New opportunities for paramagnetic materials using ultra-fast MAS

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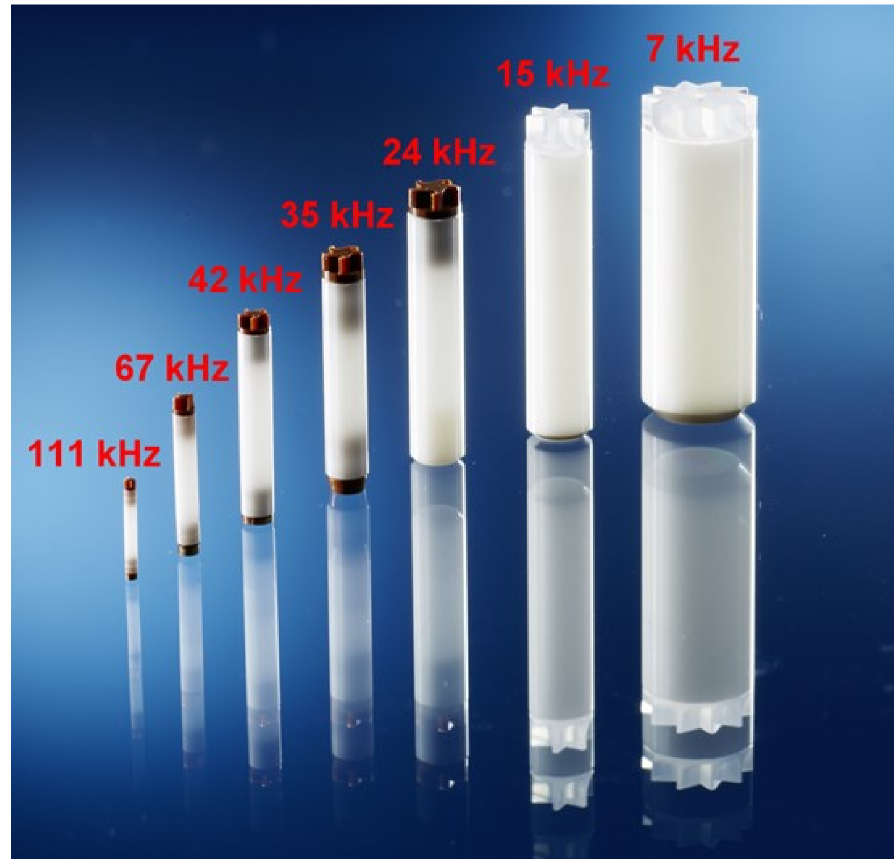

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pNMR

MARIE CURIE ACTIONS

Outline

1. Why faster MAS ?
2. What means fast MAS ?
3. Probe hardware for fast MAS
4. How about CRAMPS ?
5. Heteronuclear decoupling under fast MAS
6. Cross polarization under fast MAS
7. Some applications to paramagnetic systems
8. Fast MAS and extended VT

Why faster and faster Rotation ?

- Strong dipole – dipole interactions
  - Homonuclear dipole – dipole couplings
    - $^{1}H \leftrightarrow {}^{1}H$ and $^{19}F \leftrightarrow {}^{19}F$ (also $^{1}H \leftrightarrow {}^{19}F$)
  - Heteronuclear dipole – dipole couplings
    - MAS frequency should be 3-5 times higher than the coupling

- Quadrupolar nuclei
  - Fast MAS rotation enables the observation of undistorted central transitions, free of spinning sidebands
  - Spinning sidebands from satellites can be detected more easily und undistorted

- Paramagnetic species
  - Paramagnetically distorted samples can have anisotropies resulting in spectra with widths more than a 1.000 ppm

Some common interactions in solid state NMR

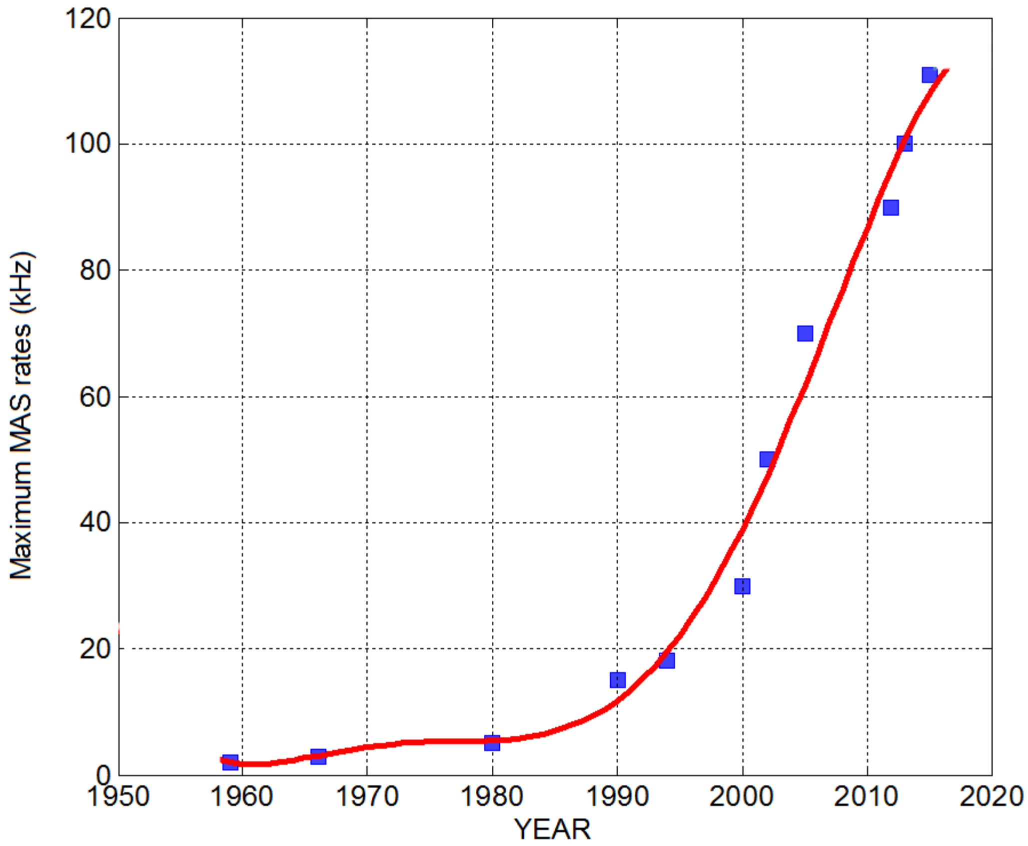
Parameter	Order of magnitude	Example
CSA, chemical shift	up to 100 kHz	^{77}Se, ^{119}Hg
Dipole dipole coupling	up to 100 kHz	^{19}F, (^{1}H)
J-coupling	up to 10 kHz	$^{1}J(^{31}P,^{31}P)$
Quadrupolar coupling	If eQ small, only 1st order important, can be averaged by MAS	^{2}H, ^{14}N, ^{6}Li
	If eQ large, than 1st and 2nd order are important, second order not averaged but only scaled by MAS	^{27}Al $^{47/49}Ti$

-> fast MAS in the regime of 100kHz can be benificial for some interactions !

What means fast MAS?

The terms "fast MAS" or "very fast MAS" or "ultrafast MAS"

are a function *f*(*t*) of time *t*.



