Investigation of local Dynamics via ^{2}H Solid-State MAS NMR

Christoph Deller

Robert Graf, Lothar Brombacher, Gunther Brunklaus and Hans-Wolfgang Spiess

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York
United Kingdom

Outlook

- **^{2}H-NMR spectroscopy under MAS**

- **Motional broadening – The effect of molecular motion on ^{2}H-MAS spectra**

- Application to model systems with one ^{2}H-site
- Application to crystalline sample with more than one ^{2}H-site
- Application to amorphous samples with more than one ^{2}H-site

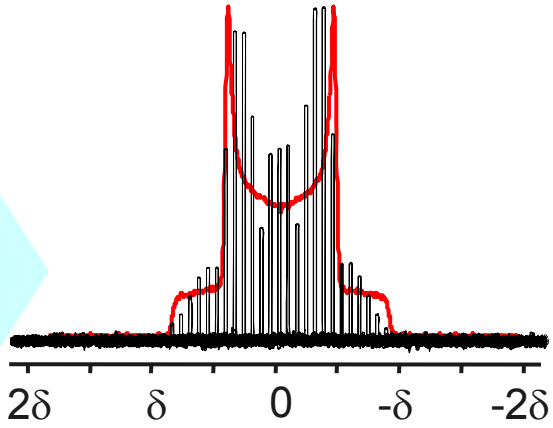
^{2}H NMR Spectroscopy under MAS

Quadrupolar coupling : ~125 kHz

→ inhomogeneous broadening

~250 kHz >> ω_{MAS}

NOT MAS synchronized detection



Complete tensor, better signal/noise

M. Schulz-Dobrick, I. Schnell,
Central European Journal of Chemistry **3**, 245 (2005)

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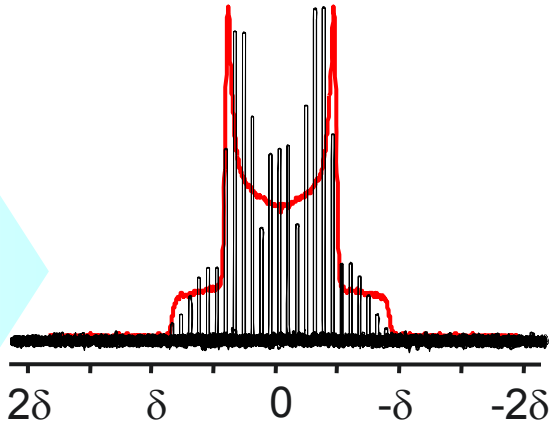

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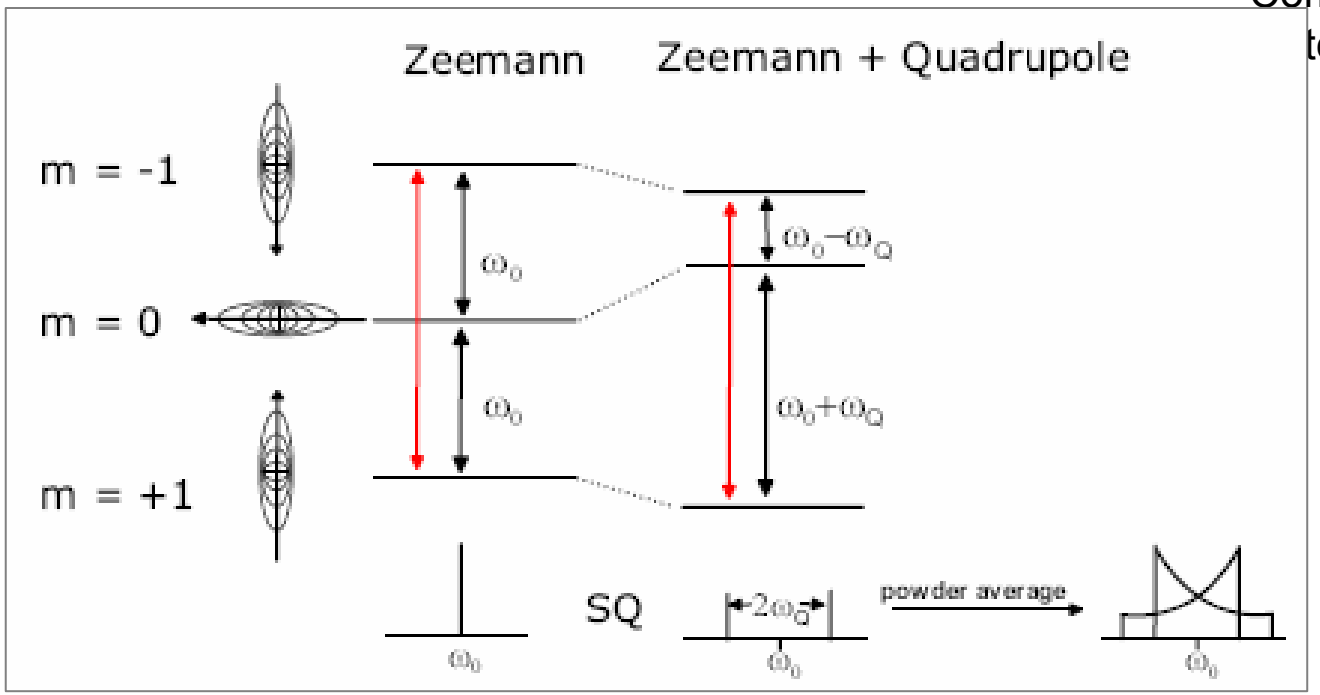

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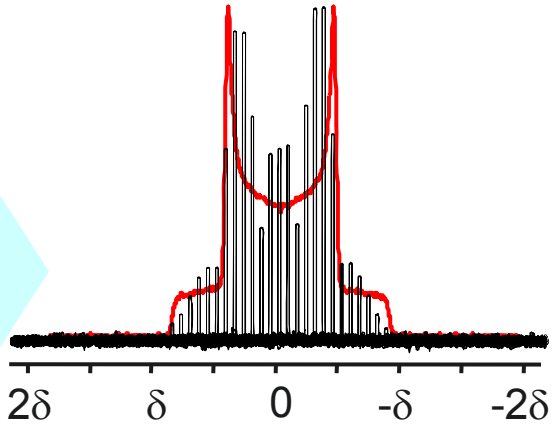

