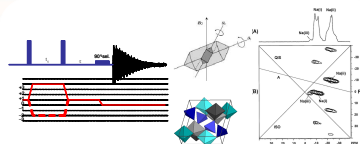
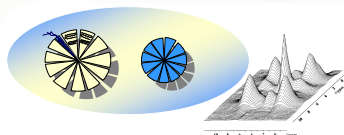


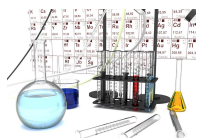


NMR spektroskopie pevného stavu

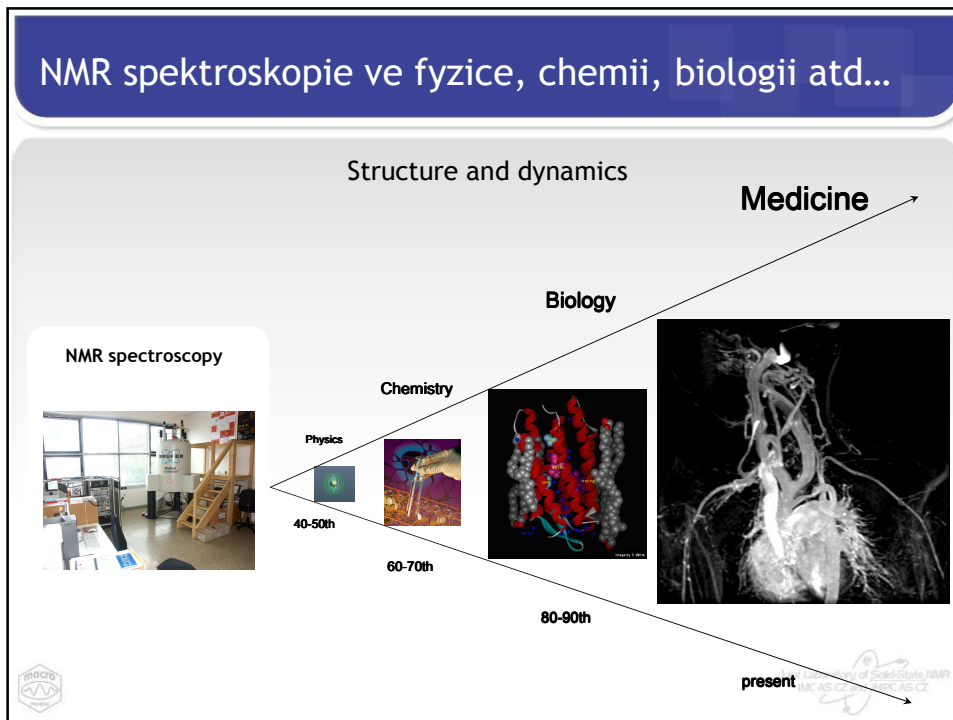


Přehled kursu ss-NMR spektroskopie

- Historický úvod do NMR spektroskopie pevné fáze
- Anizotropní interakce v pevných látkách (CSA, DC, MAS, dipolární dekaplink)
- Techniky přenosu polarizace - "cross"-polarizace
- Techniky editace 1D NMR spekter (NQS, CPPI, SoS APT)
- 2D heteronukleární experimenty - separace lokálních polí
- 2D heteronukleární korelační experimenty
- 2D homonukleární korelační experimenty
- 2D ^1H - ^1H dvou-kvantové techniky - π - π interakce a HB
- X-X a X-Y korelace - dvojitě CP, TDO-CP-INADEQUATE
- Peptidy a proteiny, přiřazení signálů a struktura
- Kvadrupolární jádra - SQ-TQ experimenty
- Technická omezení NMR spektroskopie pevného stavu



NMR spektroskopie ve fyzice, chemii, biologii atd...