Technology for fast MAS

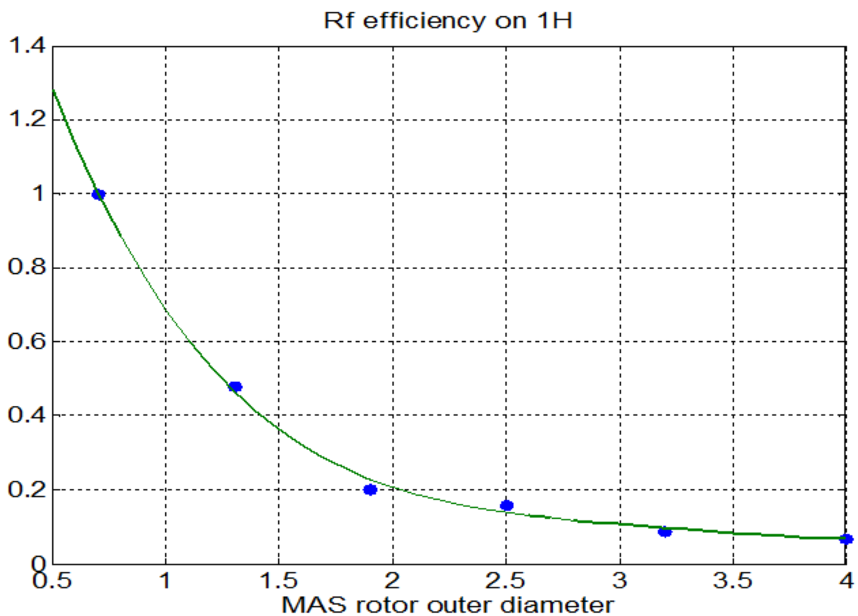
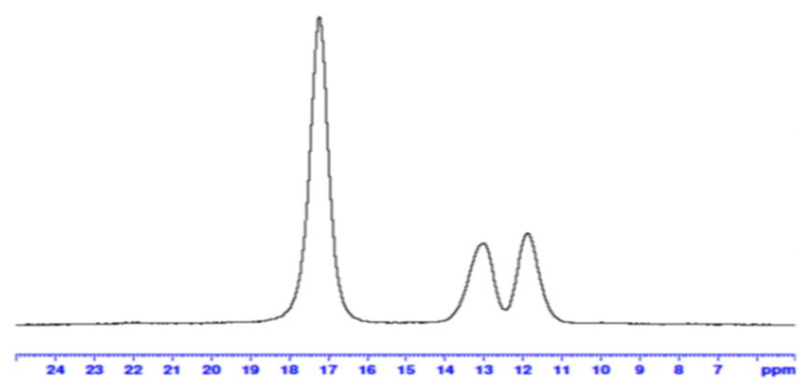


Fig. 7: Relative ¹H rf efficiencies for MAS probes with rotor diameters from 0.7mm to 4mm.



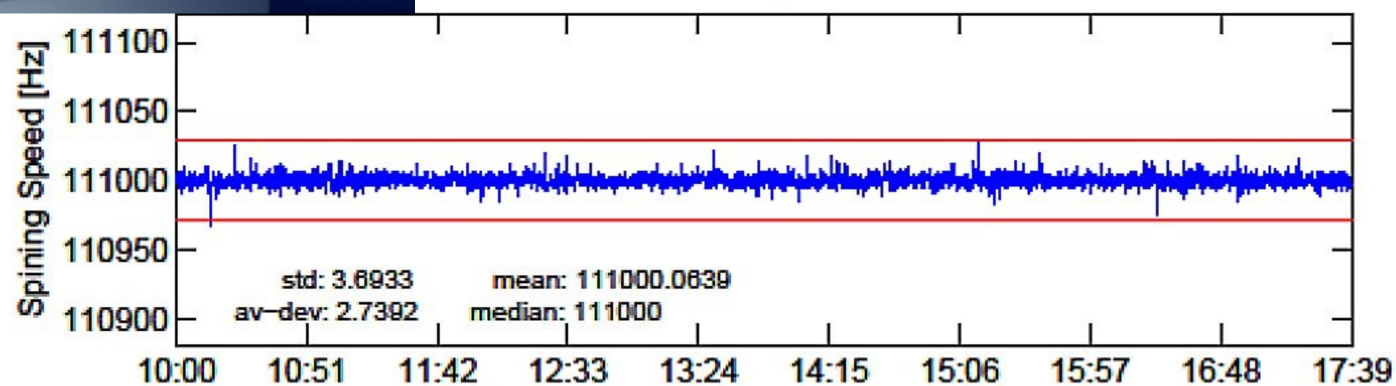
¹H spectrum of glycine at 1000 MHz and spinning at an MAS speed of 111 kHz.

Single pulse excitation (P1 = 1.1μs), single scan.
Active sample volume 350 nl

MAS 0.7mm
Control of bearing and drive flow
Frictional heating

MAS	CS difference	frictional heating	sample T
10 kHz	0	0	15
40 kHz	0	0	15
60 kHz	0,1	4	19
80 kHz	0,3	12	27
100 kHz	0,5	20	35
111 kHz	0,6	24	39
111 kHz + BCU-X	0	0	15