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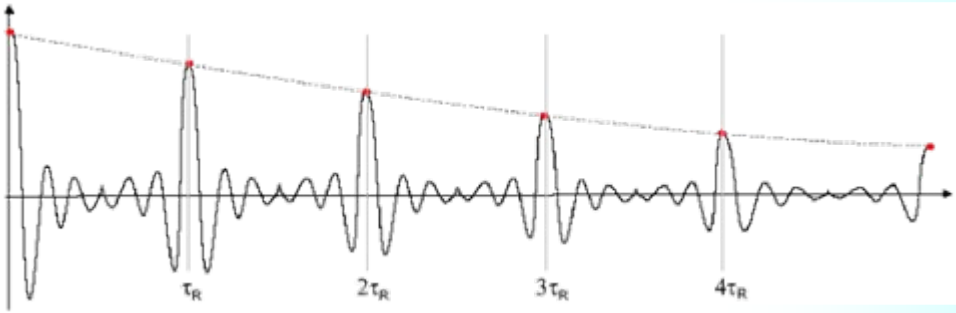
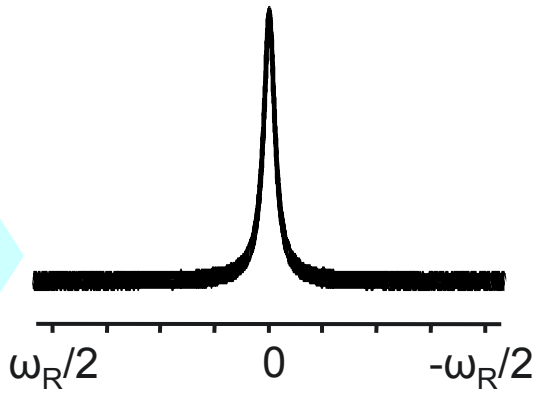


FID : sharp rotational echoes

MAS synchronized detection



CS resolved ^{2}H spectra, if more than one ^{2}H nucleus

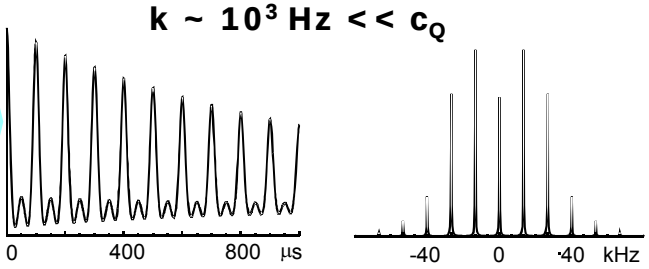
M. Schulz-Dobrick, I. Schnell,
Central European Journal of Chemistry **3**, 245 (2005)

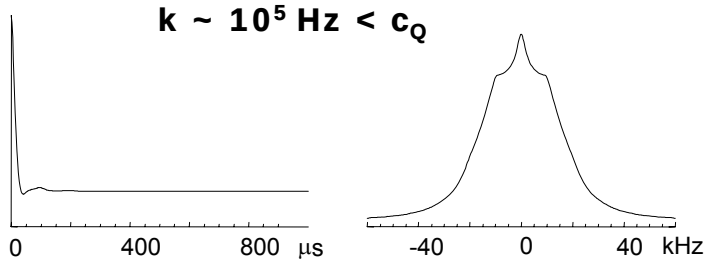
Motional Broadening of ^{2}H-MAS Spectra

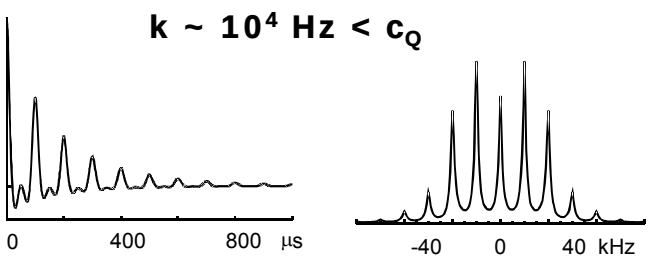
Principle: Reorientation of quadrupolar tensor with “jump rate” k = k(T)

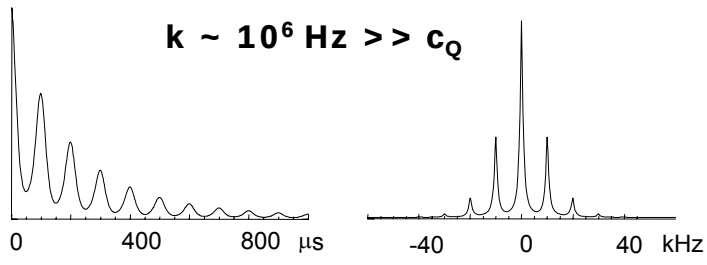
MAS: Formation of the echo at the end of the rotor period is perturbated