Úsvit vesmíru a NMR

“Epoch of Nucleosynthesis” - 3 min - 400 000 years: 10^9 -3000 K - formation of heavier nuclei

“Lepton Epoch” - 1s - 3 min: 10^{10} - 10^9 K - formation of protons

“Hadron Epoch” - 10^{-6} -1s: 10^{13} - 10^{10} K - quarks combine to form protons and neutrons

“Electroweak Epoch” - 10^{-12} - 10^{-6} s: 10^{15} - 10^{13} K - formation of electrons and pozitrons

“Grand Unification Epoch” - 10^{-35} - 10^{-12} s: 10^{27} - 10^{19} K - formation of quarks

“Planck Epoch” - 10^{-43} - 10^{-34} s: 10^{32} - 10^{27} K

The Big Bang -time 0 s

$\alpha - 1/137$

Spin predicted by W. Pauli in 1924 as the 4-th quantum number
1945 - Nobel Prize

Logo: JINPAC AS CR and JHPC AS CR

Historie - měření magnetického momentu 1938



Isidor Isaac Rabi
1898-1988
1944 - Nobel Prize



RADAR technologie



Rabi I., Zacharias JR, Millman S, Kusch P.
A new method of measuring nuclear magnetic moment.
Phys Rev 1938; 53: 318.

$$E = h \cdot \nu = 6,6262 \cdot 10^{-34} \times 5 \cdot 10^8 = 3,31 \cdot 10^{-25} \text{ J}$$

$$0,001 \text{ g hmoty} \dots\dots 2 \cdot 10^{-4} \text{ J}$$

$$E = mc^2 \dots \text{ v } 0,001 \text{ g hmoty se ukrývá } 9 \cdot 10^{10} \text{ J}$$

Atomové hodiny



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Historie - první NMR signály 1946-51



Felix Bloch
1905-1983



Edward M. Purcell
1912-1997



1952 - Nobel Prize



Laboratoř F. Blocha

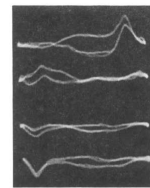
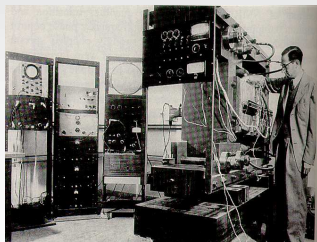
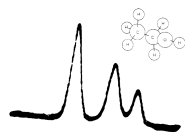
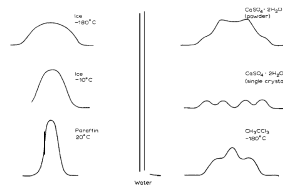


Fig. 10. Photographic record of the proton signal in water. The four traces from top to bottom correspond to the times t_1, t_2, t_3, t_4 of Fig. 9. In the text they are referred to as a, b, c, d , respectively.

Bloch, F.; Hansen, W. W.; Packard, M.
The nuclear induction experiment
Physical Review (1946), 70 474-85.



Arnold, J.T., S.S. Dharmatti, and M.E. Packard,
J. Chem. Phys., 1951, 19: p. 507.



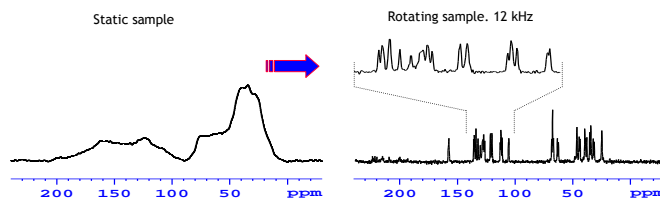
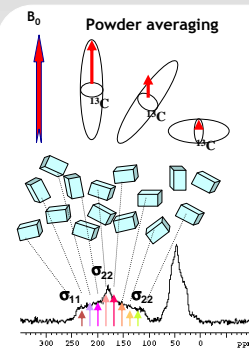
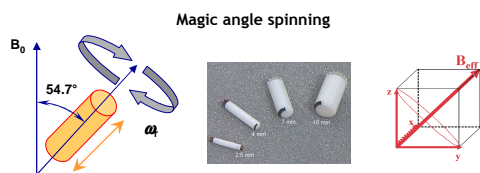
Historie - rotace vzorku pod magickým úhlem 1958



I.J. Lowe

Lowe, I.J.,
Free Induction Decays in Rotating Solids, *Phys. Rev. Lett.* (1959); 2: 285.