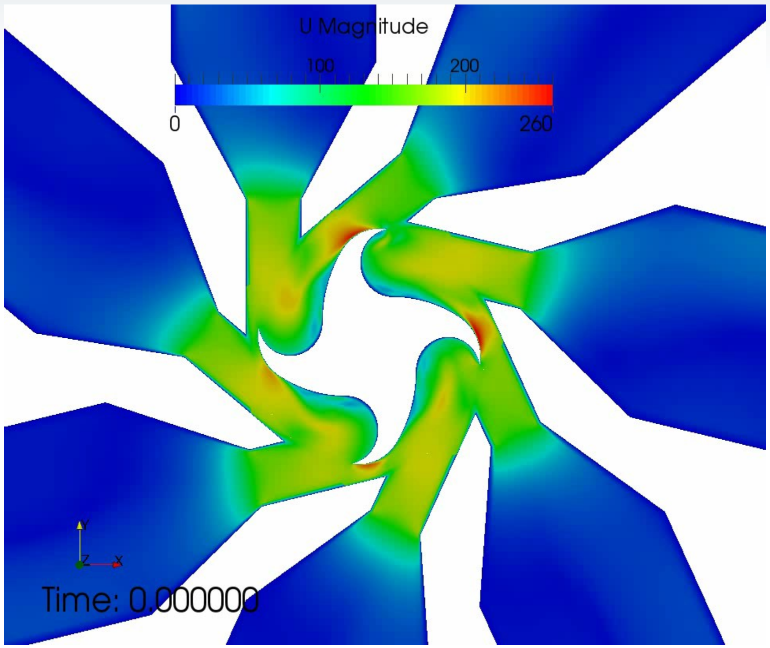
MAS 3 PNEUMATIC CONTROL UNIT

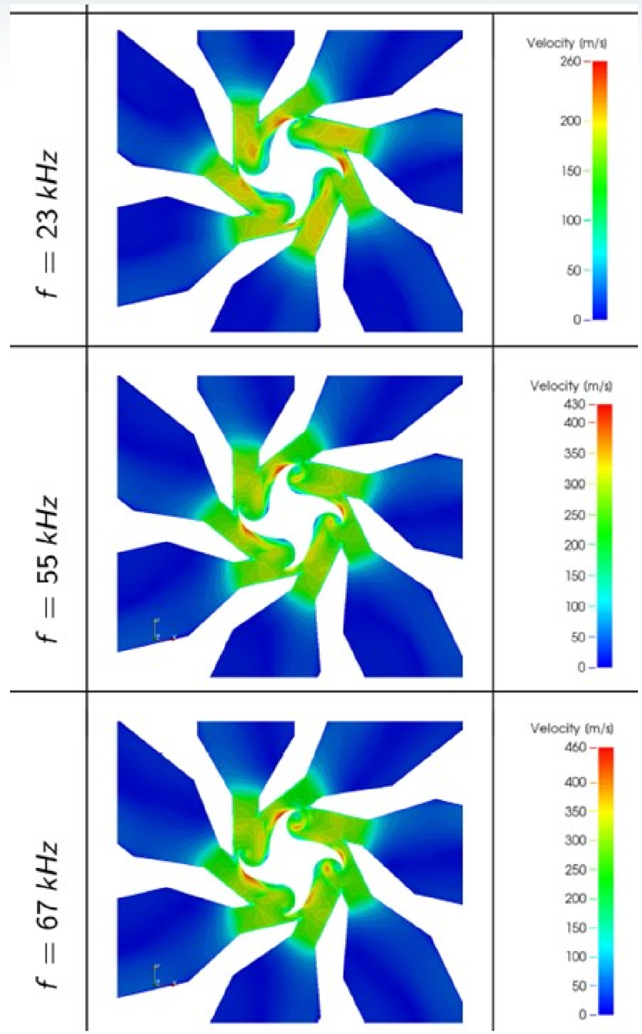


Technology for fast MAS – MAS 3

- Spin regulation up to 200kHz
- Fiberoptical spin-signal-interface to the probe
  (and backward compatible spin-interface)
- New spinrate readout resolution: 0,1Hz
- Additional pneumatic channels for future probe designs
- Safer and faster communication using ethernet and CAN-bus
- Several logging functions
- Internal 3-axis magnetic field sensors for coarse stray field measurements
- Easy probe profile management therefore easy A2B conversion

Fast MAS – technological limits

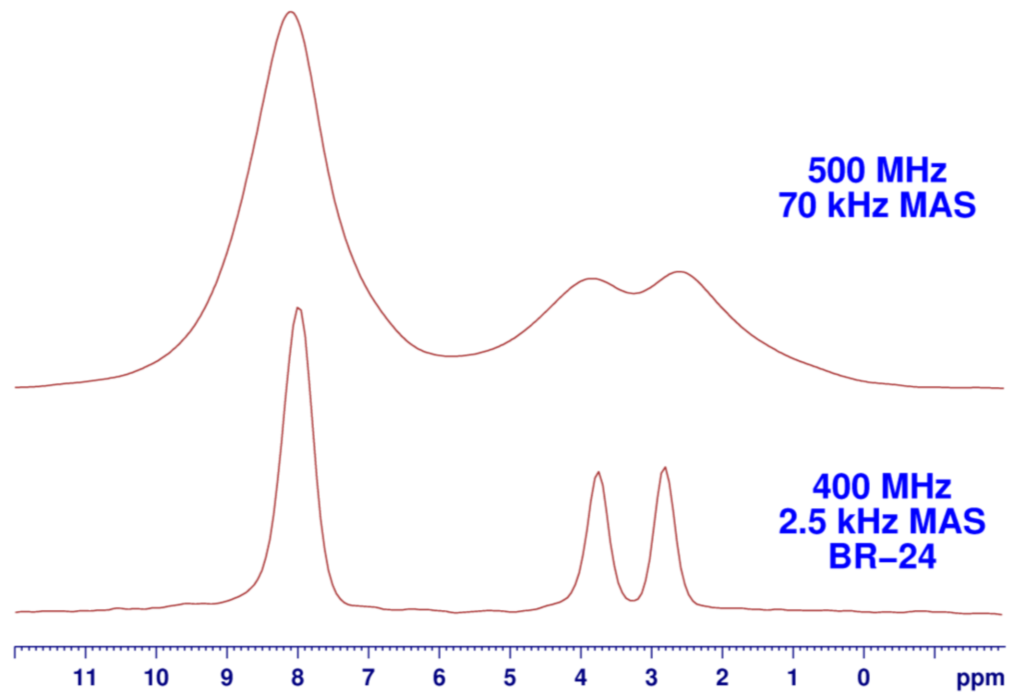




Gas velocity profiles for MAS 1.3mm turbines

Spectral resolution:
What about the good old CRAMPS ?

- @ 70kHz -> 1.3mm probe
  the result seems disappointing, since 70kHz is not fast enough

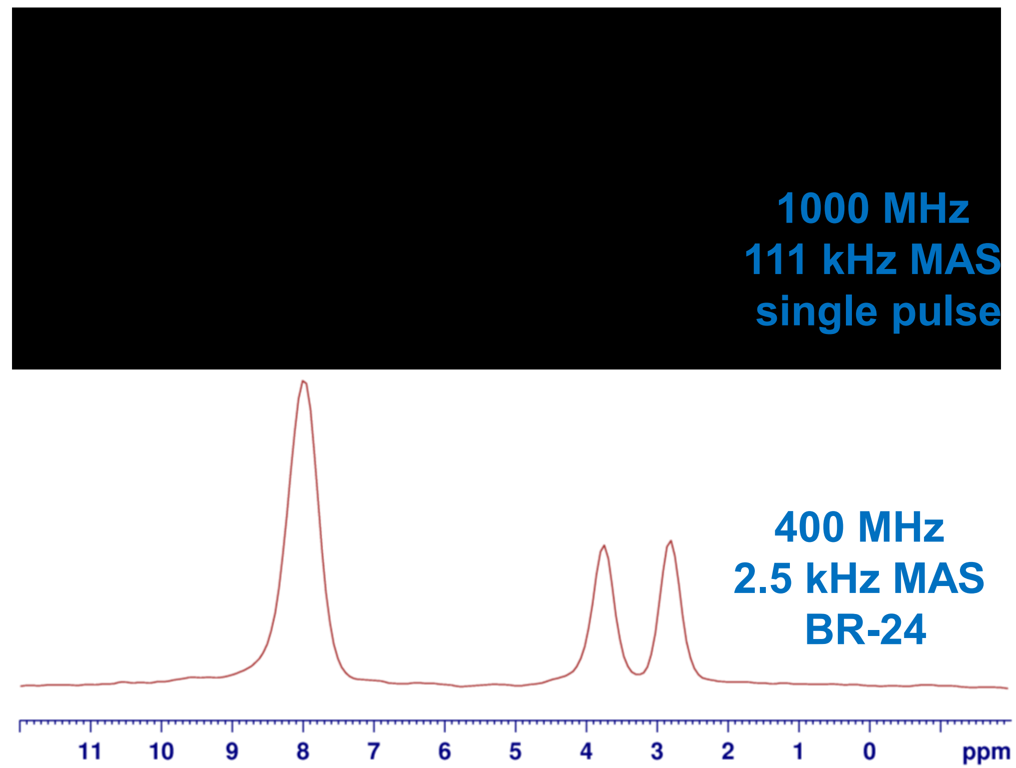


Resolution:
What about the good old CRAMPS ?

