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

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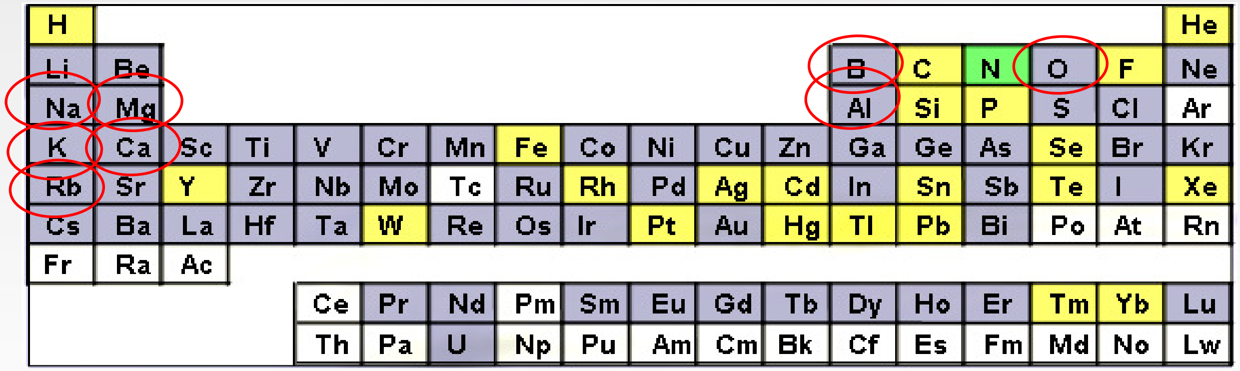
Advanced NMR spectroscopy of quadrupolar nuclei

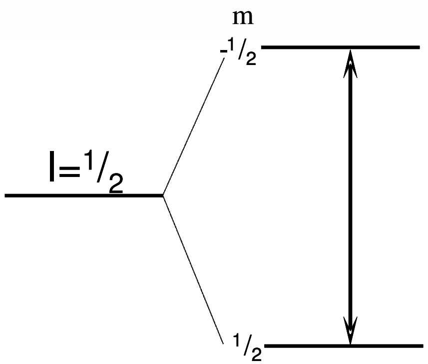
NMR active nuclei – problem of inorganic systems; *I*>1/2

22 spins *I*=1/2

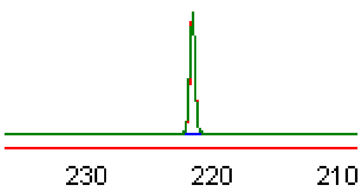
77 spins *I*=3/2, 5/2,9/2

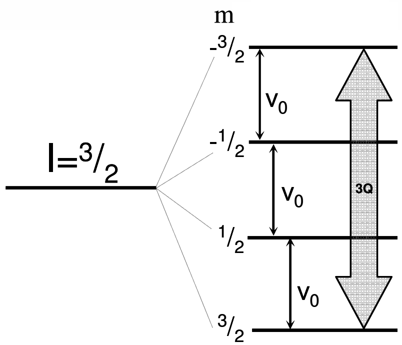
1 spin *I*=1



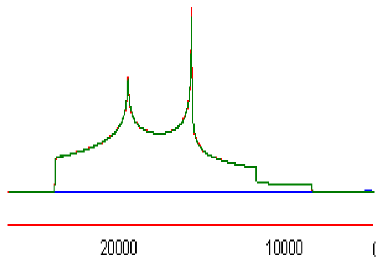


Spectrum: narrow signal
0,1-100 Hz





Spectrum: broad signal
1000-100000 Hz



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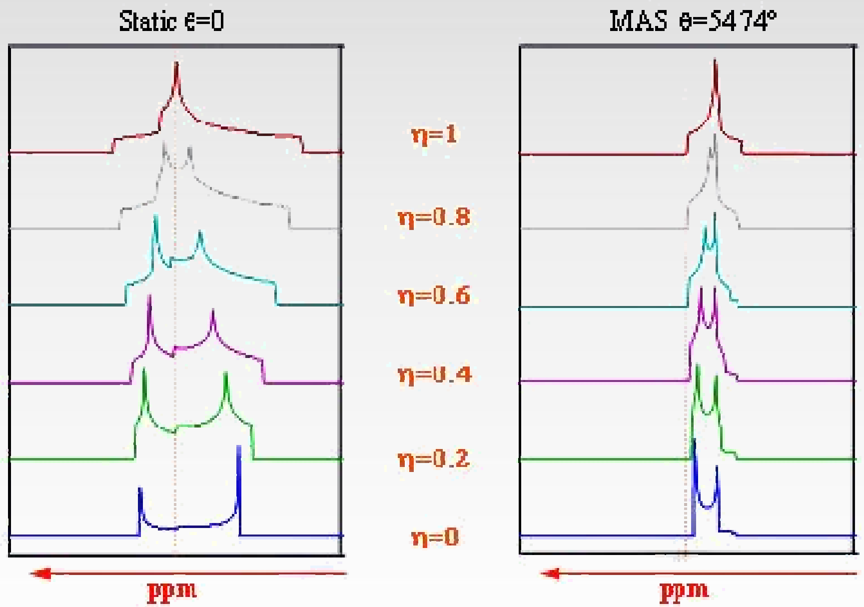
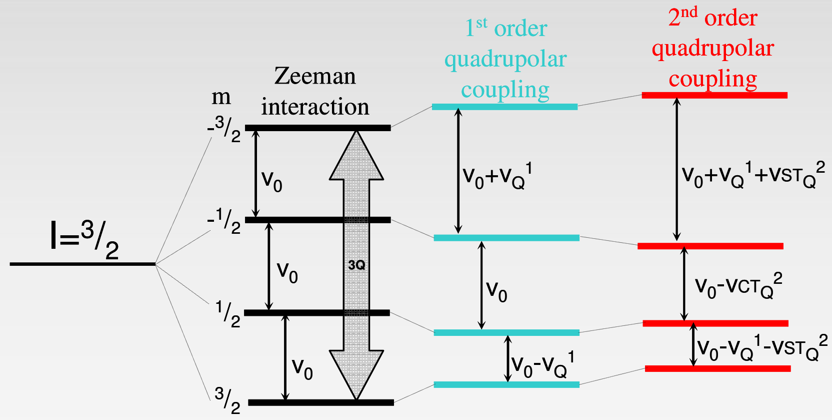
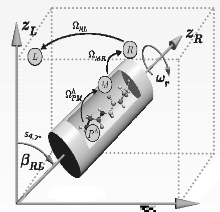
Quadrupolar broadening





