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# **NMR Spectroscopy of Organic Compounds**

## **Lesson 9: Solid-state NMR**



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**Martin Dračínský**

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# Overview

- NMR interactions
- Magic-angle spinning, cross polarization
- Examples

# NMR interactions

## SOLIDS

- Chemical shift anisotropy
- $J$ -coupling (indirect coupling)
- Direct spin-spin interaction (dipolar coupling)
- Quadrupolar interaction

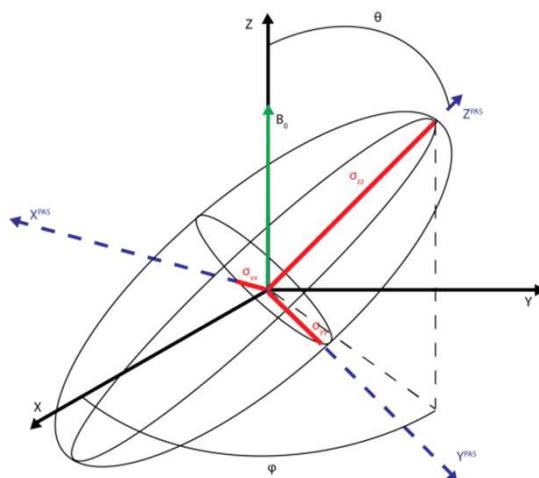
## SOLUTIONS

$\delta$

$J$

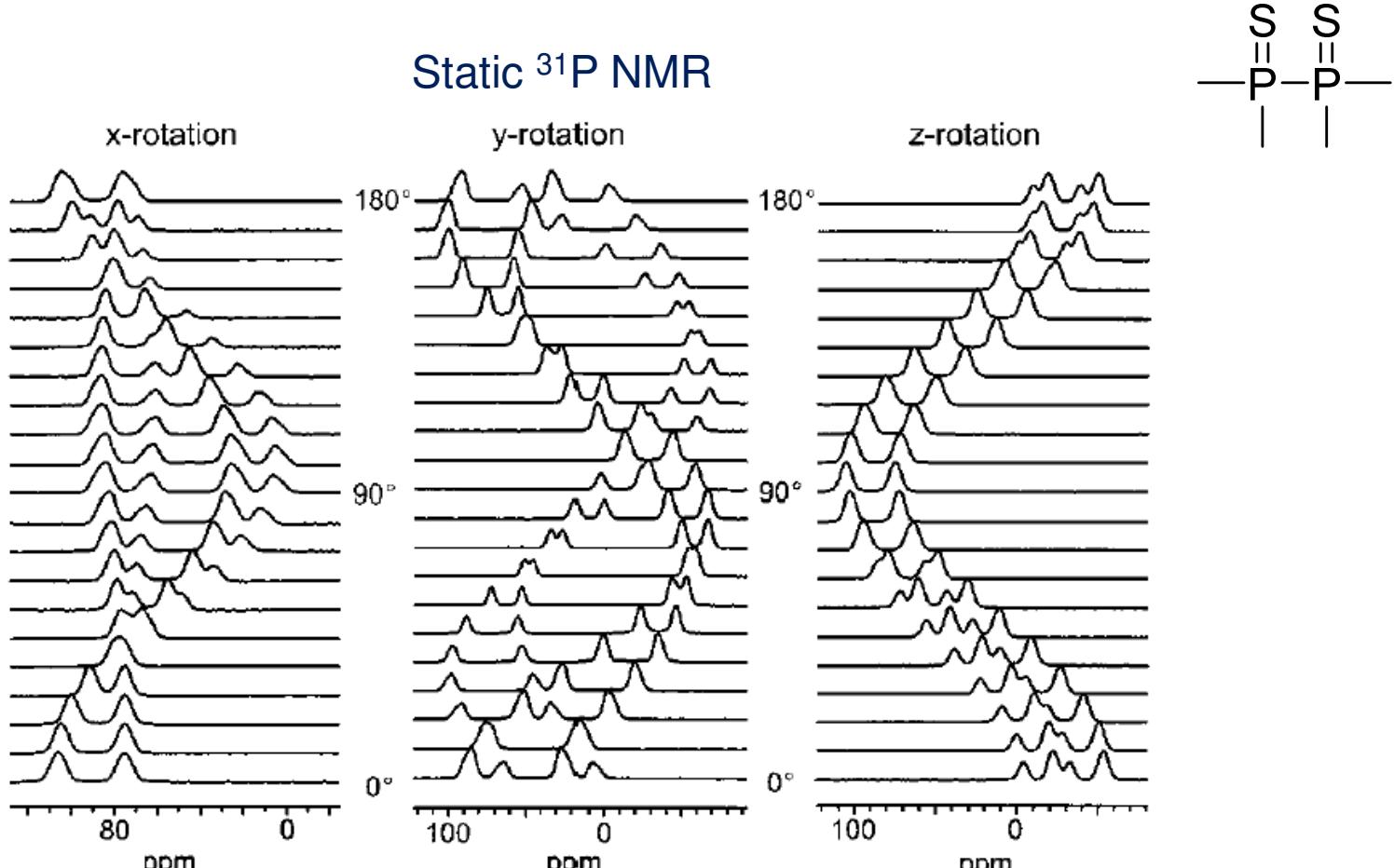
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$$(3 \cos^2 \theta - 1)$$