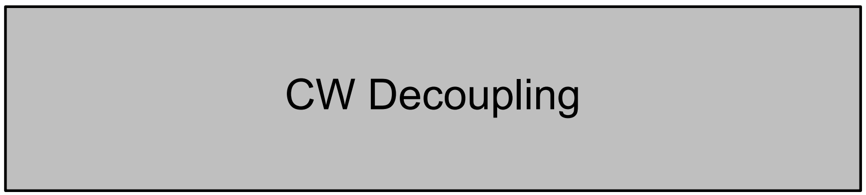
- @ 70kHz → 1.3mm probe the result seems to be insufficient, since spinning at 70kHz is not fast enough.

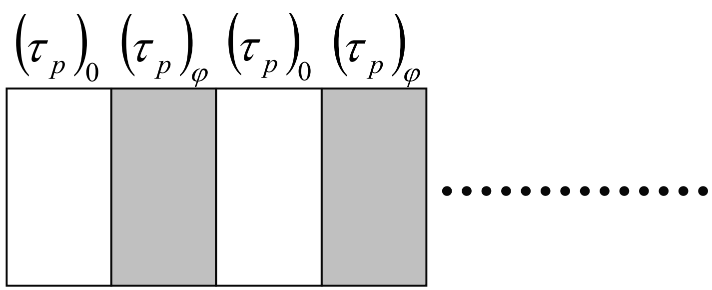
- @ 111kHz it looks better

→ 111kHz exceeds the homonuclear coupling strength of glycine



Decoupling under fast MAS

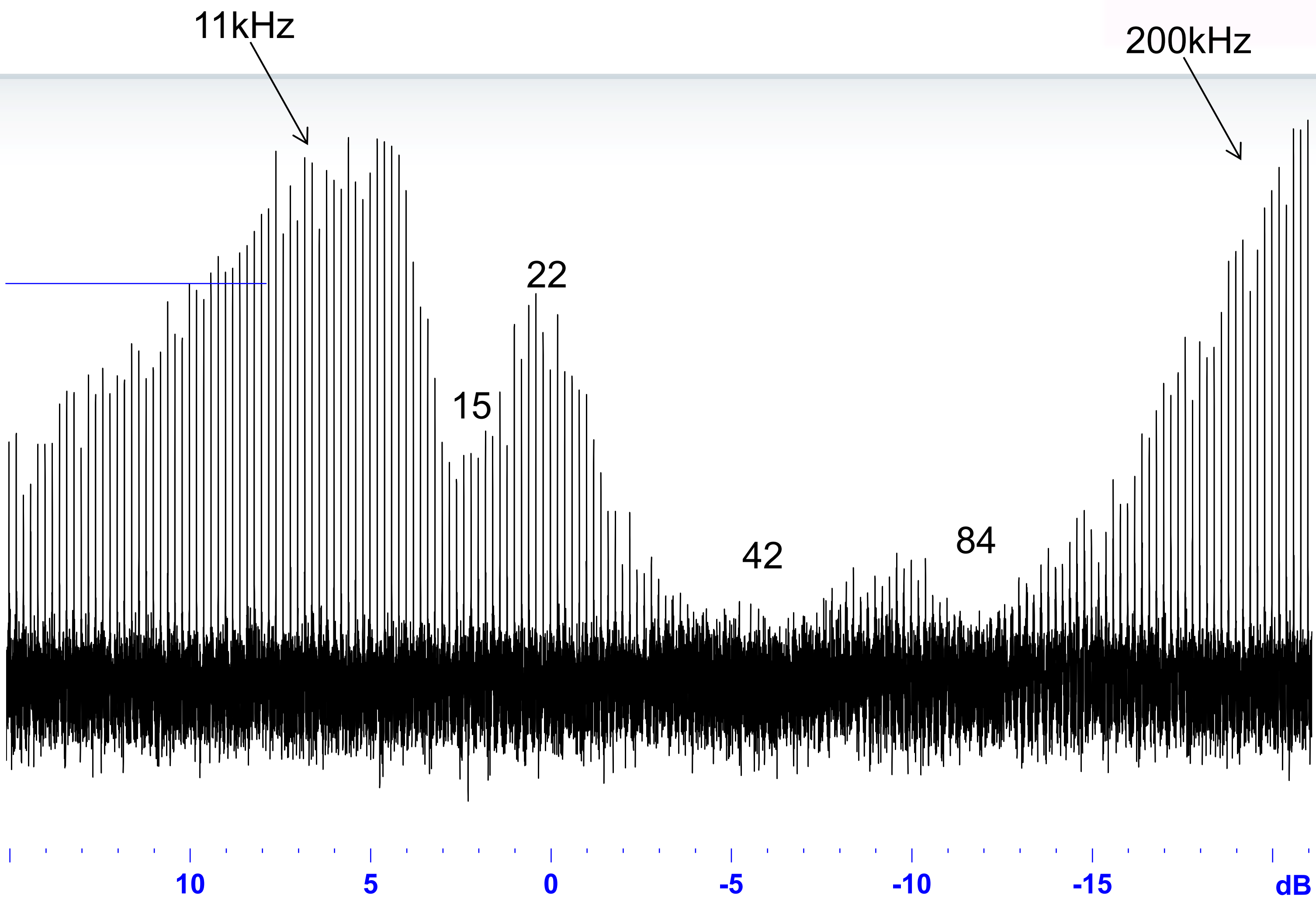




TPPM / SPINAL

- Heteronuclear decoupling can be done with different approaches
  - High power decoupling
  - Low power CW decoupling matched to MAS speed

CW Decoupling at 42kHz (MAS 1.9mm)



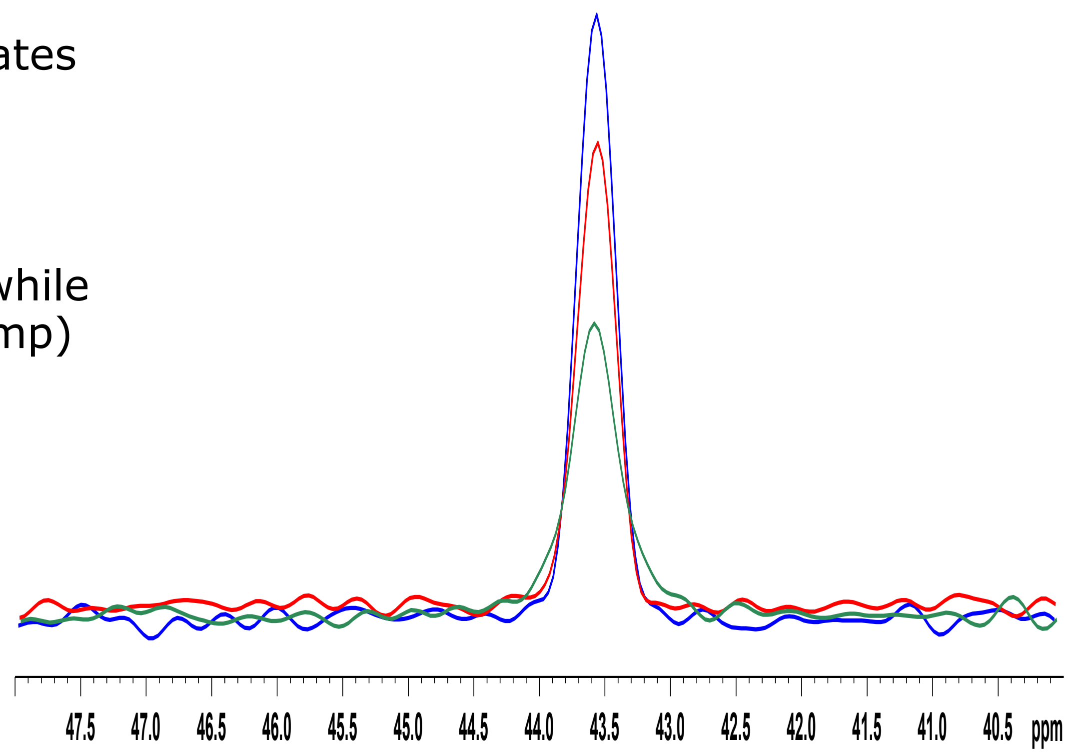
See, e.g., M. Weingarth, et al., Chem.Phys.Lett. 466, 247-251, 2009.
M. Ernst, J. Magn. Reson. 162, 1-34, 2003.