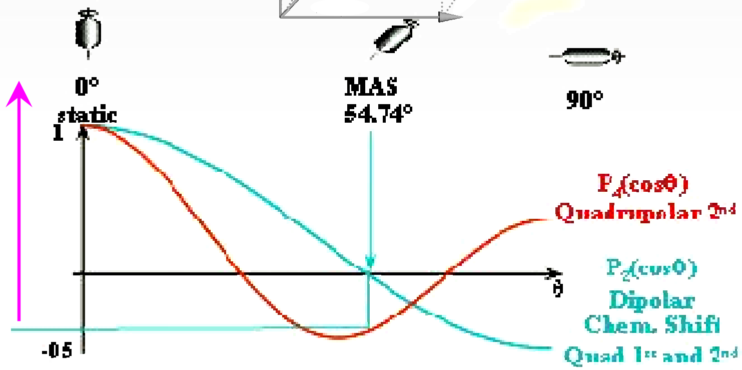


1st order quadrupolar coupling

$$P_2(\cos\theta)=\frac{1}{2}\left(3\cos^2\theta-1\right)$$

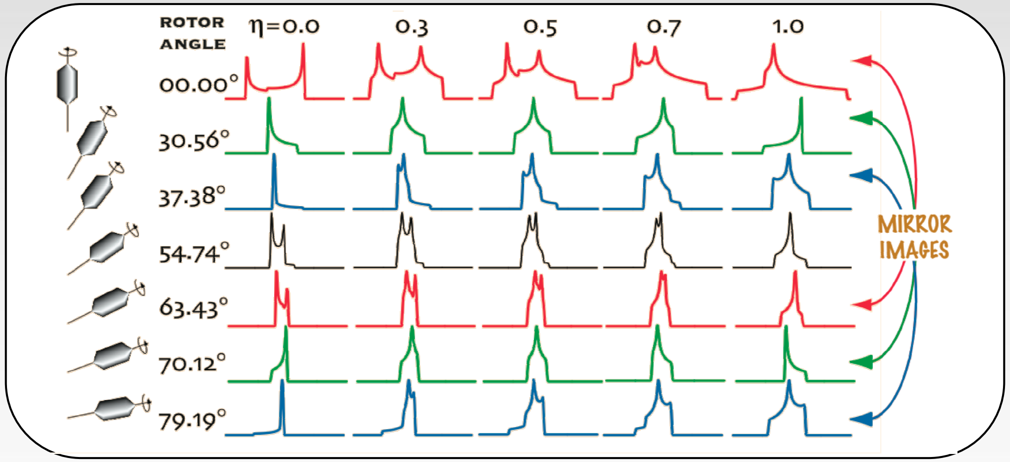
2nd order quadrupolar coupling

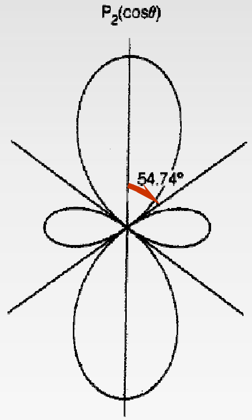
$$P_4(\cos\theta)=\frac{1}{8}\left(35\cos^4\theta-30\cos^2\theta+3\right)$$

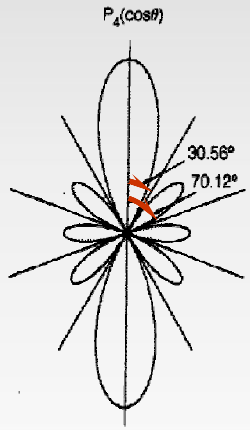


MAS narrows 2nd order broadening by a factor 3 to 4

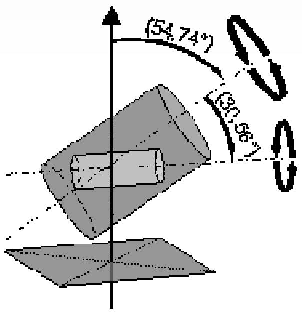
NMR techniques for quadrupolar nuclei
DOR/DAS/MQMAS