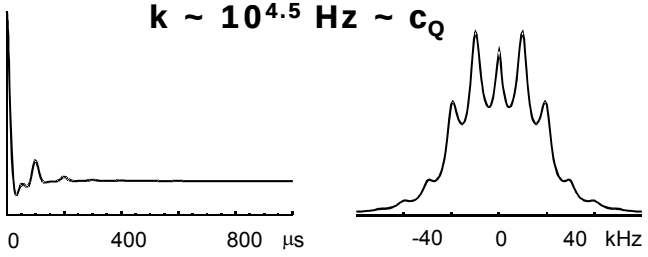
slow limit

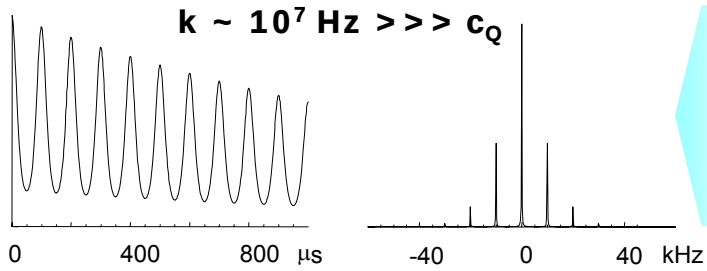












fast limit

M. Cutajar, S. E. Ashbrook, S. Wimperis, *Chemical Physics Letters* **423**, 276 (2006).

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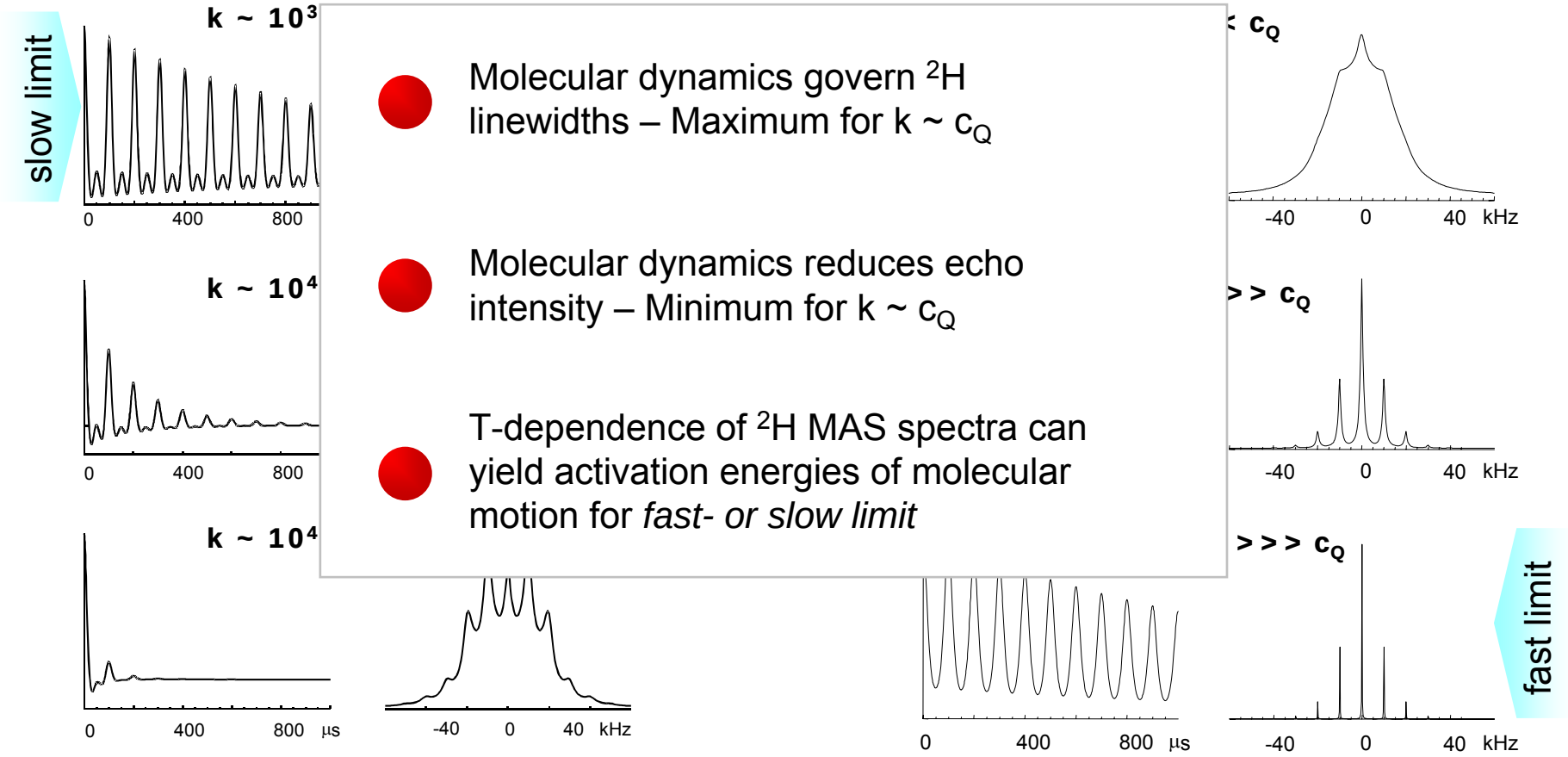

- Molecular dynamics govern ^{2}H linewidths – Maximum for k ~ c_Q
- Molecular dynamics reduces echo intensity – Minimum for k ~ c_Q
- T-dependence of ^{2}H MAS spectra can yield activation energies of molecular motion for *fast- or slow limit*

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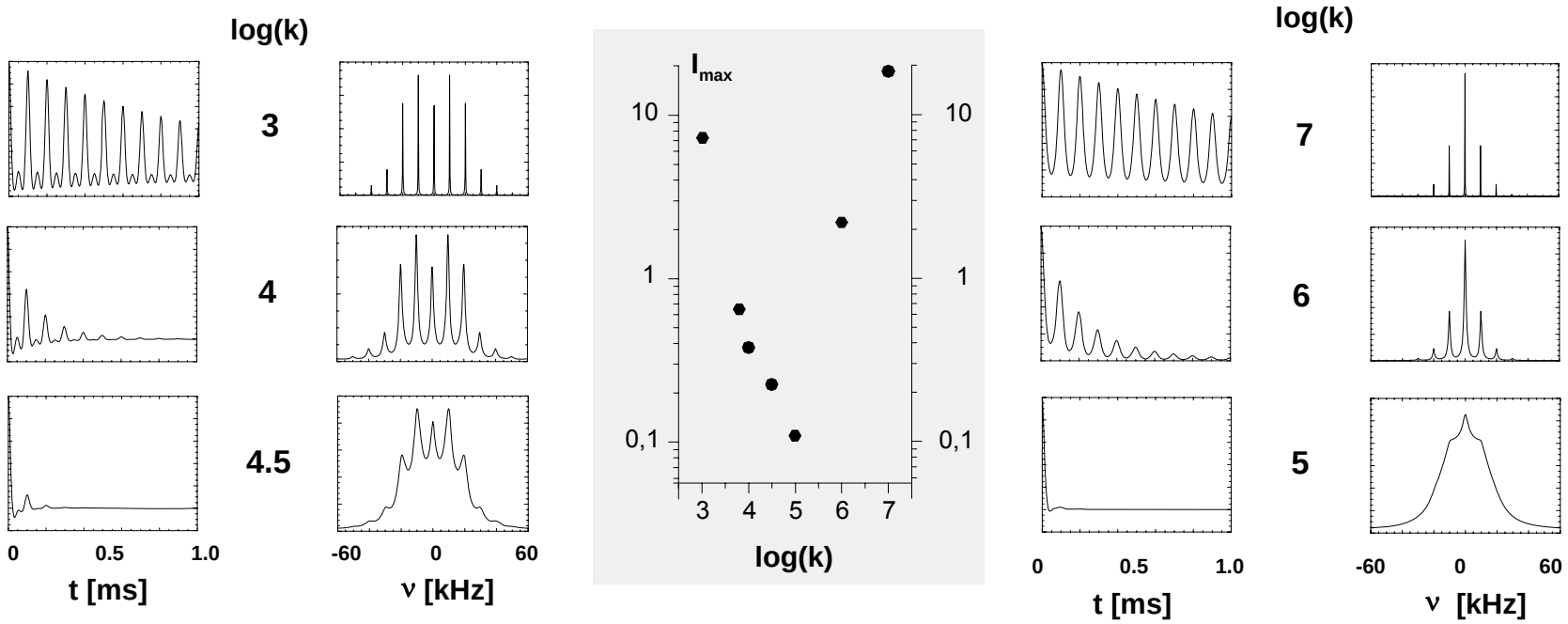
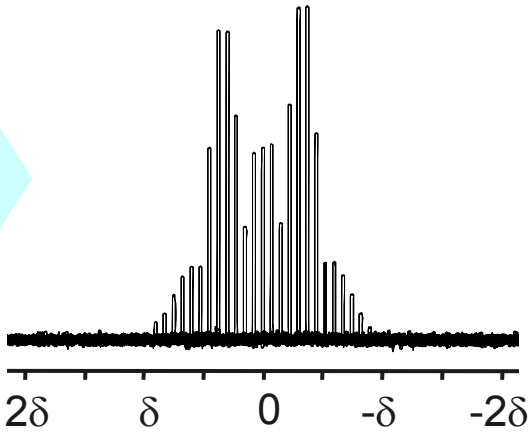
Motional Broadening of ^{2}H-MAS Spectra