CP efficiency at fast MAS
example @ 42kHz (MAS 1.9mm)

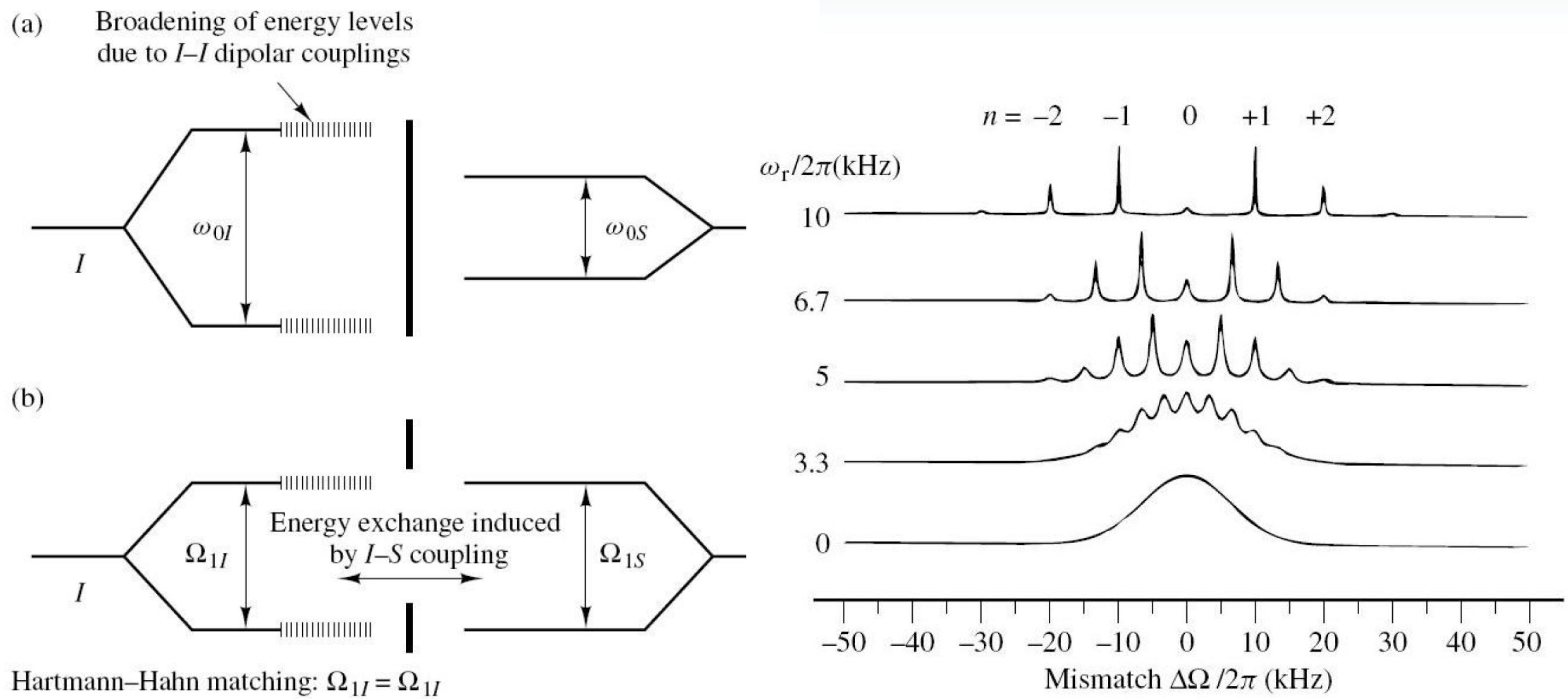
- Approaching very fast Magic Angle Spinning the dipolar coupling gets averaged -> what about cp efficiencies?

- Intensity of $^{13}CH_2$ signal

  in glycine at various spinning rates
  - Same contact time
  - Same ^{13}C RF-field
  - ^{1}H RF-field was adjusted while (using a 50% to 100% ramp)
    - MAS 10 kHz
    - MAS 25 kHz
    - MAS 42 kHz



CP and MAS



See, e.g., E.O. Stejskal, et al, J. Magn. Reson. 57, 471, 1984

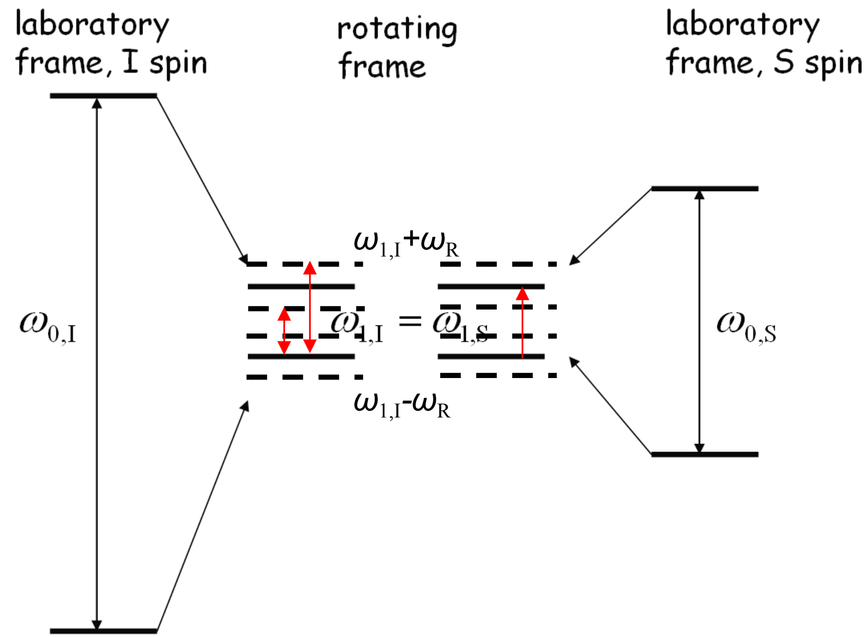
CP MAS dynamics

Using MAS the energy levels in the rotating frame are modulated by the magic angle rotation.