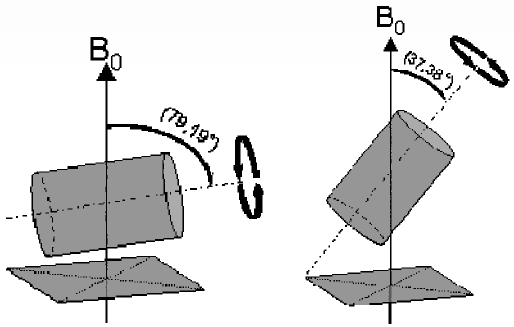


DOR NMR



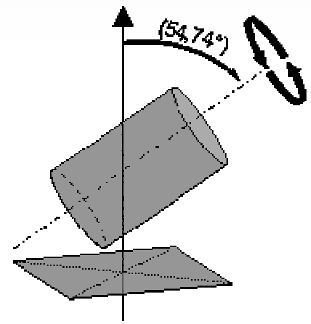
1D spectrum

DAS NMR



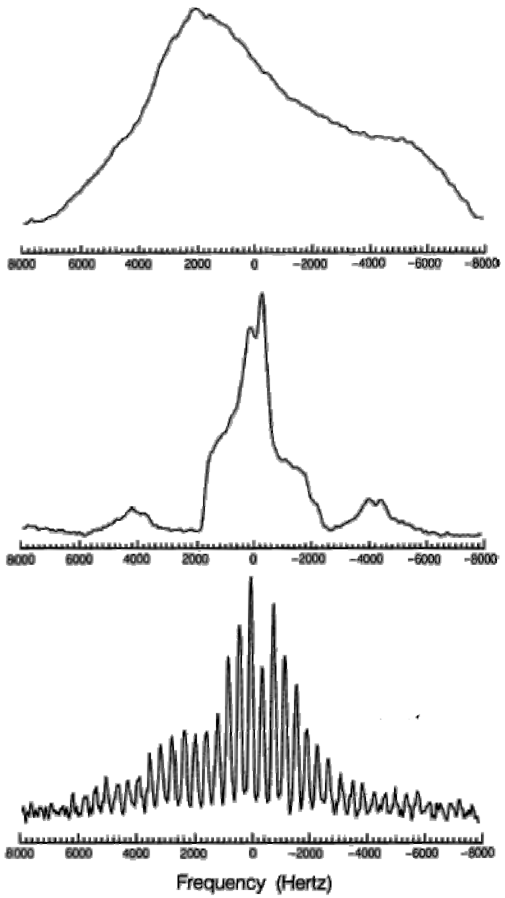
2D spectrum

MQ/MAS NMR

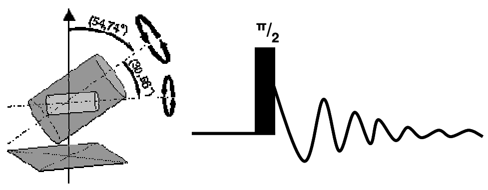


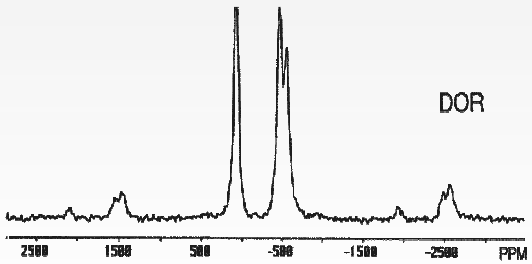
2D spectrum

DOR: DOuble Rotation



^{23}Na Static(top),
MAS(middle),
DOR(bottom)
NMR spectra of sodium oxalate



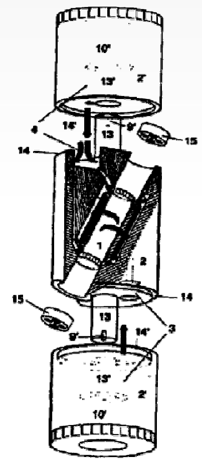


Advantages

- quantitative
- high sensitivity
- low rf field requirement
- fast 1D experiment

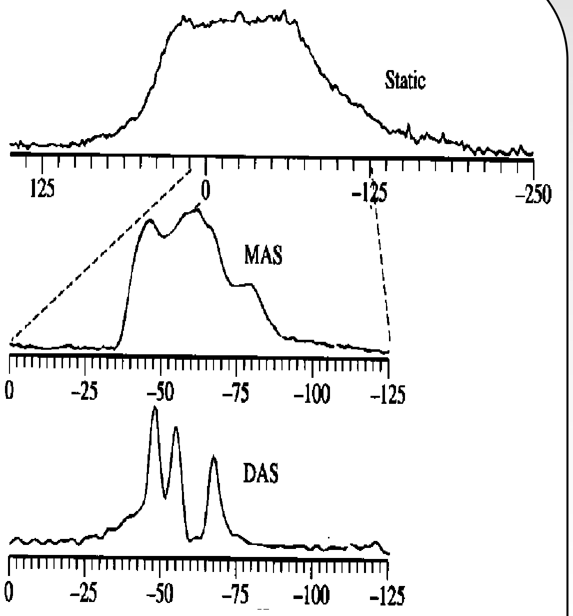
Disadvantages

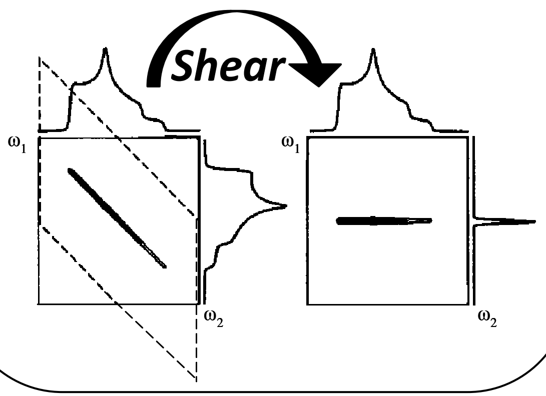
- special and expensive probes required
- low spinning frequency
  stable spinning is difficult
- Only for crystalline compounds

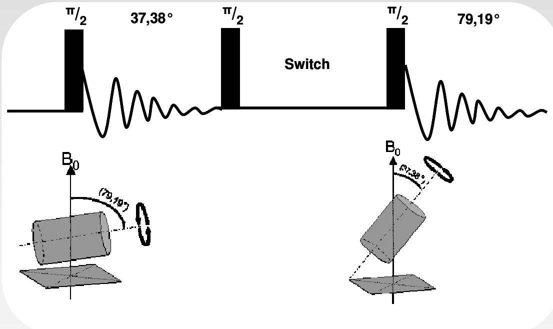


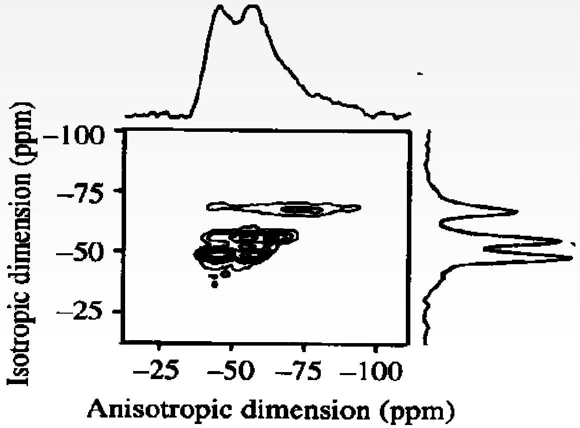
In practice:
ν_0 7-8 kHz
ν_1 1-2 kHz

DAS: Dynamic Angle Spinning







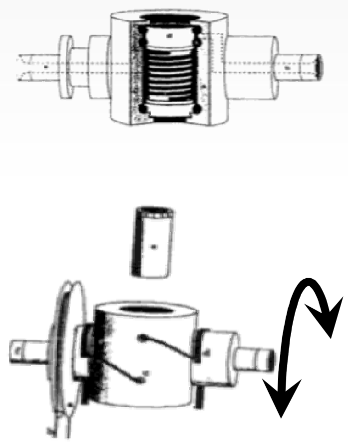


Advantages

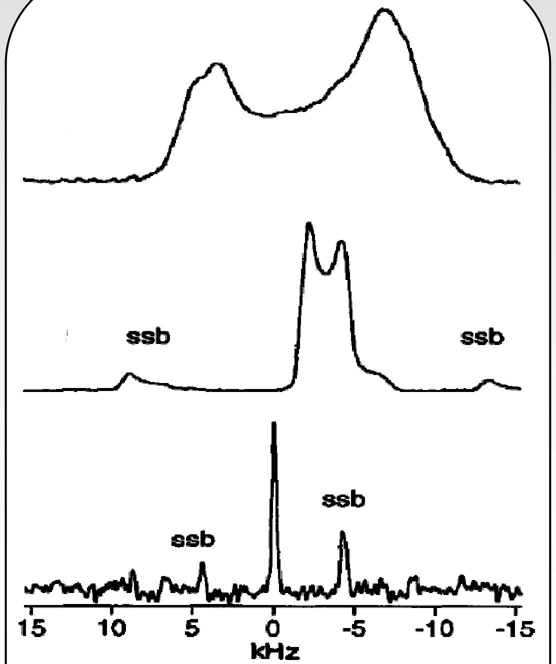
- quantitative
- high sensitivity
- low rf field requirement
- For amorphous compounds