Andrew E.R., Bradbury A., Eades R.G.
NMR spectra from a Crystal Rotated at High Speed, *Nature* (1958); 182: 1659.

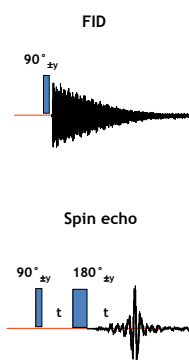


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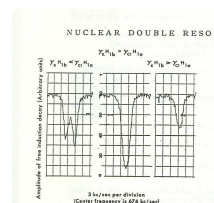
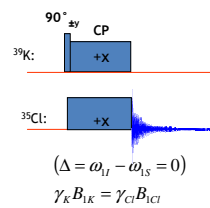
Historie - Hahnovi experimenty (1950-1962)



Erwin L. Hahn
*1921



Cross polarization



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.



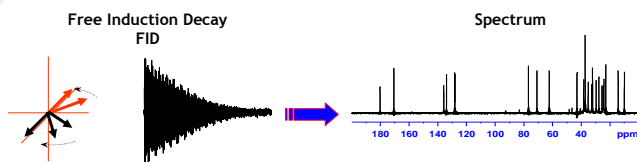
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Historie - Pulsní NMR (1966.....1822)

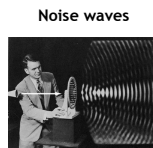


Richard R. Ernst
*1933
1991 - Nobel Prize

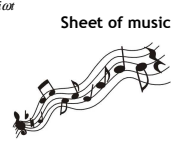
Ernst R.R., Anderson W.A.
Application of FT Spectroscopy to Magnetic resonance, *Rev.Sci.Instr.* (1966); 37: 93.



Jean Baptiste Joseph
Fourier
1768-1830



$$F(\omega) = \int_{-\infty}^{\infty} dt. f(t) e^{-i\omega t}$$



Fourier J.B.J.
Théorie analytique de la chaleur, *Firmin Didot, pere et fils, Paris.* (1822).

Joint Laboratory of Solid State NMR
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Objev více-rozměrné NMR spektroskopie (1971)

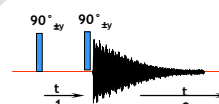
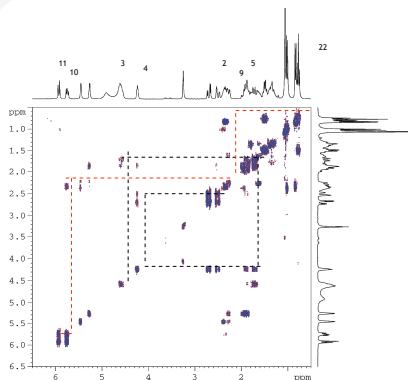
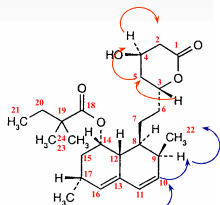


Jean Luis Charles Jeener
*1931

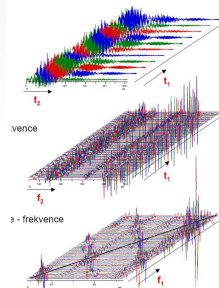
Přenos magnetizace přes vazebné elektrony
(konektivita řetězce)