For the case when ω_R is small compared to the RF-fields $\omega_{1,I}$ and $\omega_{1,S}$ the CP Hartmann-Hahn matching conditions is given by:

$$\omega_{1,I} \pm n\,\omega_R = \omega_{1,S}$$

$$\omega_{1,I} - \omega_{1,S} = \pm n\,\omega_R$$

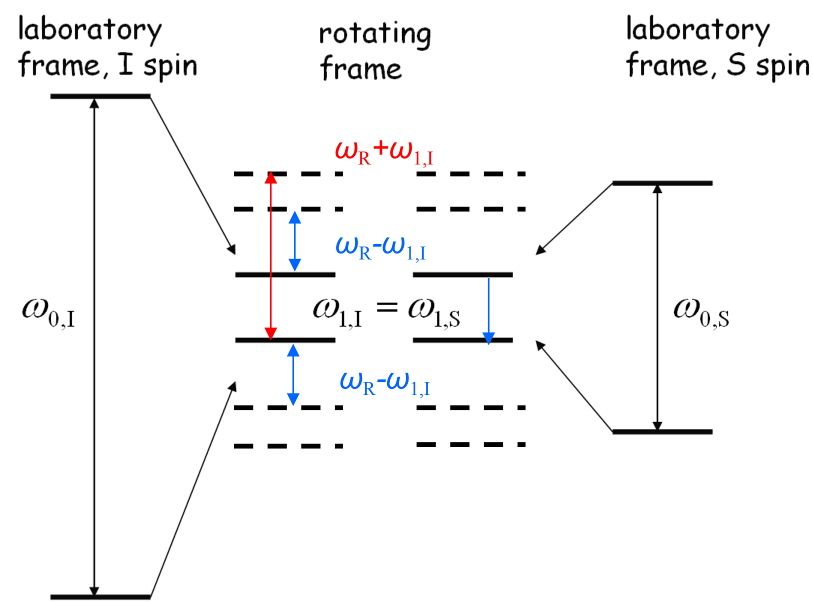


This is shown on the right side for n=1: The polarisation transfer is supported by *flip-flop* terms (zero-quantum transitions)

CP and very fast MAS

When the MAS speed ω_{R} is approaching a regime, where ω_R is faster (stronger) than the RF-fields $\omega_{1,I}$ and $\omega_{1,S}$ the CP Hartmann-Hahn condition can also be:

$$\boxed{\begin{aligned} \omega_{1,I} \pm n\,\omega_R &= -\,\omega_{1,S} \\ \omega_{1,I} + \omega_{1,S} &= \pm n\,\omega_R \end{aligned}}$$



Shown on the right for n = 1; now the polarisation transfer is also supported by *flop-flop* processes, the elemental CP step is now a double-quantum transition.

See, e.g., S. Laage, et al., J. Magn. Reson. 196, 133, 2009

Hartmann-Hahn at 111kHz MAS

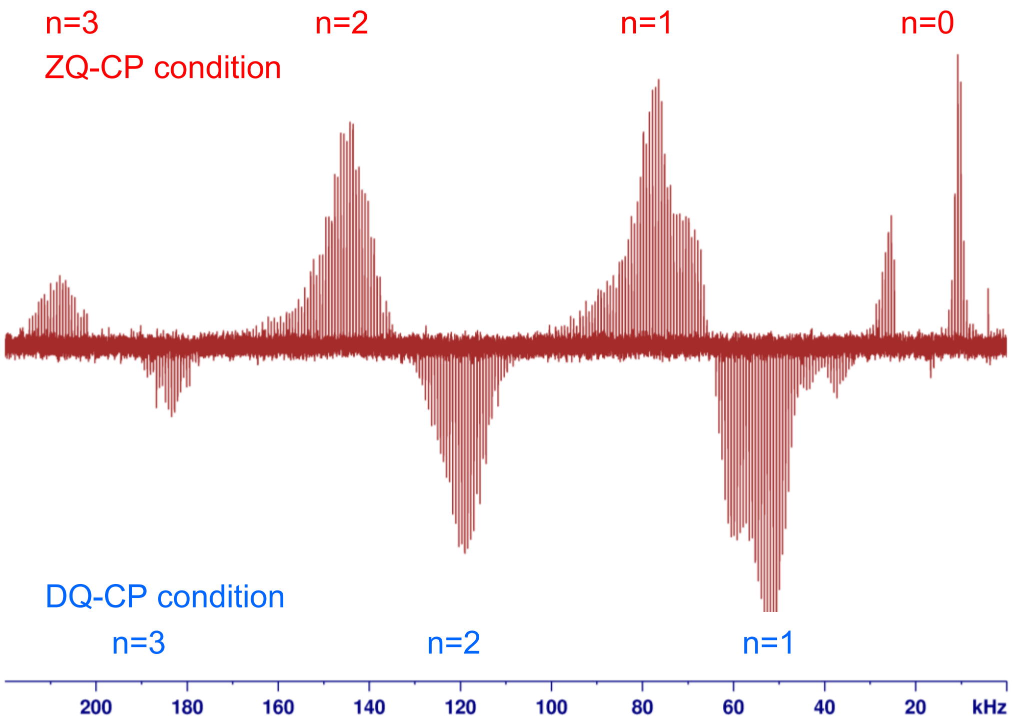
ZQ condition: $$\boxed{\frac{\omega_{1I} - \omega_{1S}}{\omega_R} = \pm n}$$

DQ condition: $$\boxed{\frac{\omega_{1I} + \omega_{1S}}{\omega_R} = \pm n}$$

For ω_R = 111 kHz, ω_{1S} = 15 kHz matching conditions:

ω_{1I}(ZQ,n=0) = 15 kHz
ω_{1I}(ZQ,n=1) = 126 kHz
ω_{1I}(ZQ,n=2) = 237 kHz
ω_{1I}(ZQ,n=3) = 348 kHz

ω_{1I}(DQ,n=1) = 96 kHz
ω_{1I}(DQ,n=2) = 207 kHz
ω_{1I}(DQ,n=3) = 318 kHz



Hartmann-Hahn at 111kHz MAS destructive overlay of H-H conditions

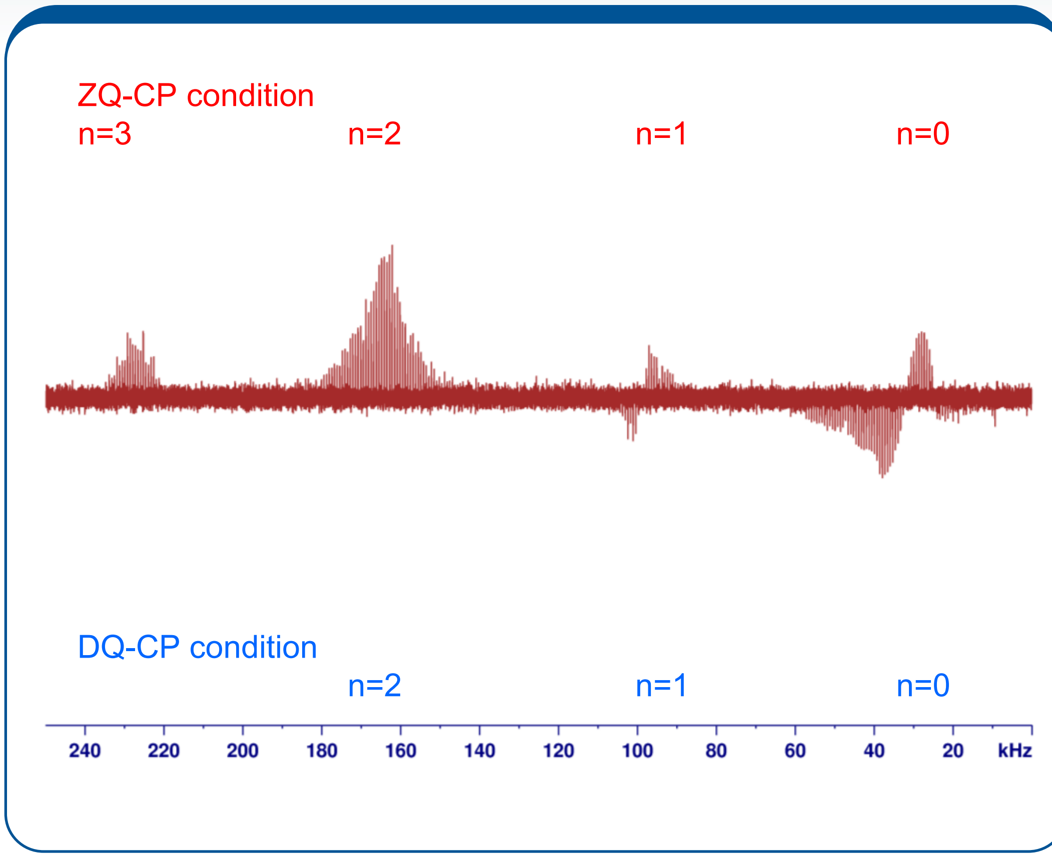
ZQ Kondition: $$\boxed{\frac{\omega_{1S} - \omega_{2S}}{\omega_R} = \pm n}$$