RS vs. NRS ^{2}H-MAS Spectra

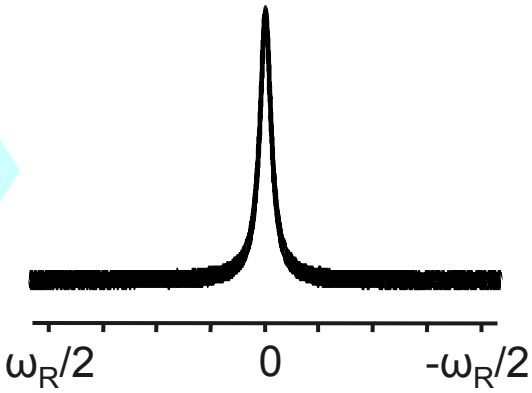
NOT MAS synchronized detection



- jump rate (k)
- jump geometry (Θ)
- anisotropy/assymetry (c_Q/η)
- Activation energy (E_A)

$$k = \frac{3\pi e^2 qQ}{4h}\Omega = \nu_0 \exp\left(-\frac{E_A}{RT}\right)$$

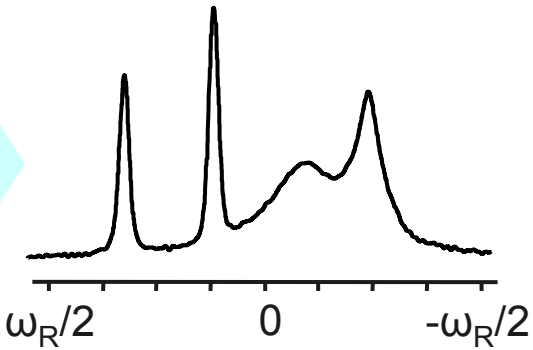
MAS synchronized detection **(one site)**



- linewidth/intensity
- Activation energy (E_A)

$$\text{linewidth} = \nu_0 \exp\left(-\frac{E_A}{RT}\right)$$

MAS synchronized detection **(> one site)**



- linewidth/intensity
- site selectivity (δ_{CS})
- Activation energy (E_A) for **> one site**

Outlook

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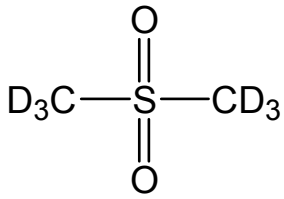
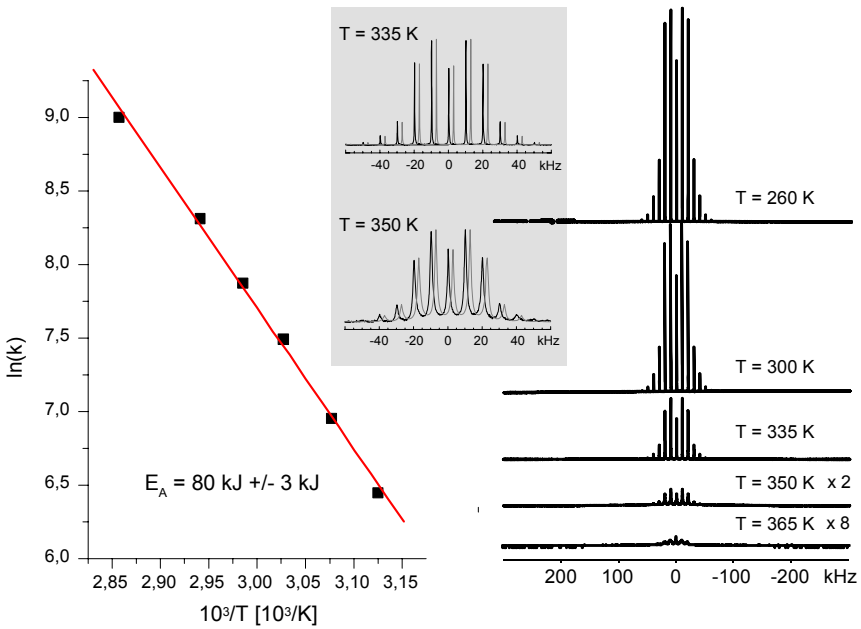
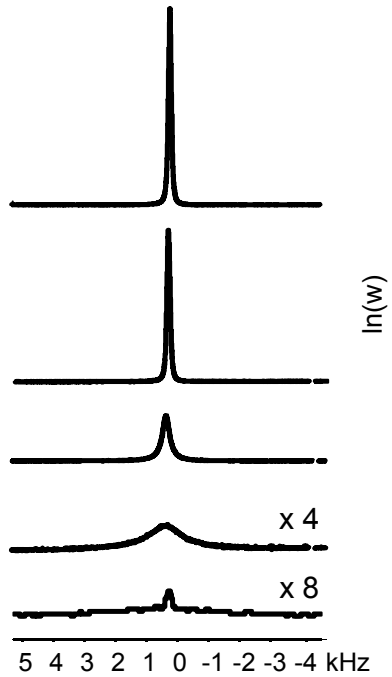
System I : d_6-Dimethylsulfon