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

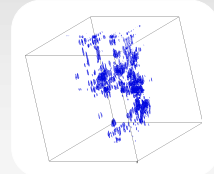
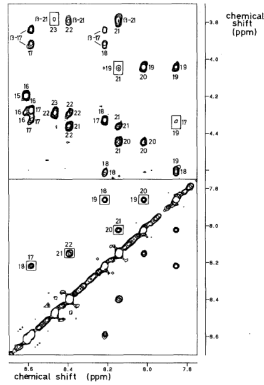
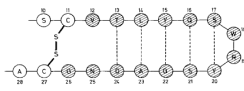


Historie - 3D struktura proteinů (1986)

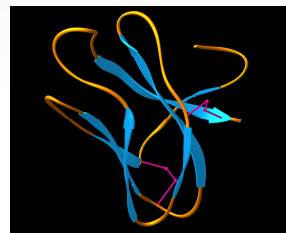
Allen D. Kline, Werner Braun and Kurt Wüthrich,
 Studies by ^1H nuclear magnetic resonance and distance geometry of the
 solution conformation of the α -amylase inhibitor Tendamistat. *J. MOL. BIOL.* 189
 (2): 377-382 MAY 20 1986



Kurt Wüthrich
 *1938
 2002 - Nobel Prize



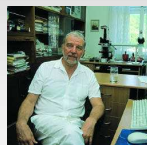
TENDEMISTAT



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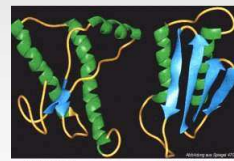
Prionová onemocnění mozku



František Koukolík
 *1954

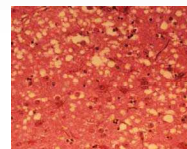
Neuropatolog, primář patologie Fakultní Thomayerovy
 nemocnice v Praze a vedoucí Národní referenční
 laboratoře TSE/CJN

Konformační
 polymorfismus proteinů

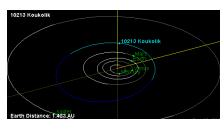


Zdravý PrPc

Poškozený PrPc



Bublinky vzniklé v nemocné mozkové
 tkáni



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Křížová-polarizace - 1972

Zvýšení citlivosti NMR experimentu

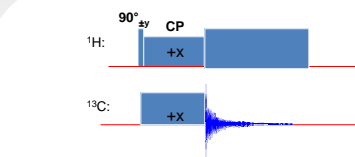
Pines A., Gibby M.G., Waugh J.S.
Proton-Enhanced Nuclear Induction Spectroscopy. A Method for High Resolution NMR of Dilute Spins in Solids, *J. Chem. Phys.* (1972); 56: 1776.



Alex Pines
*1945

Zvýšení citlivosti až 1000-krát

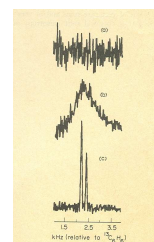
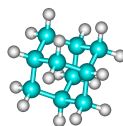
- 1) Polarizace izotopicky hojných jader I .
- 2) Snižování spinové teploty jader I v rotující soustavě souřadné.
- 3) Ustavení kontaktu mezi I a S - spin-lock a HH kontakt.
- 4) Detekce magnetizace S při současném dekaplinku I .



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

$$\gamma_H B_{1H} = \gamma_C B_{1C}$$

Adamantan



Křížová-polarizace - 1976

Zvýšení citlivosti NMR experimentu

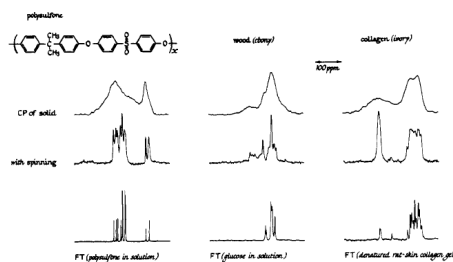
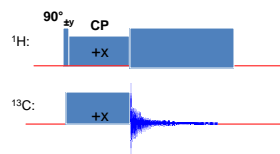
Schaefer J., Stejskal E.O.J.
 ^{13}C NMR of Polymers Spinning at Magic Angle, *J. Am. Chem. Soc.* (1976); 98: 1031.



