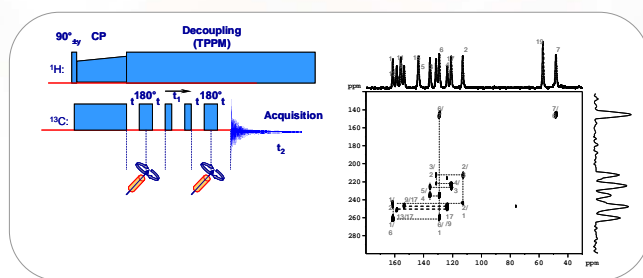
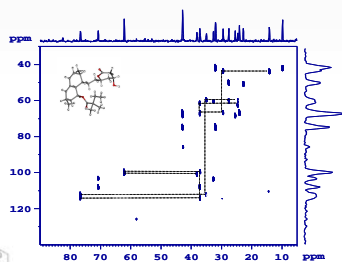
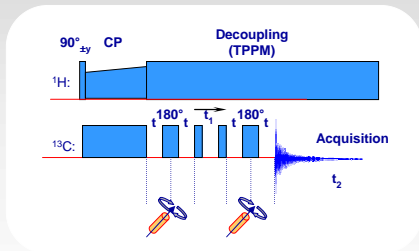


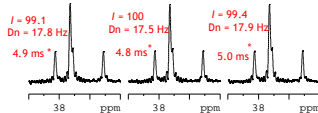
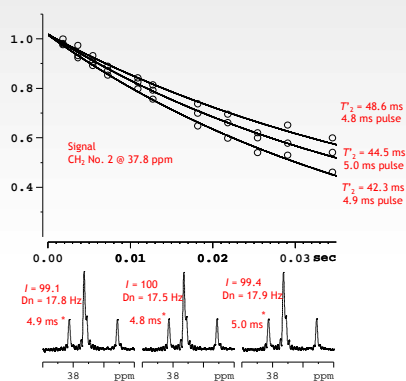
X-X a X-Y korelace - zvýšení spektrálního rozlišení



T_2 -optimalizovaný INADEQUATE

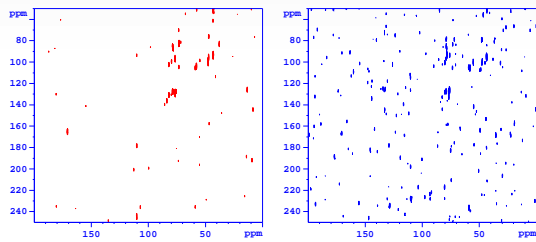
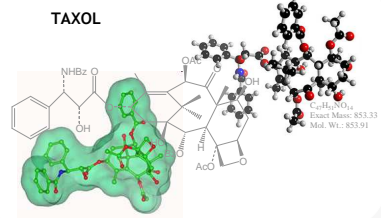
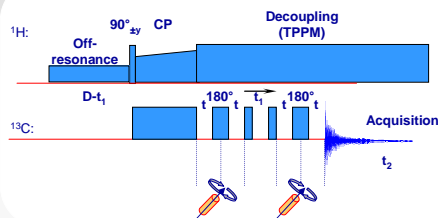


^{13}C coherence lifetime T_2^* at various length of decoupling pulse (TPPM)



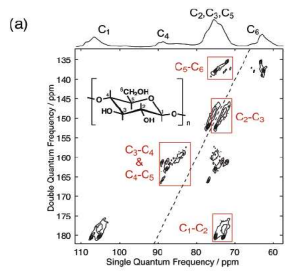
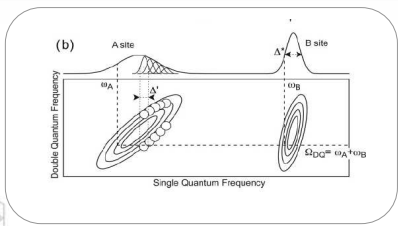
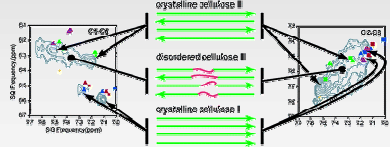
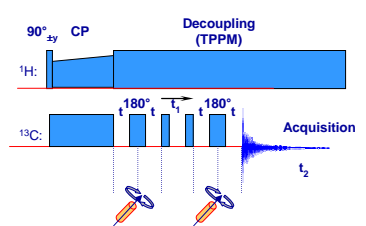
Linewidth and intensity of the signal CH₂ (2) at various length of decoupling pulse (TPPM)