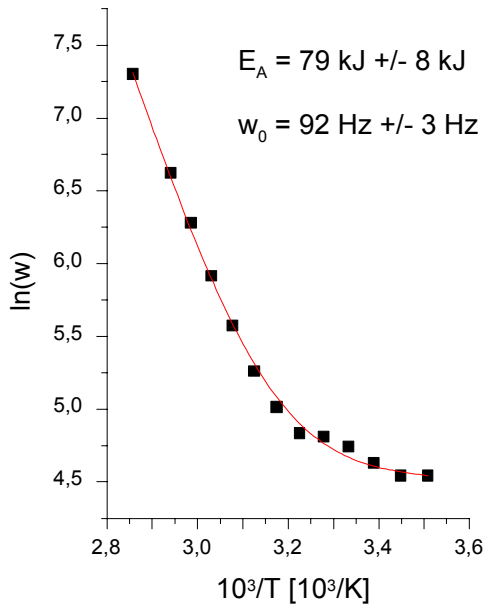
c_Q ~ 42 kHz
Θ_{jump} = 106°
two positions



Relaxation:
T_1 = 5 s
Temperature:
260 K – 370 K



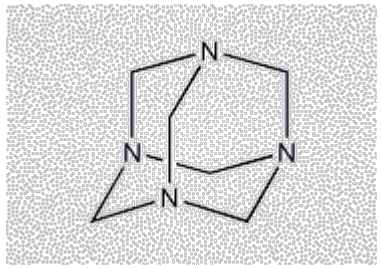




J. Kristensen et al., JMR, **100**, 437 (1992)

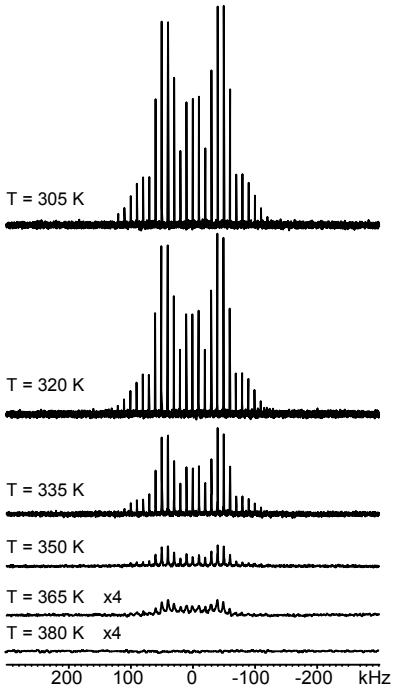
System II : d_{12}-Hexamethylentetramin

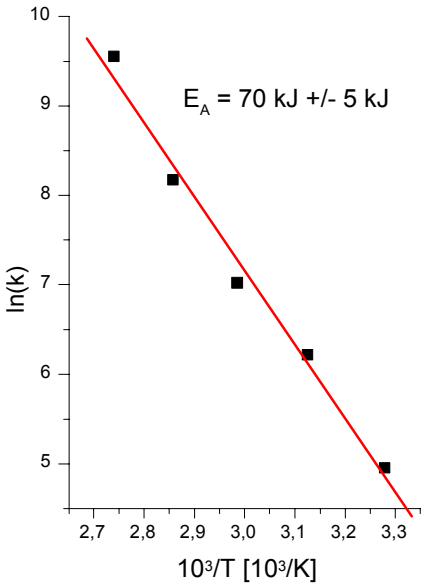
c_Q = 119 kHz
Θ = 109,5°
Four Positions
Ω = ¼

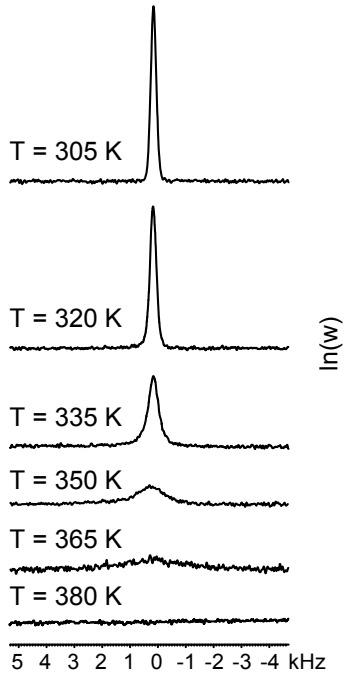


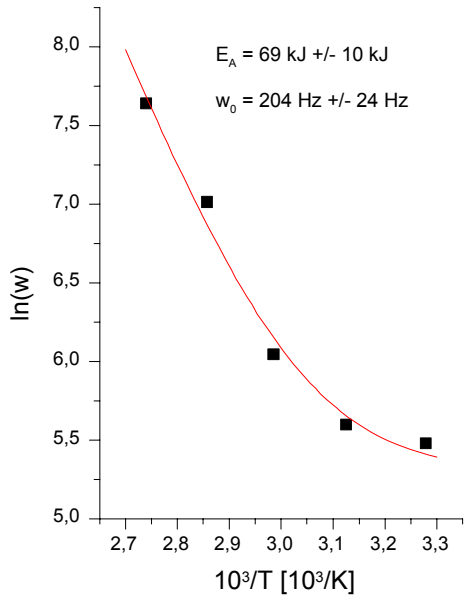
Relaxation:
T_1 > 900 s

Temperature:
200 K – 500 K









H.W. Spiess, O. Pschorn, *JMR*, **39**, 217 (1980)