DQ Kondition: $$\boxed{\frac{\omega_{1S} + \omega_{2S}}{\omega_R} = \pm n}$$

Für ω_R = 111 kHz, ω_{1I} = 55 kHz
the matching conditions are:

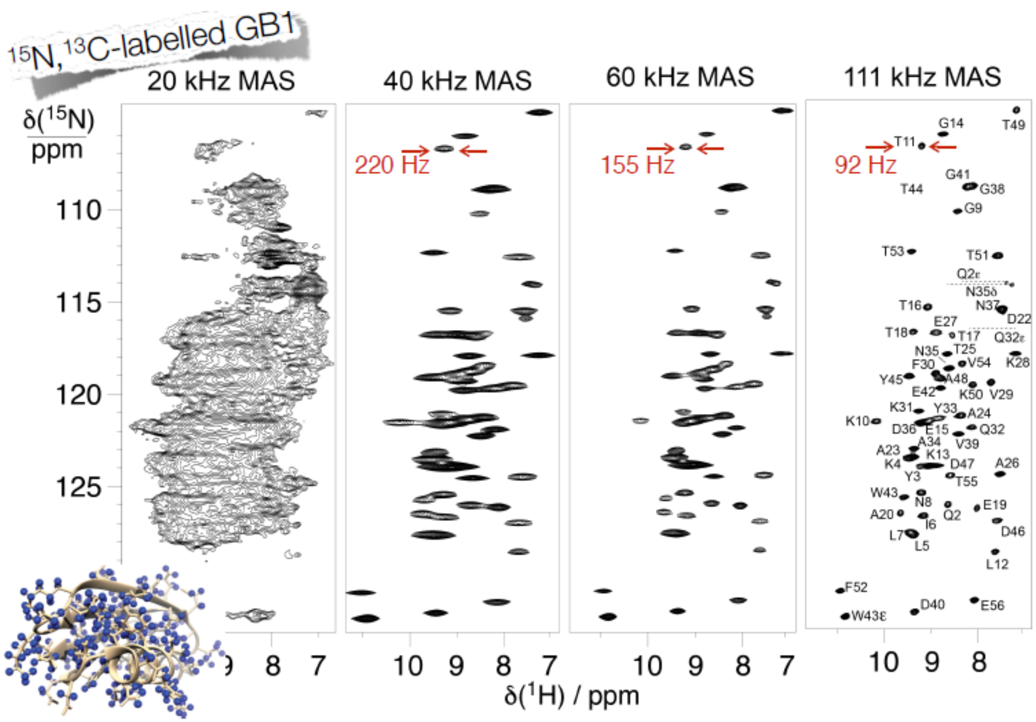
ω_{1S}(ZQ,n=0) = 55 kHz
ω_{1S}(ZQ,n=1) = 166 kHz
ω_{1S}(ZQ,n=2) = 277 kHz
ω_{1S}(ZQ,n=3) = 388 kHz

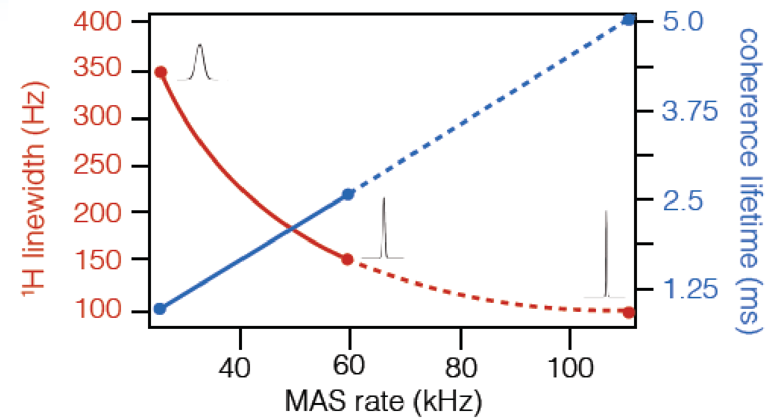
ω_{1S}(DQ,n=1) = 56 kHz
ω_{1S}(DQ,n=2) = 167 kHz
ω_{1S}(DQ,n=3) = 278 kHz