T_2 -optimalizovaný INADEQUATE



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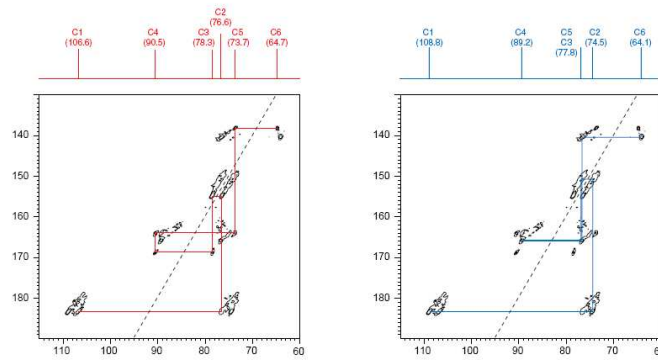
Korelace disperze chemických posunů



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Korelace disperze chemických posunů - disorder

Celuloza

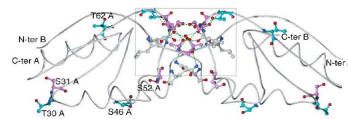
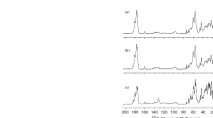
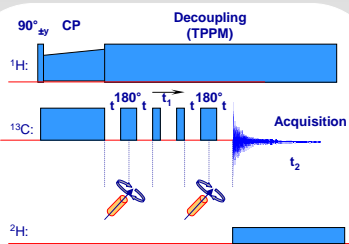
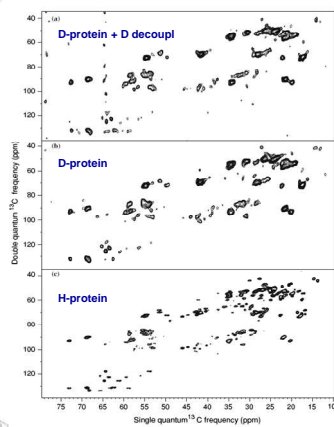


In more complex systems, correlations can be exploited to extract *chains of correlated shifts*. Each chain corresponds to the chemical shifts of an entire subunit with a given conformation.



Korelace disperze chemických posunů - deuterače

Mikrokrytalický protein Crh
(catabolite repression histidine containing phosphocarrier protein)

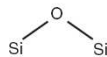


Korelace disperze chemických posunů - susceptibilita

Chemical Disorder (local effect)

a change in the isotropic chemical shift from one molecule to another

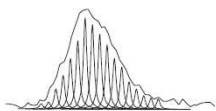
e.g., glasses, catalysts, polymers



Magnetic Susceptibility (bulk effect)

a change in the Larmor frequency from one part of the sample to another

heterogeneous samples



How can the chemical shift differences due to disorder be removed without removing the chemical shift differences that distinguish sites from each other?



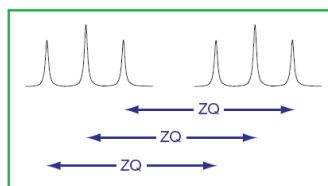
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Korelace disperze chemických posunů - refokusace

Zero-Quantum Spectroscopy

For susceptibility broadening or broadening due to an inhomogeneous applied field, the shifts at one nucleus are perfectly correlated in a one-to-one fashion with the shifts at another nearby nucleus

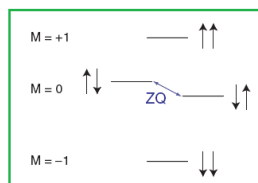
Thus, while the individual chemical shifts change, the chemical shift differences remain the same



Hall et al. 1981: Zero-quantum NMR spectra are free of B_0 broadening

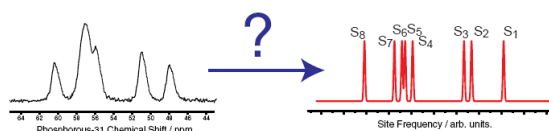
Warren et al. 1996: Intermolecular solvent-solute ZQ coherences yield high-resolution spectra in unstable very high magnetic fields

Terao et al. 1999: ZQ sideband spectra are free of susceptibility broadening in paramagnetic solids



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Korelace disperze chemických posunů - refokusace



To record this red spectrum we must refocus the chemical shift distribution due to disorder within a site, **without** refocusing the chemical shifts that distinguish sites from each other.