Disadvantages

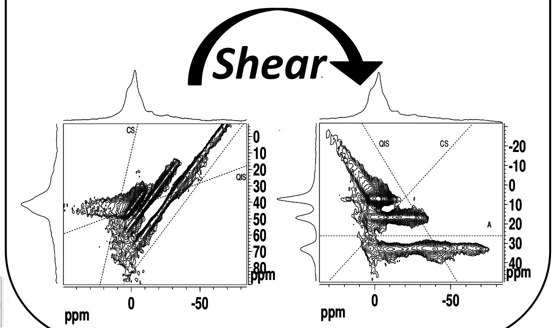
- special and expensive probes required
- nuclei with long T_1
- Impossible decoupling (β_1 and $\beta_2 \neq 54.7°$)

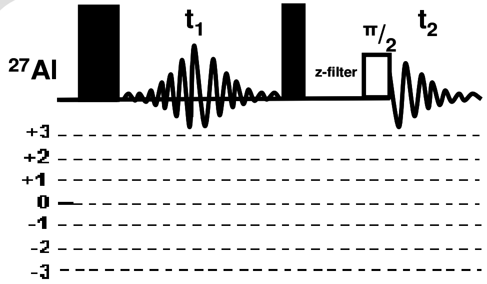


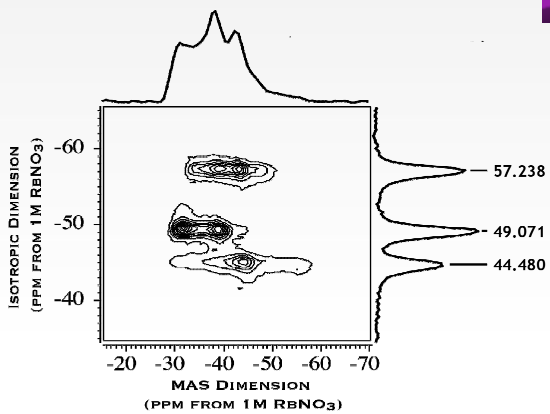
MQ/MAS: Multi Quantum Magic Angle Spinning



^{17}O NMR spectra of hydroxyapatite





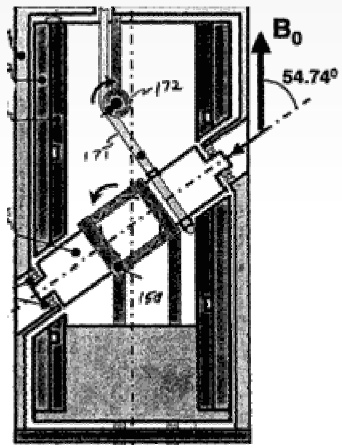


Avantages

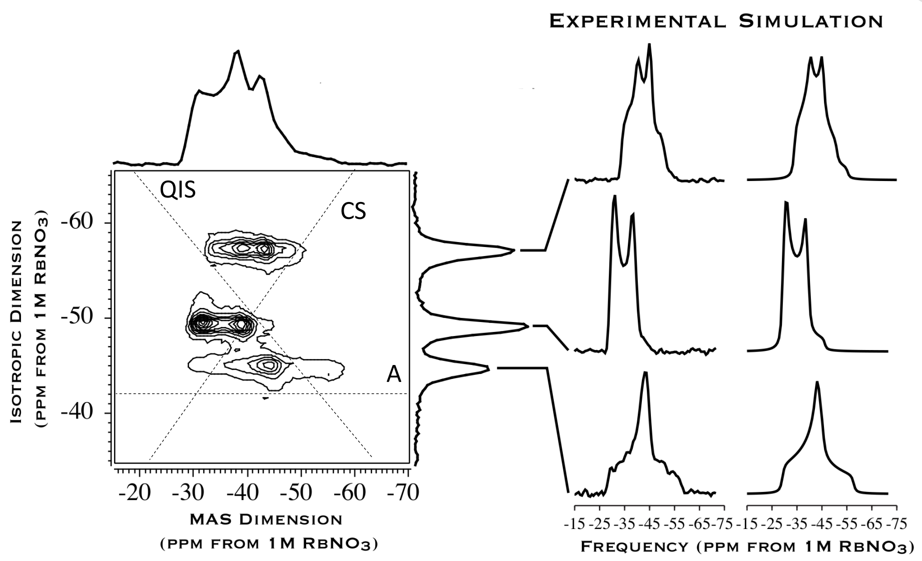
- Easy to implement and no special probe required
- Good for abundant nuclei
- Good for nuclei with short T_1

Disadvantages

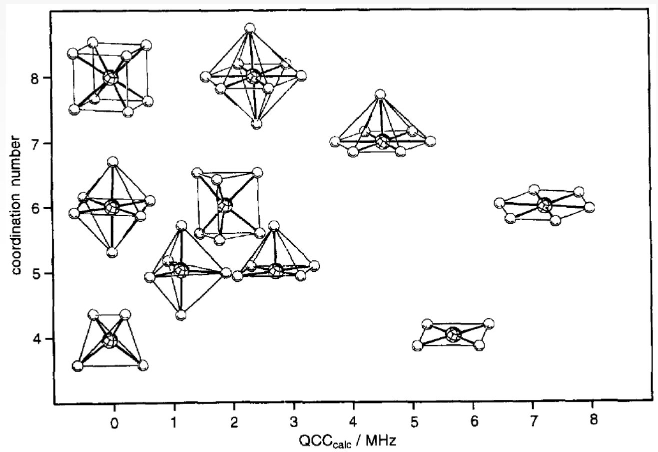
- Not quantitative
- High rf field required for the excitation pulse
- Poor sensivity for large C_Q