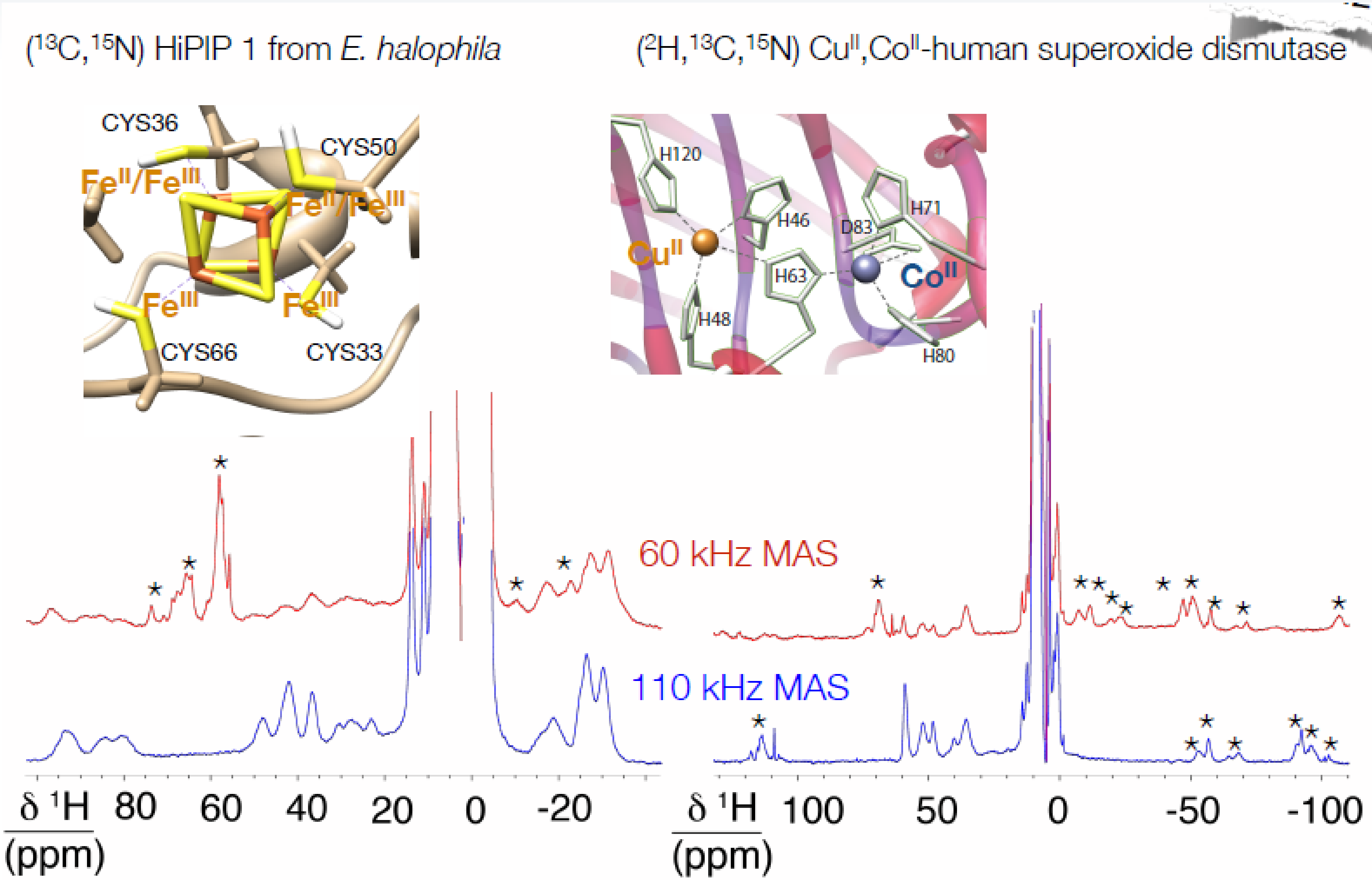
MAS 0.7 mm
^{1}H detected ^{15}N-^{1}H 2D correlation @ 111kHz

Coherence Lifetimes & Linewidths (GB1)

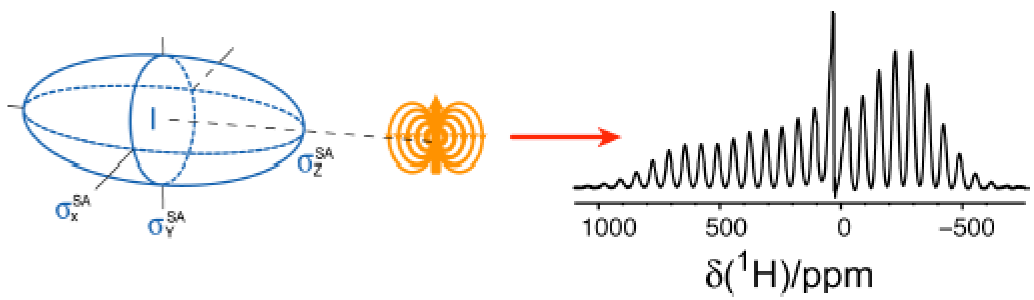


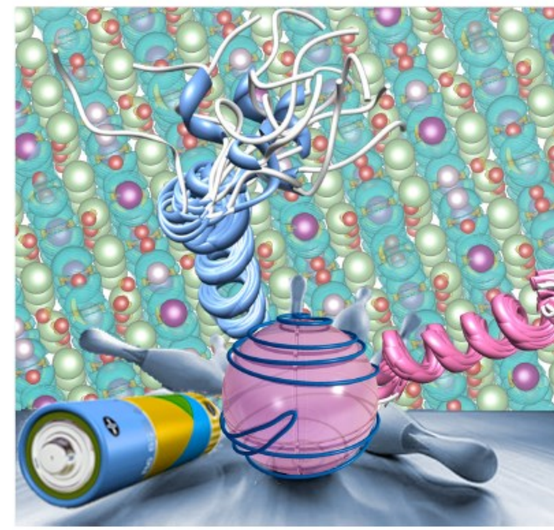


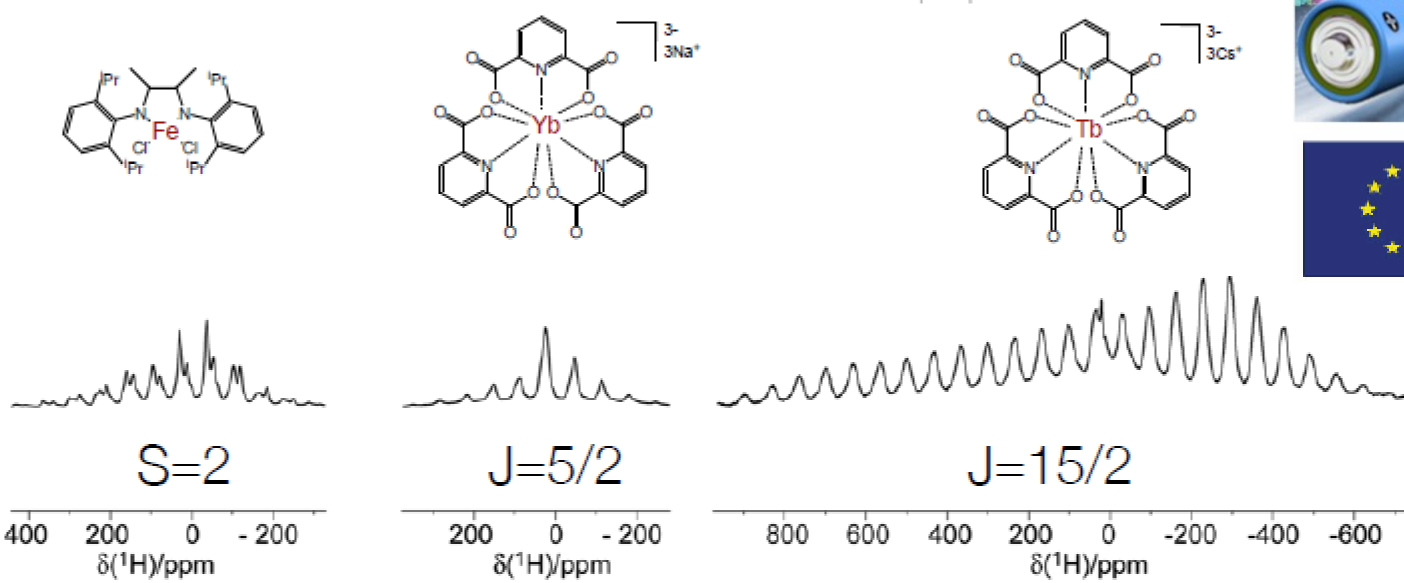
Paramagnetic metalloproteins: Metal-ion coordination



Paramagnetic Solids
Large Offsets and Large Shift Anisotropies







pNMR Network

Fast MAS and extended VT

- Ultrafast MAS (0.7 mm)
  (ENS Lyon February 2015)
- Fast MAS (1.3 mm) low temperature (100 K) DNP probe
  (ENS Lyon 2016, ETHZ 2017)
- Fast MAS (1.3 mm) non-DNP with extended VT capabilities
  (functional prototype July 2016)

Thank you

for your attention !