This cannot be done if the sites are isolated from each other.

It can be achieved if

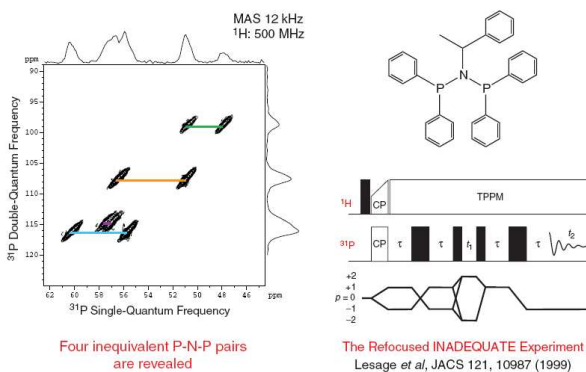
- (i) the sites can be connected in a multi-dimensional spectrum
- (ii) the chemical shifts between coupled pairs of spins are highly correlated.



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Korelace disperze chemických posunů - refokusace

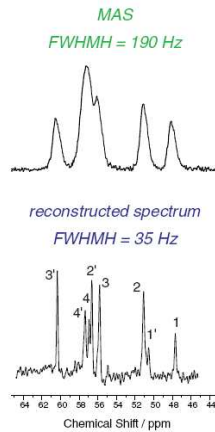
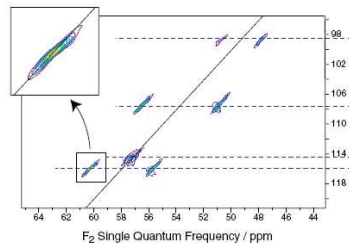
³¹P-³¹P Through-Bond Connectivities



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Korelace disperze chemických posunů - refokusace

The shifts are well correlated,
but there are deviations
from a 1:2 ratio for the
SQ and DQ frequencies

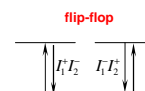
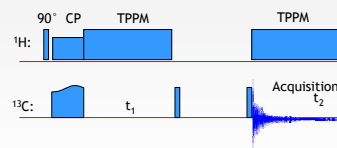
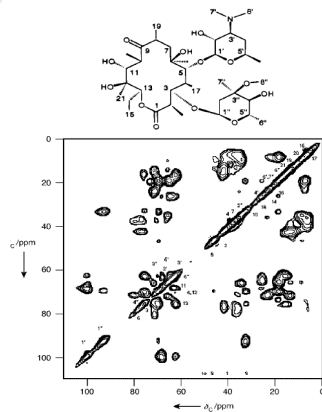


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¹³C-¹³C korelace (PDSD) - dipolární interakce

Proton Driven Spin Diffusion

$$P(t) = \frac{1}{2} \pi g_0^{jk} (\omega_j - \omega_k \omega_D^2) t$$



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3D struktura prionových proteinů (2005)

Meier B.H. et al.,
Correlation of Structural Elements and Infectivity of the
HET-s prion, *Nature* (2005); 435(9): 844.

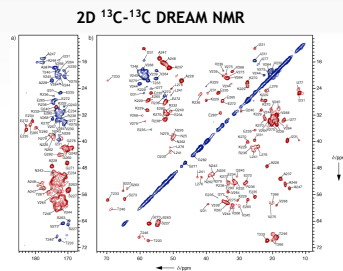


Beat.H. Meier
*1954

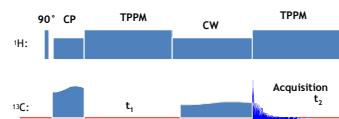


PrPC

PrPSc



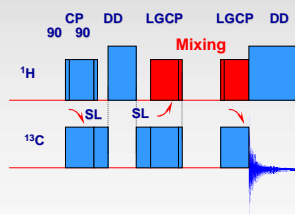
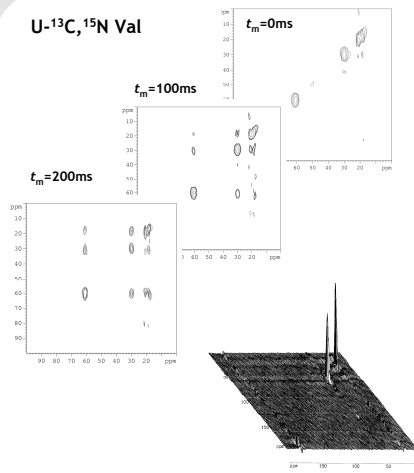
Dipolar Recoupling Enhancement through Amplitude Modulation