J. Schaefer

Zvýšení citlivosti až 1000-krát

- 1) Polarizace izotopicky hojných jader I .
- 2) Snižování 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 .



3D struktura prionových proteinů (2005)

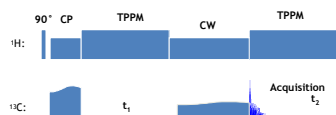
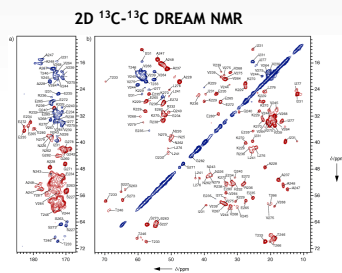


Beat H. Meier
*1954

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



PrPC PrPSc



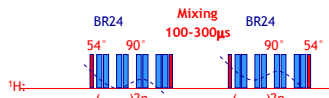
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2D korelační NMR v pevné fázi - 1985

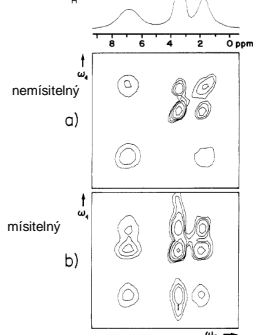
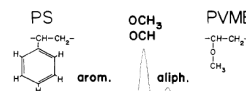
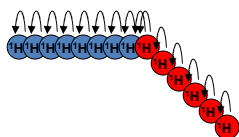
Morfologie polymerních směsí

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

2D ^1H MAS NMR pulse sequence



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

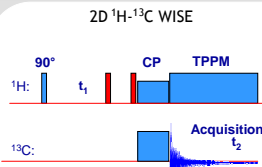


Joint Laboratory of Solid State NMR
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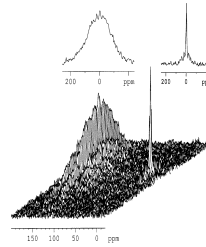
Dipolární separační experimenty (1987 - 1995)



Hans W. Spiess
*1933

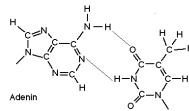


Schmidt-Rohr K., Clauss J., Spiess H.W.
Correlation of Structure and Mobility and Morphology by 2D Wideline-Separation NMR, *Macromolecules*. (1992); 25: 3273.

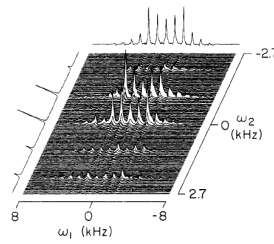


RG Griffin

2D ^1H - ^{15}N SLF NMR



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



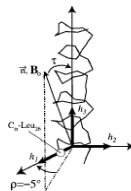
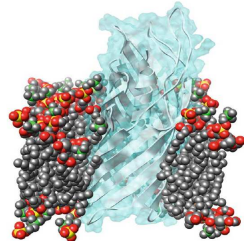
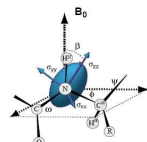
Orientované systémy (1995 - 2000)

Strukturní biologie a membránové proteiny

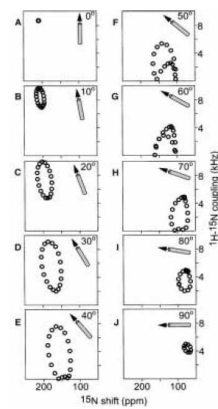


Opella S.J.

Wu C.H., Ramamoorthy A., Opella S.J., High Resolution Dipolar Solid-State NMR, *J. Magn. Reson. A* (1994); 109: 270.