MQ/MAS spectrum - analysis



- Information about
  - Number of species
  - Orderliness
  - Local geometry
  - determine of C_Q, η_Q by simulation



Chemical shift

$$\delta_{CS} = \frac{17\delta_{F_1} + 10\delta_{F_2}}{27}$$

Quadrupolar coupling constant

$$P_Q = \frac{\delta_{F_1} - \delta_{F_2}}{k}$$

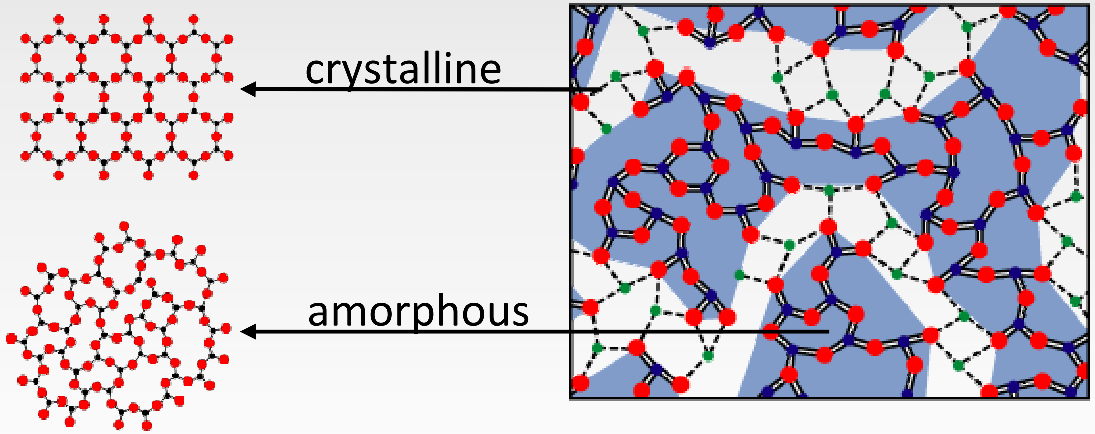
$$k = \frac{3}{10} \cdot \frac{4I(I+1)-3}{[4I(2I-1)\nu_0]} \cdot 10^6$$

$$P_Q = C_Q\sqrt{1+\frac{\eta^2}{3}}$$

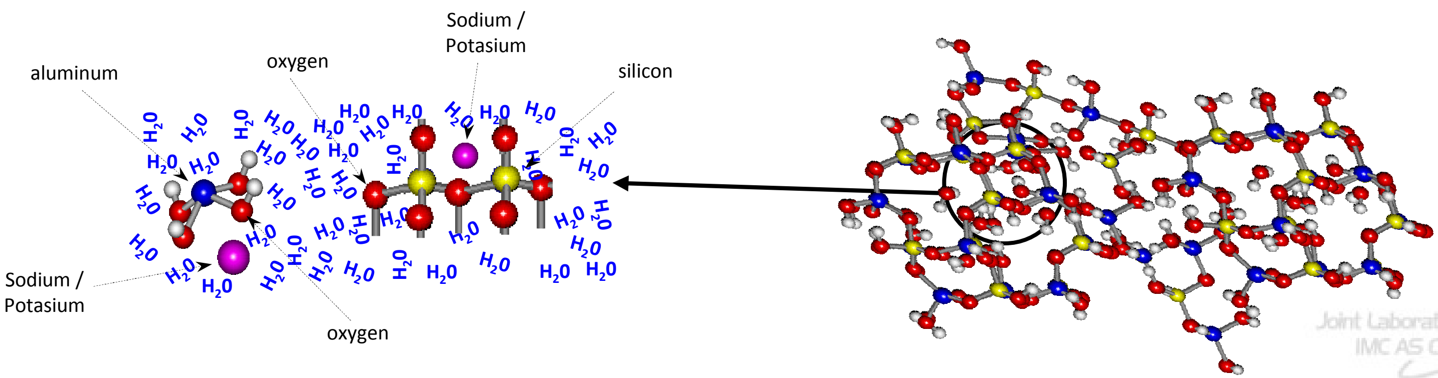
MQ-MAS NMR spectra exhibit a higher resolution than DAS or DOR spectra

Amorphous materials –glasses, cements, AlPs etc…

Boron glasses



Amorphous alumino-silicate polymers AIP`s



Preparation and properties of AlP`s

1. Calcination

Kaolin → **Metakaolin**

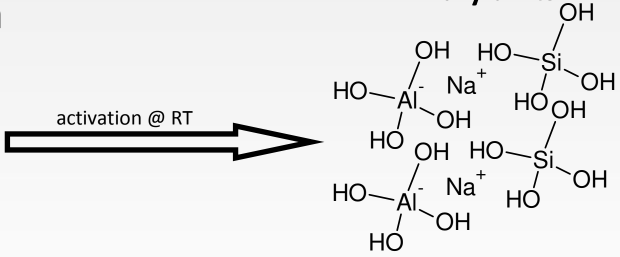
$Al_4(OH)_8Si_4O_{10}$ $\xrightarrow[-4H_2O]{650°C}$ $Si_2O_5.Al_2O_2$

2.Activation

Metakaolin

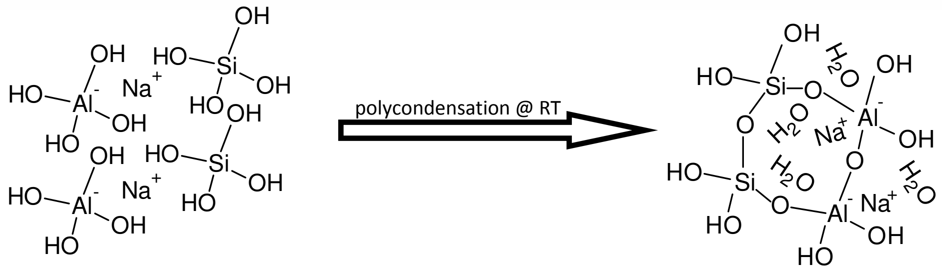
$Si_2O_5.Al_2O_2 + 5H_2O{+}2NaOH$

Primary units



3. Polycondensation

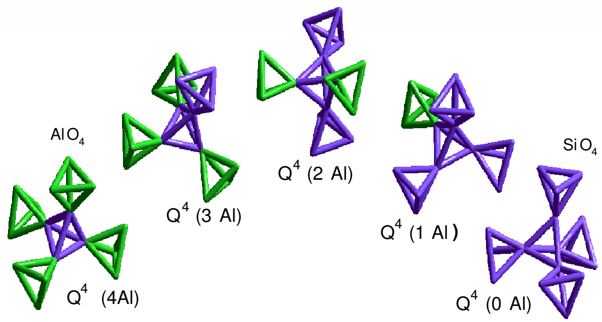
Primary building units → **Amorphous network**