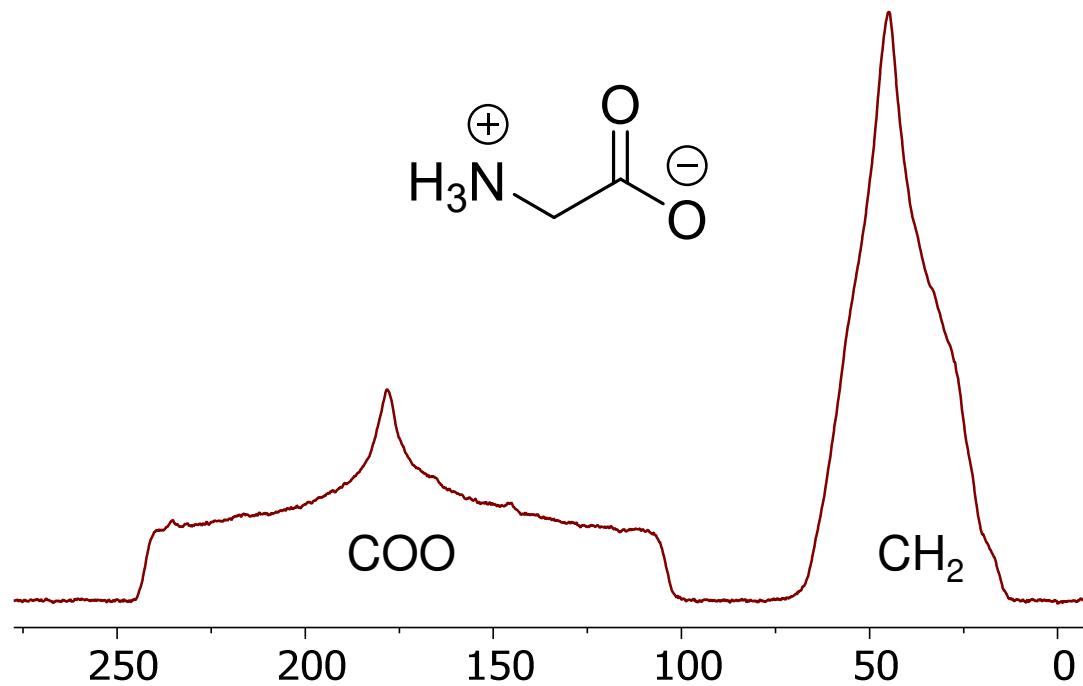
# Chemical shift anisotropy – single crystal