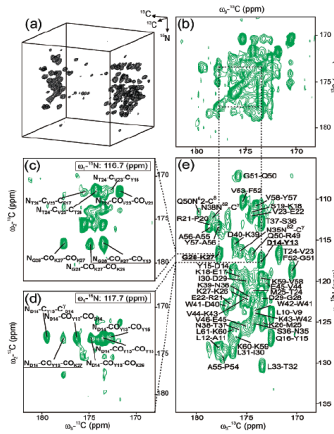
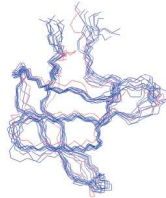
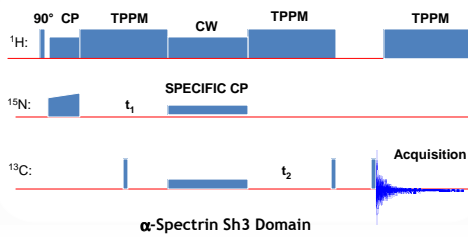
PISEMA: Polarization Inversion Spin Exchange at Magic Angle



Mikrokrystalické proteiny - 2002

Experimenty s dvojitou cross-polarizací

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



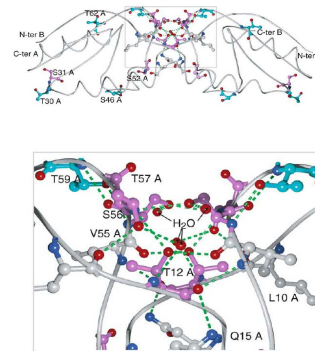
Mikrokrystalické proteiny - 2005-2006

Lokalizace vody - detekce 1H NMR signálu

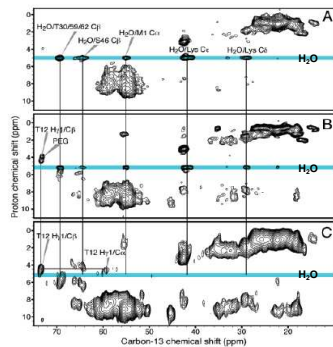
A. Böckmann, M. Juy, E. Bettler, L. Emsley, A. Galinier, F. Penin, A. Lesage, Water-Protein Hydrogen Exchange in the Micro-Crystalline Protein Crh as Observed by Solid State NMR Spectroscopy, *Journal of Biomolecular NMR*, 32, 195 (2005).

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

Mikrokrystalický protein Crh (catabolite repression histidine containing phosphocarrier protein)



2D 1H-13C HETCOR - mikrokrystalický systém



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

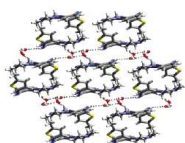
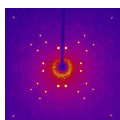
B Přímá chemická výměna H2O-OH

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



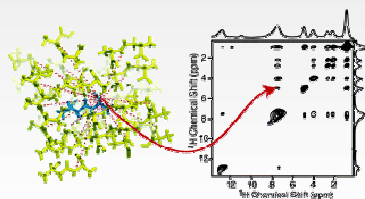
NMR kristalografie - 2006...

XRD



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

ss-NMR

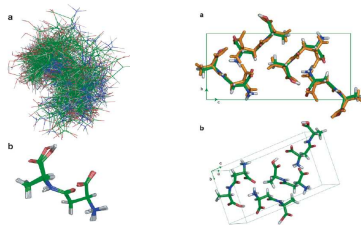


Elena B. et al. *J. Am. Chem. Soc.* (2006); 128, 9555.



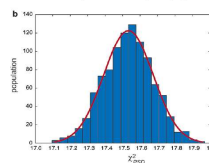
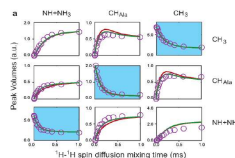
Jiří Labánek
Jiří Štěpánek
Jiří Štěpánek
IMC AS CZ and JNEPC AS CZ

NMR kristalografie - 2006...