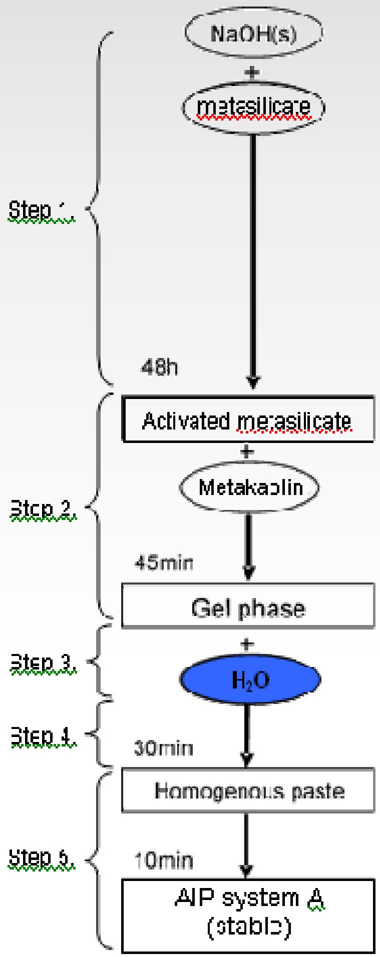
Properties

- excellent mechanical strength
- resistance to high temperatures
- easy recycling
- low production of CO_2
- long-time stability