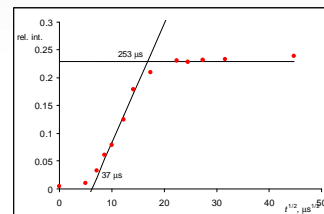
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2D ^{13}C - ^{13}C korelace - ^1H - ^1H spinová difuze

$\text{U-}^{13}\text{C}$, ^{15}N Val

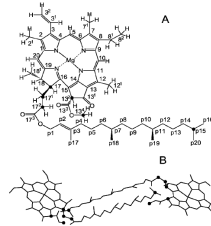
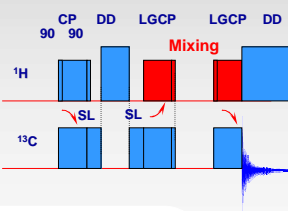
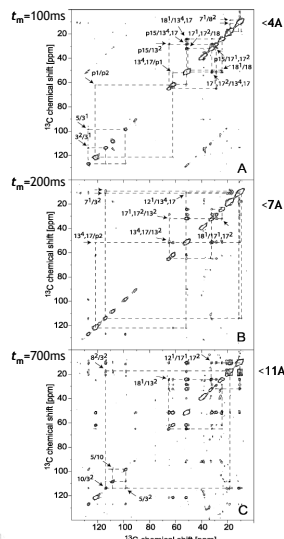


$t_m = 0\mu\text{s}$;
CP1=500 μs ;
CP2=100 μs ;
CP3=100 μs



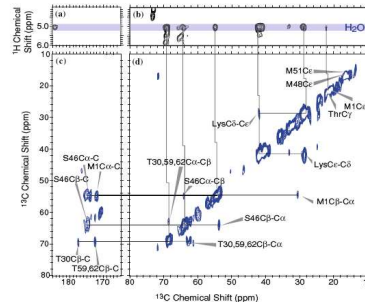
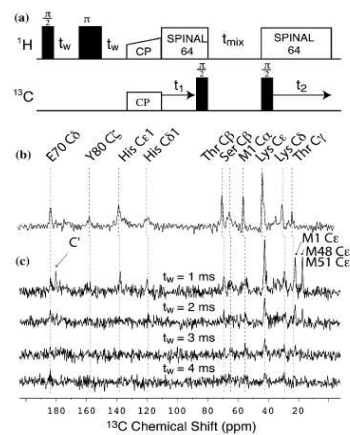
Joint Laboratory of Solid-State NMR
IMC AS CZ and JHPC AS CZ

2D ^{13}C - ^{13}C korelace - ^1H - ^1H spinová difuze



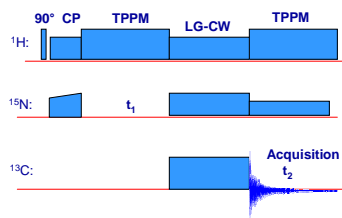
Ido de Boer, L. Bosman, J. Raap, H. Oschkinat and H. J. M. de Groot.
2D ^{13}C - ^{13}C MAS NMR Correlation Spectroscopy with Mixing by True ^1H Spin Diffusion Reveals Long-Range Intermolecular Distance Restraints in Ultra High Magnetic Field, *J. Magn. Reson.* 157, (2002) 286-291.

Lokalizace molekul vody - ^{13}C - ^{13}C

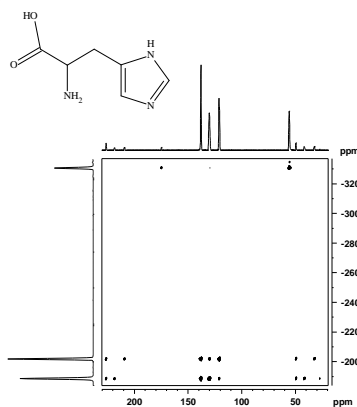


A. Böckmann, M. Juy, E. Bettler, L. Emsley, A. Galinier, F. Penin, A. Lesage.
Water-Protein Hydrogen Exchange in the Micro-Crystalline Protein Crh as Observed by Solid State NMR Spectroscopy, *Journal of Biomolecular NMR*, 32 195 (2005).