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.



$$\frac{dM}{dt} = -K(M - M_0) \quad k_{ij} = \sum_k \left(\frac{\mu_0 \gamma^2 \hbar}{4\pi} \right)^2 \frac{A}{(r_{ij}^k)^3} \quad k_{ii} = -\sum_j k_{ij}$$

$$M(t, \tau_{SD}) = \exp(-K \tau_{SD}) M_i(t, 0) \quad P(\tau_{SD}) = \exp(-K \tau_{SD}) M_i^t$$

n ... Functional dependence on internuclear distance

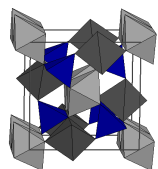
$$\chi^2 = \sum \frac{(calc_i - t_i)^2}{\sigma_i^2}$$



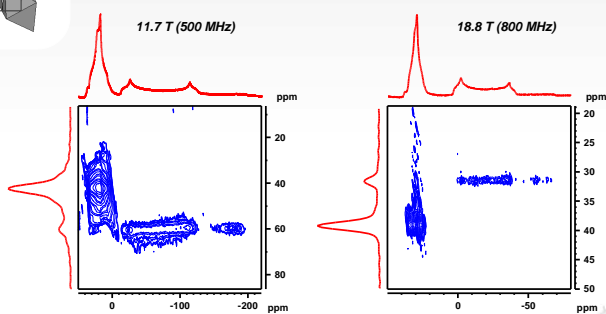
IMC
AS CZ

Vícekvantová NMR spektroskopie

²⁷Al 3Q MAS of Andalusite at different fields



$$\delta_{3Q} = \delta_{iso} - \frac{10}{17} \delta_{qis}$$

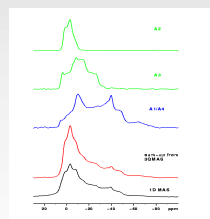
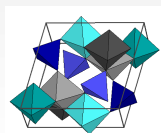


Joint Laboratory of Solid State NMR
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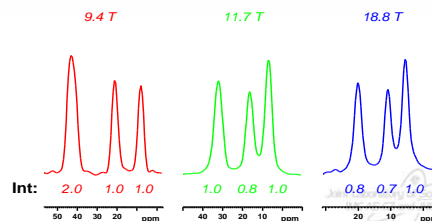
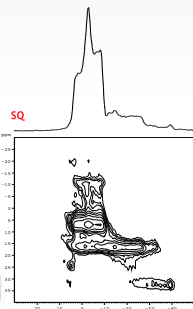
Vícekvantová NMR spektroskopie

²⁷Al 3Q MAS of Kyanite at different fields

- Kyanite, z-filtered experiment at 11.7 T
- anisotropic traces
- traces for A1 and A4 cannot be resolved
- 27 kHz MAS frequency
- 250 kHz RF
- excitation pulse: 1.9 μs
- conversion pulse: 0.7 μs
- 90° selective pulse: 11 μs



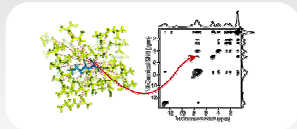
Al-27 3Q MAS traces of Kyanite at different fields



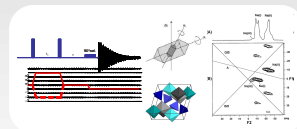
Joint Laboratory of Solid State NMR
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Souhrn

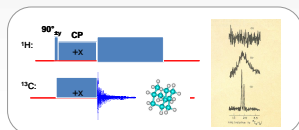
NMR krystalografie



MQ/MAS NMR - anorganické systémy

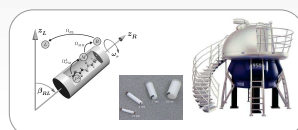


Cross-polarizace

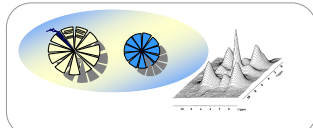


Solid-state NMR
and

MAS - rotace vzorku pod magickým úhlem



Spinová difuze a morfologie polymerů



Struktura proteinů