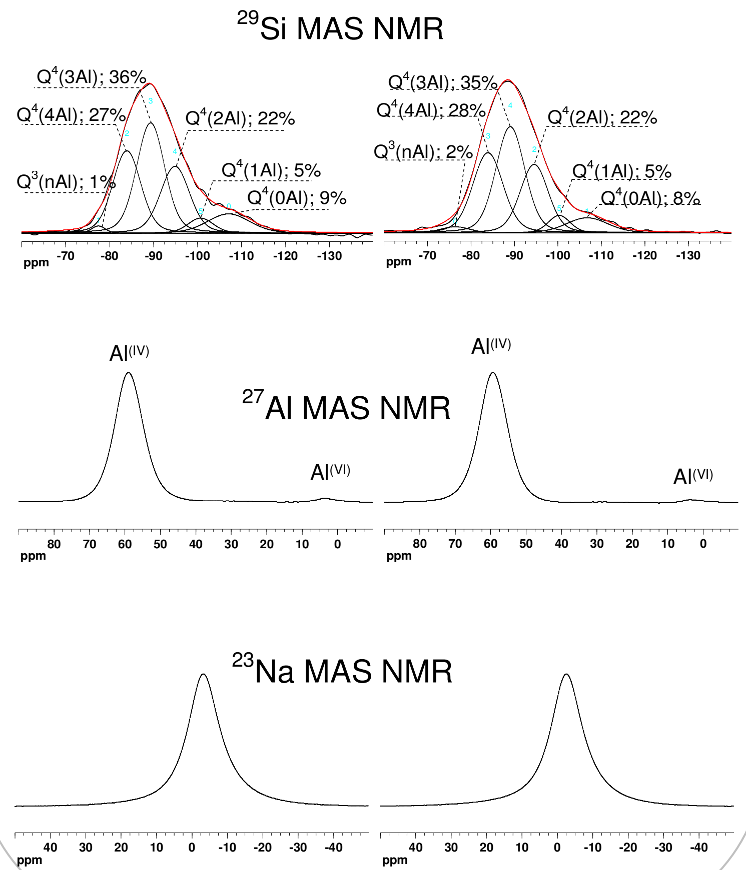
Building units

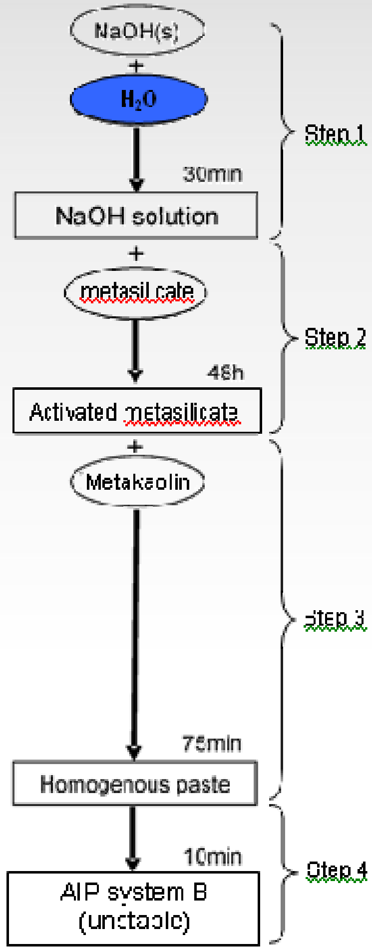


Preparation and basic characterization



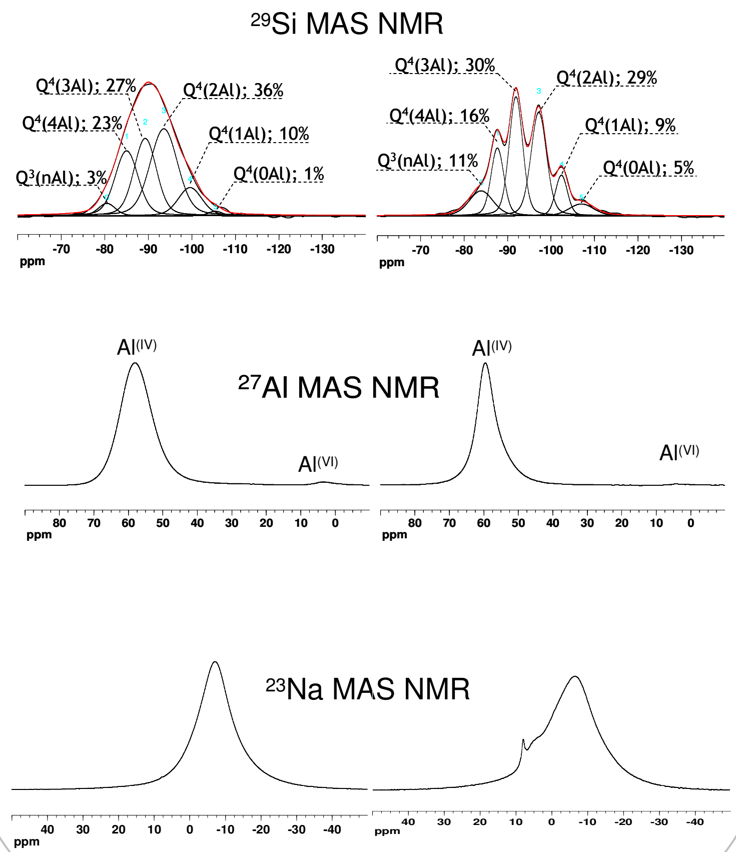
stable vs. unstable





Characterization after accelerated aging

stable vs. unstable

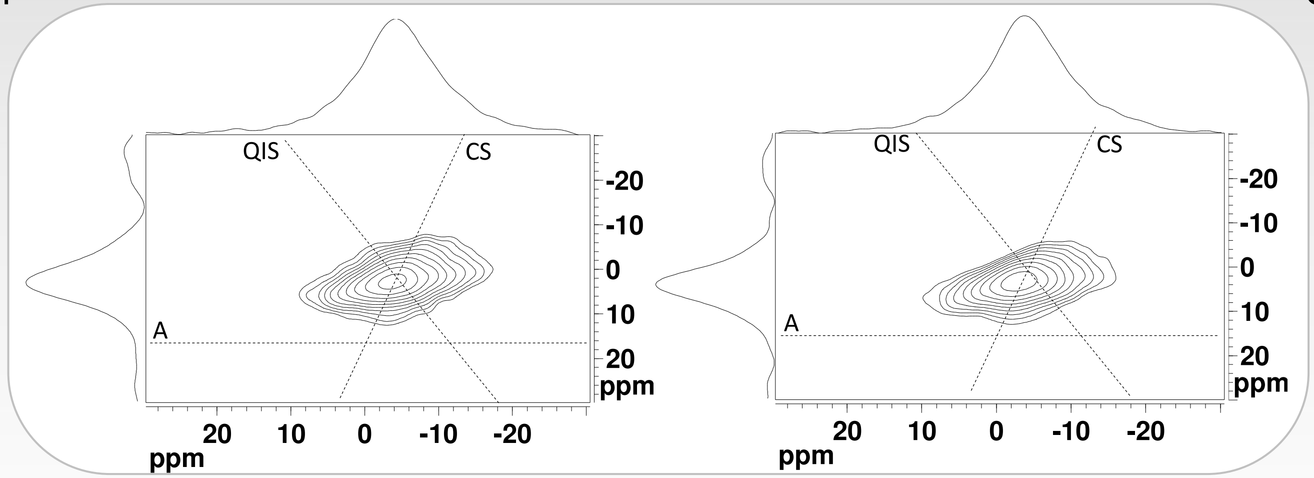


^{23}Na MQ/MAS of AlP systems

stable vs. unstable

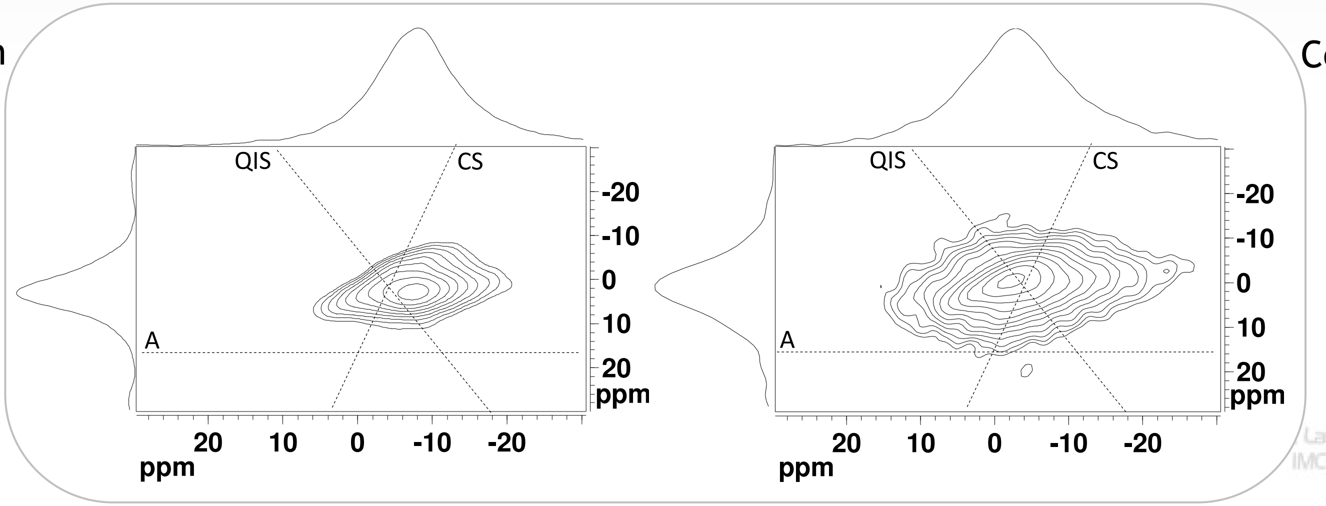
Compression strength **70 MPa**

Compression strength **70 MPa**



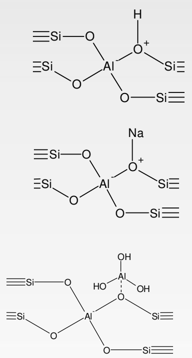
Compression strength **70 MPa**

Compression strength **30 MPa**



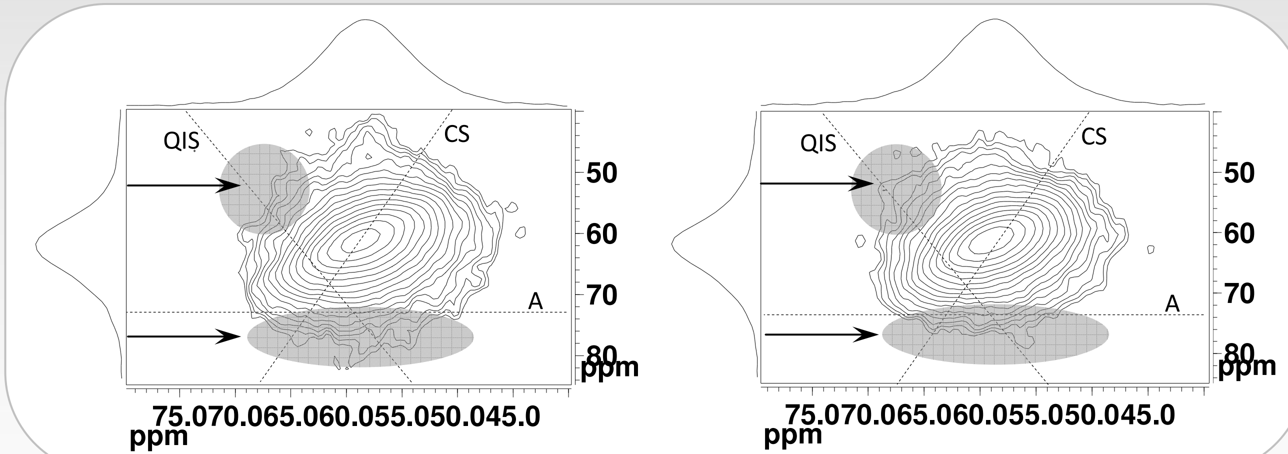
^{27}Al MQ/MAS of AlP systems

Compression strength **70 MPa**



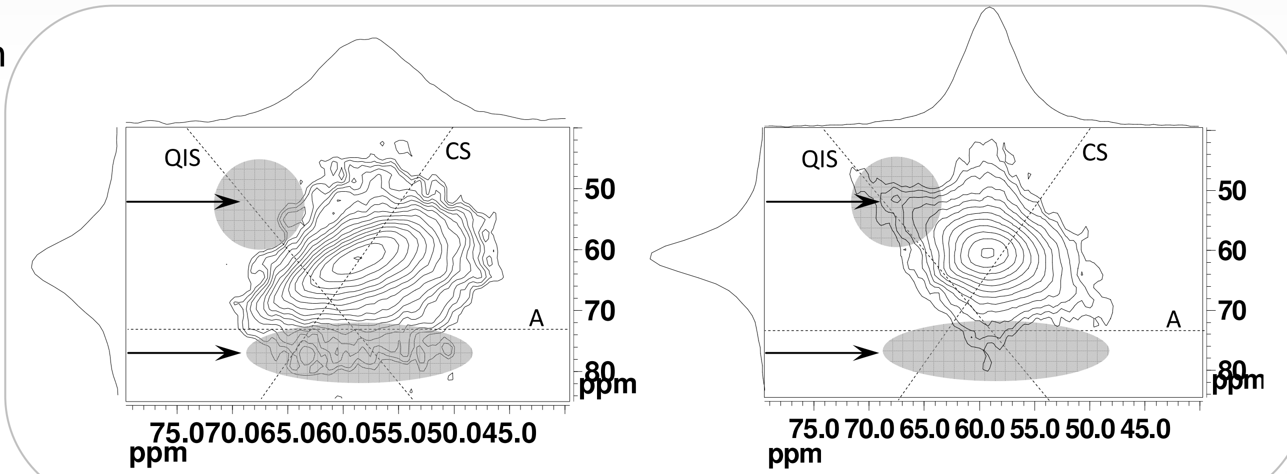
stable vs. unstable

Compression strength **70 MPa**



Accelerated aging