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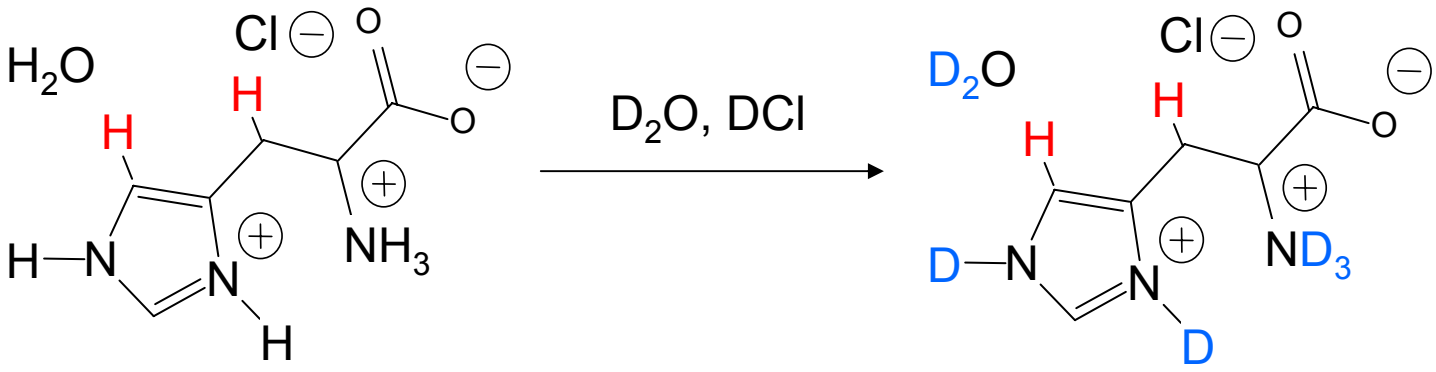
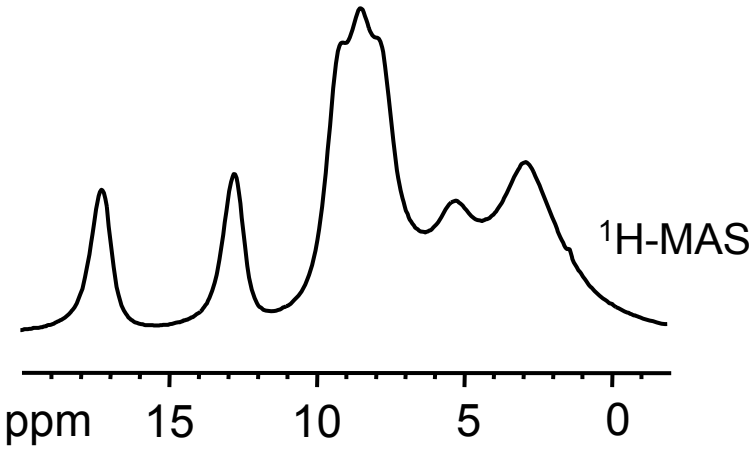
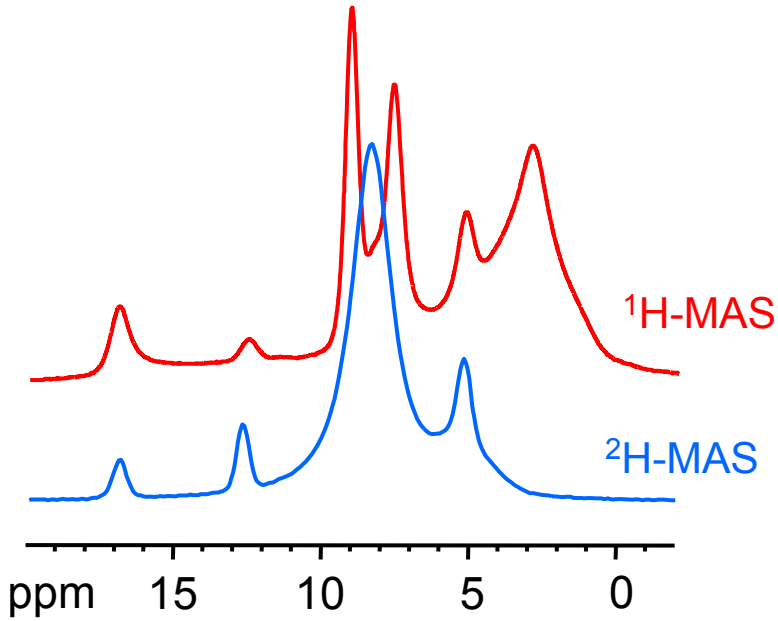
Selective Deuteration of acidic protons: Histidine HCl Monohydrate







