crh as Observed by Solid State NMR Spectroscopy, *Journal of Biomolecular NMR*, 32 195 (2005).

Anne Lesage, Lyndon Emsley, Francois Penin, and Anja Bockmann, Investigation of Dipolar-Mediated Water-Protein Interactions in Microcrystalline Crh by Solid-State NMR Spectroscopy, *J Am Chem Soc* 128, 8246 (2006).

2D ^1H - ^{13}C HETCOR – mikrokrytalický systém

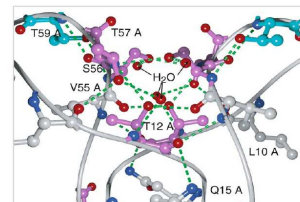
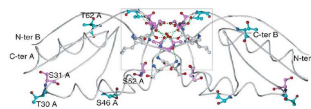


Detekce imobilizovaných i pohyblivých molekul (rezidenční čas – jednotky ns)

Přímá chemická výměna H_2O -OH

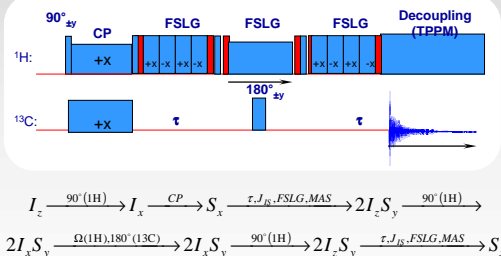
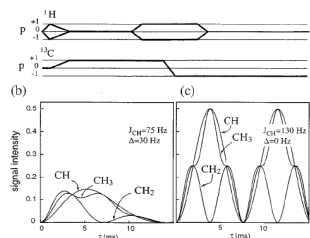
Detekce zcela imobilizovaných a fixovaných molekul (rezidenční čas – jednotky μs)

Mikrokrytalický protein Crh (catabolite repression histidine containing phosphocarrier protein)



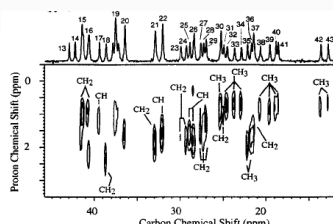
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2D ^1H - ^{13}C HMQC-J-MAS - maximální selektivita



HMQC-J-MAS

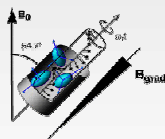
1. CP - ^{13}C magnetizace (S_y)
2. t - S_x podle skalární interakce J_{CH} na anti-fázovou $I_z S_y$
3. FSLG a MAS - potlačí // a J S dipolární interakce + CSA
4. $90^\circ(^1\text{H})$ - anti-fázovou $I_z S_y$ na dvoukvantovou $I_x S_y$
5. t_1 - koherence $I_x S_y$ se vyvíjí podle ^1H chemického posunu
6. $180^\circ(^{13}\text{C})$ - refokusace ^{13}C chemického posunu
7. DQ koherence necitlivá na J_{CH} , FSLG, MAS a $180^\circ(^{13}\text{C})$
8. $90^\circ(^1\text{H})$ - dvoukvantovou $I_x S_y$ na anti-fázovou $I_z S_y$
9. t - anti-fázová $I_z S_y$ se refokusuje podle J_{CH} na S_x
10. detekce



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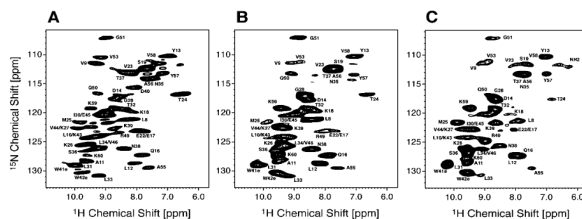
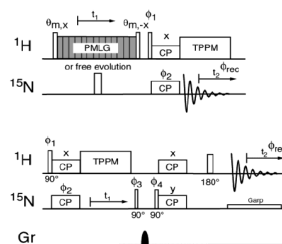
Inverzní detekce a gradientová spektroskopie

Veniamin Chevelkov, et al. ^1H Detection in MAS Solid-State NMR Spectroscopy of Biomacromolecules Employing Pulsed Field Gradients for Residual Solvent Suppression, *J. Am. Chem. Soc.*, 125 7788 2003.



Speciální podmínky pro inverzní experiment:

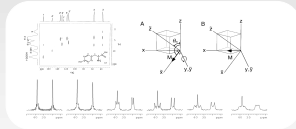
1. CP/MAS sonda s gradientovými cívkami
2. Peptidy, proteiny.
3. Plně obohacení deuteriem + následná výměna labilních ND na NH.
4. Potlačení signálů zbytkové vody - vzorky musí být hydratované



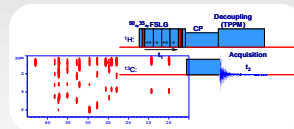
Laboratory of Solid-State NMR
IMC AS CZ and JHPC AS CZ

Souhrn

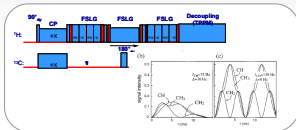
FSLG a jeho optimalizace



2D FSLG HETCOR

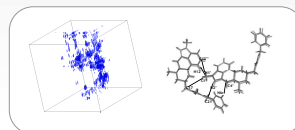


Selektivita HHCP, LGCP a HMQC-J-MAS

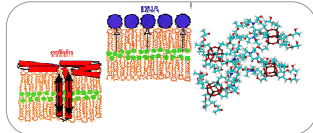


Solid-state NMR
and

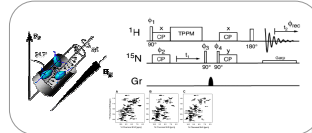
3D FSLG HETCOR



Spinová difúze a morfologie polymerů



Inverzní detekce



Institute of Solid-State NMR
and JHPC AS, CZ