2D ^{13}C - ^{15}N dvojitá cross-polarizace



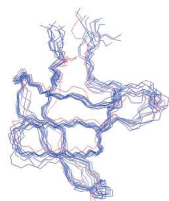
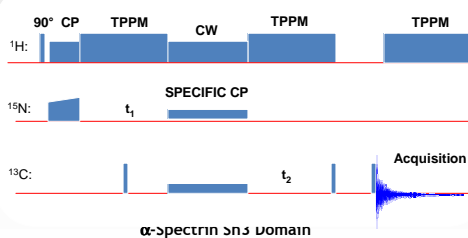
- Avance 500 WB
- 4 mm sonda
- $^1\text{H}/^{15}\text{N}$, 2 ms kontakt
- $^{15}\text{N}/^{13}\text{C}$, 1 ms kontakt
- variable amplitude (50 % ramp)
- ^{15}N RF field: 64 kHz
- ^{13}C RF field: 64 kHz
- ^1H RF field: 89 kHz



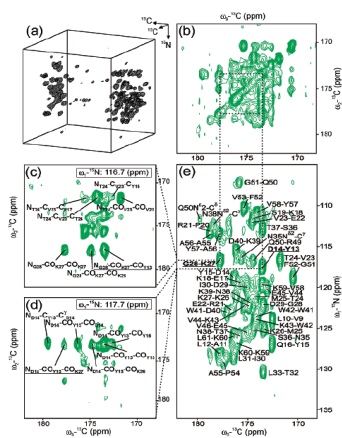
Jiří Labárek, Institute of Organic Chemistry and Biochemistry, Academy of Sciences of the Czech Republic, Prague, Czech Republic

3D: ^{13}C - ^{15}N dvojitá CP + ^{13}C - ^{13}C PDSD

Experimenty s dvojitou cross-polarizací

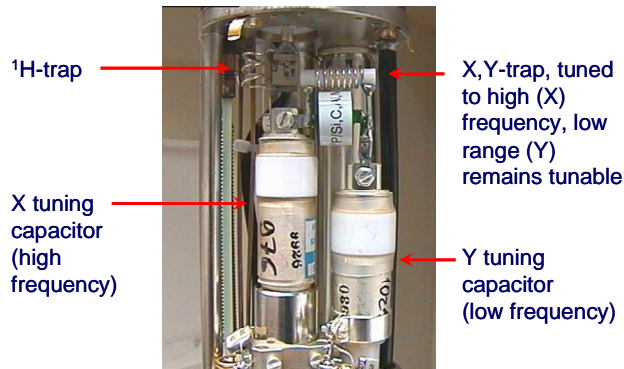


Castellani, F., van Rossum, B.J., Diehl, A., Schubert, M., Rehbein, K., and Oschkinat, H. Structure of a protein determined by solid-state magic-angle-spinning NMR spectroscopy, *Nature* 420, 98-102 (2002).



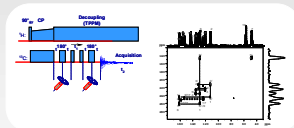
Tří-rezonanční experimenty ^{13}C - ^{15}N korelace

Experimenty s dvojitou cross-polarizací
Konstrukce sondy

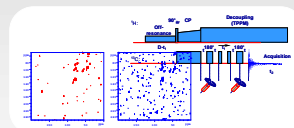


Souhrn

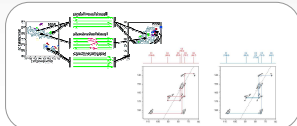
J-DQ: INADEQUATE



T2-optimizovaný INADEQUATE

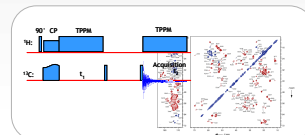


Korelovaný disorder

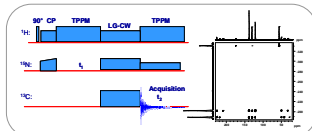


Solid-state NMR
and

^{13}C - ^{13}C PDSD



Double-CP- ^{13}C - ^{15}N



3D Double CP-PDSD