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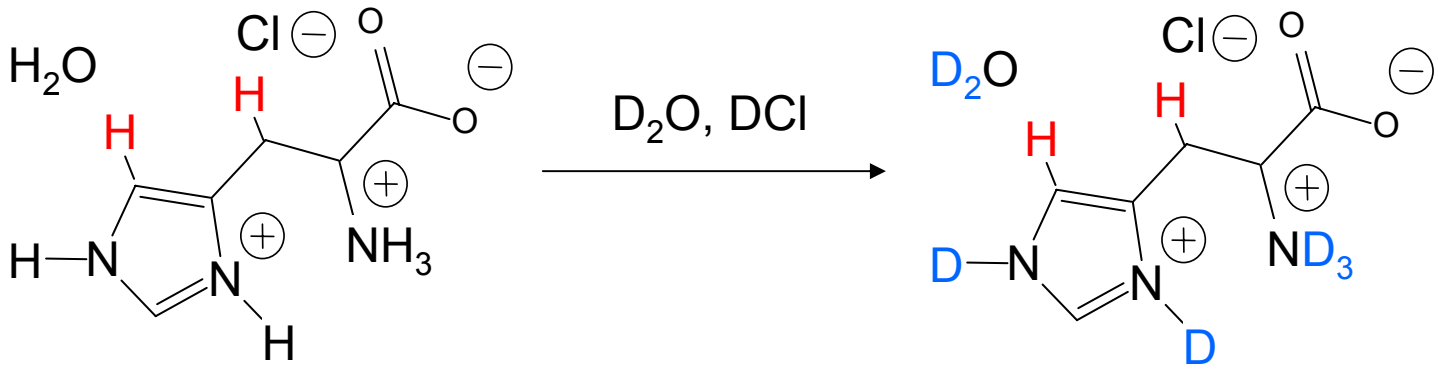
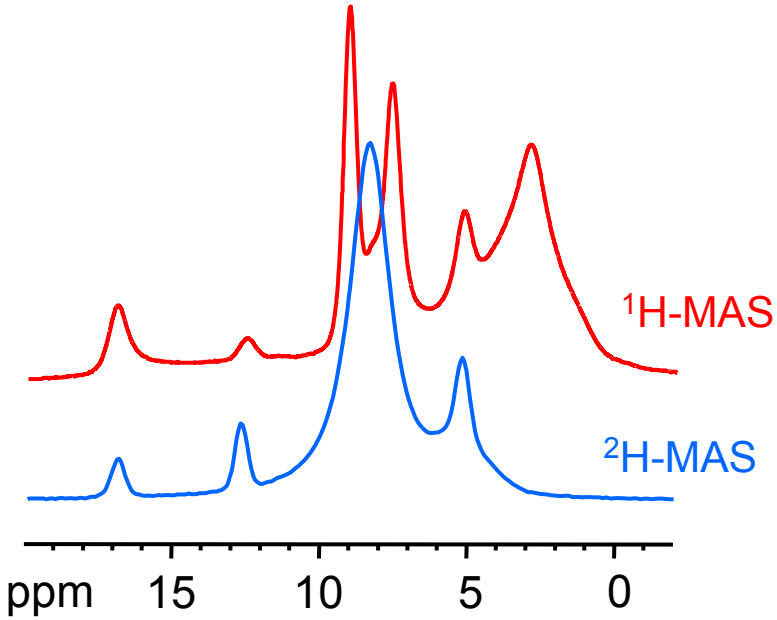
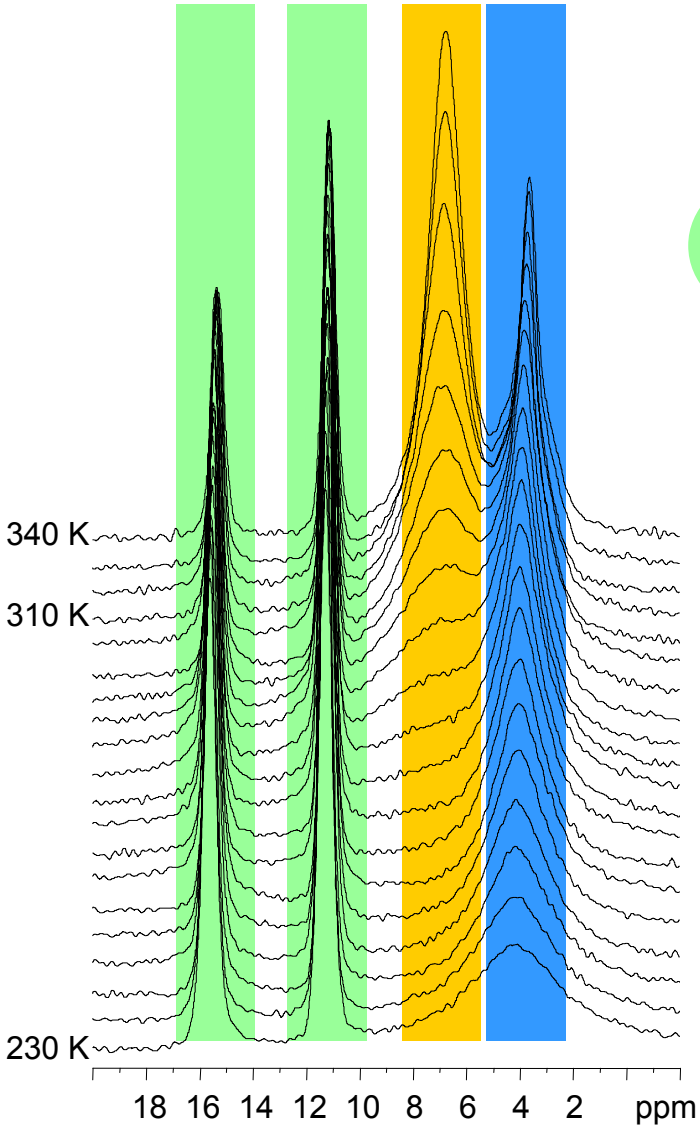


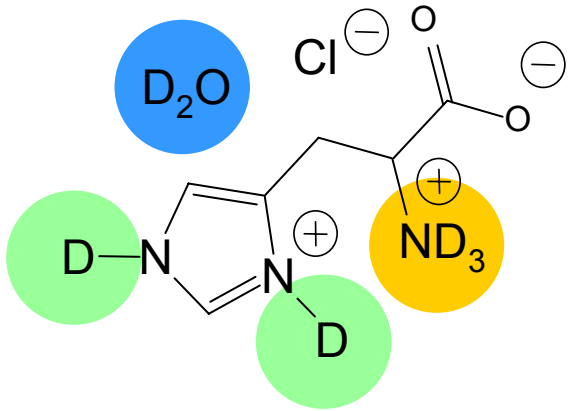
Recrystallization from D_2O :

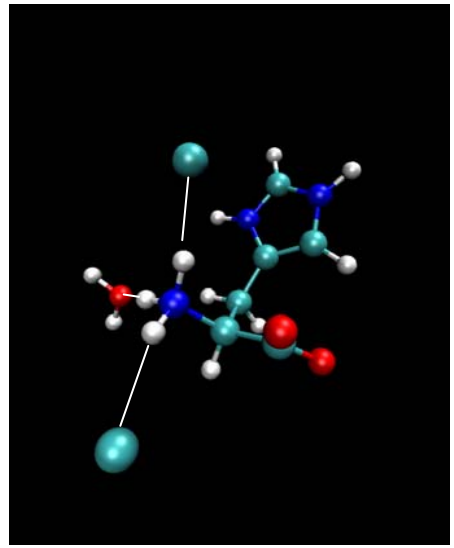
1. Distinction of acidic and non-acidic positions in the compound
2. Peak assignement
3. Resolution enhancement due to reduction of homonuclear ^1H-^1H coupling network
4. Exploring of structural features using correlation techniques