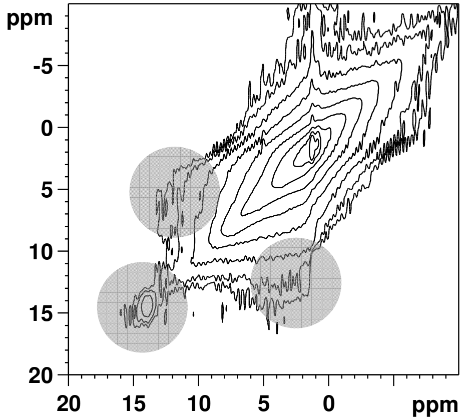
Compression strength **70 MPa**

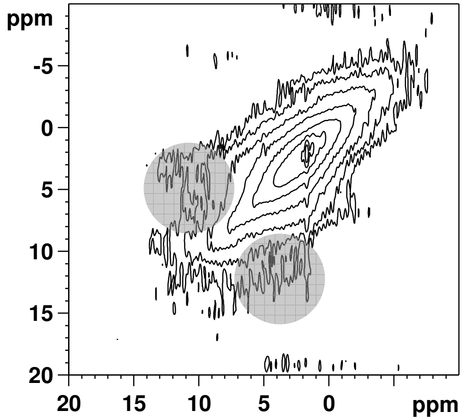


Compression strength **30 MPa**

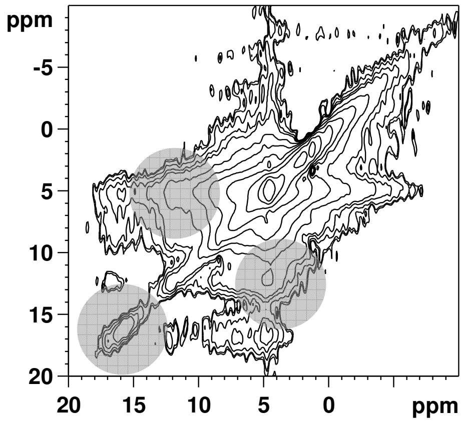
^1H-^1H MAS NMR correlation spectra

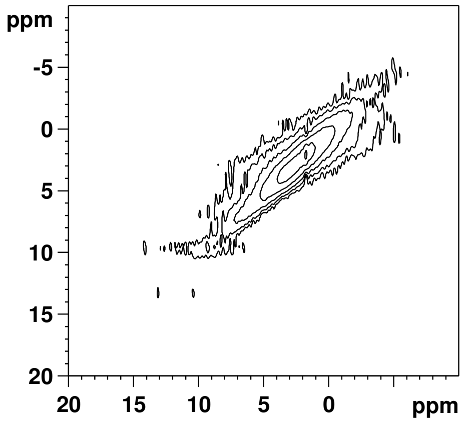
stable vs. unstable





Accelerated aging





Summary

- Since 74% of all magnetically active naturally occurring isotopes are quadrupolar nuclei
- Suitable for descriptions of local geometry to long distance
- Combination of high magnetic field and 2D MQ/MAS NMR experiments allow obtaining high-resolution spectra with usual MAS probe
- Possible for all types of materials (crystalline or amorphous)

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Thanks for your attention

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