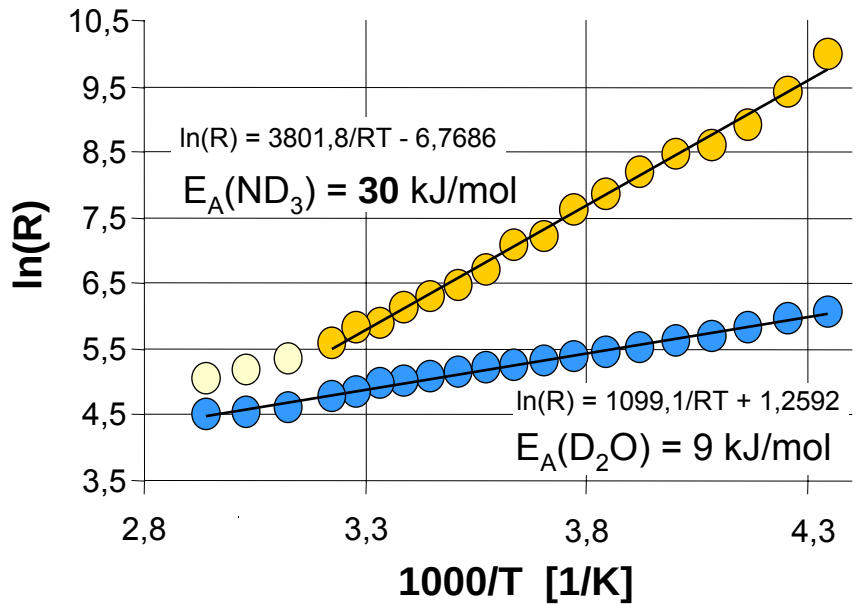


RS-^{2}H-MAS NMR Spectroscopy

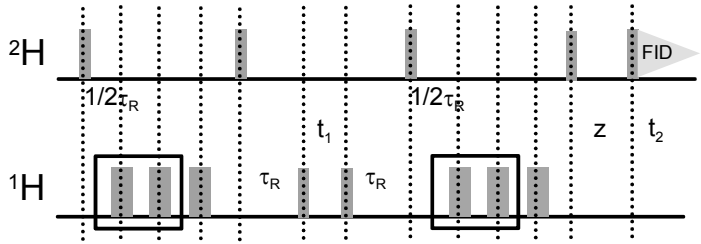




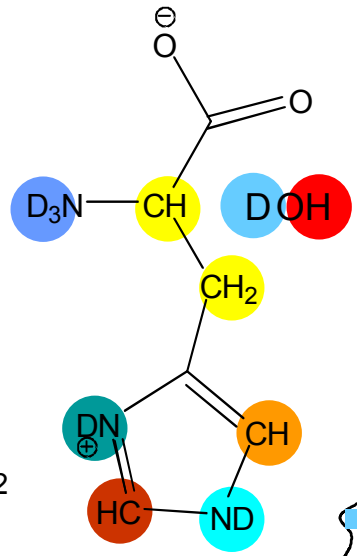




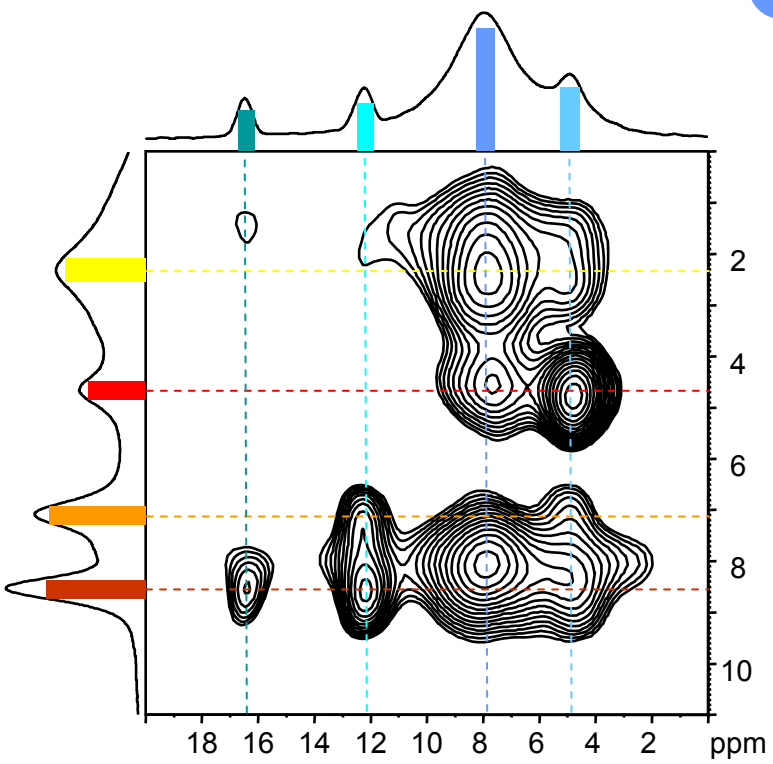
Structural Features:
^{1}H - ^{2}H Correlation Measurements



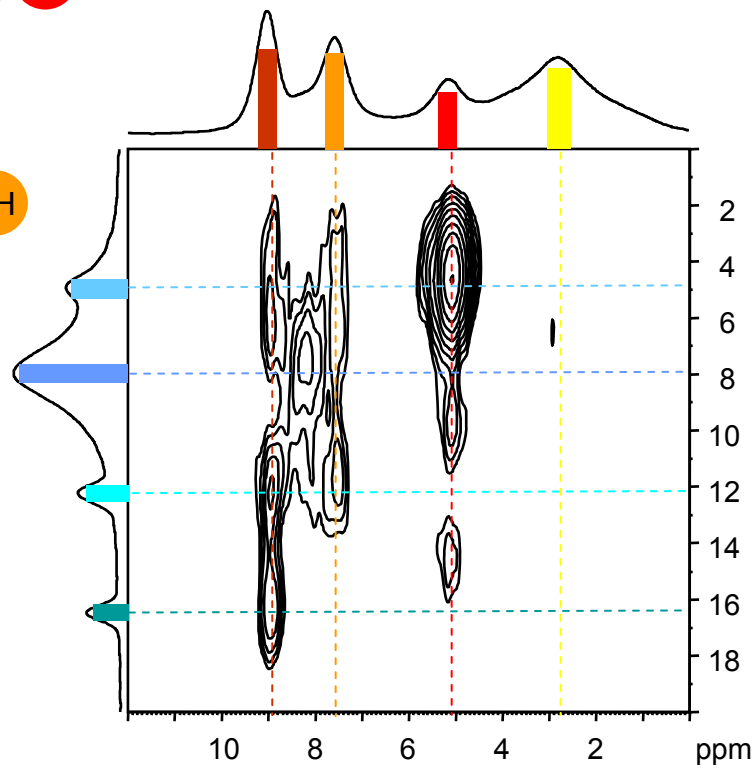
700 MHz 1H ,
30 kHz MAS,
134 µs ^{1}H-^{2}H Recoupling



^{2}H-Detection



^{1}H-Detection



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