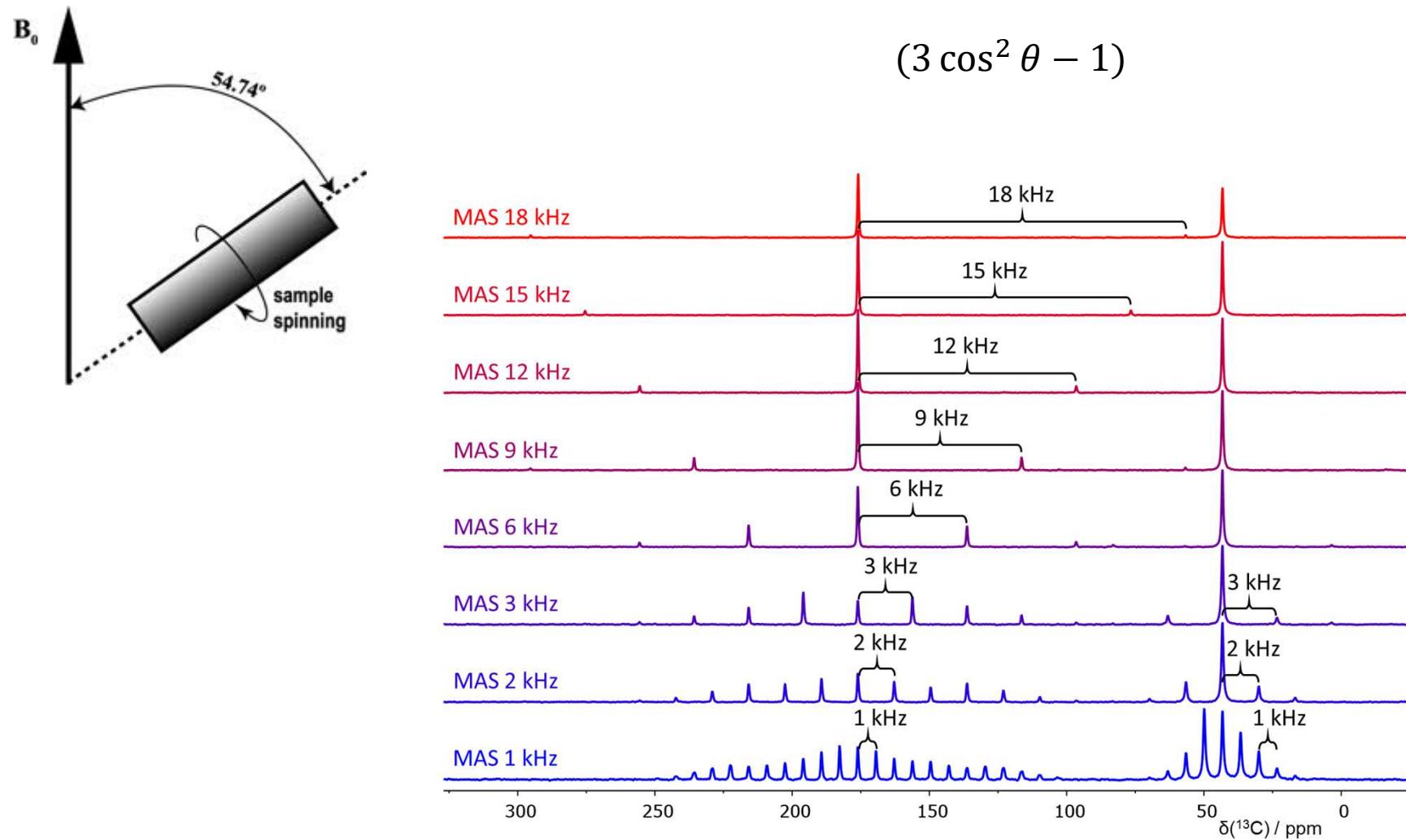
Gee et al. *J. Phys. Chem. A* 2000, 104, 4598.

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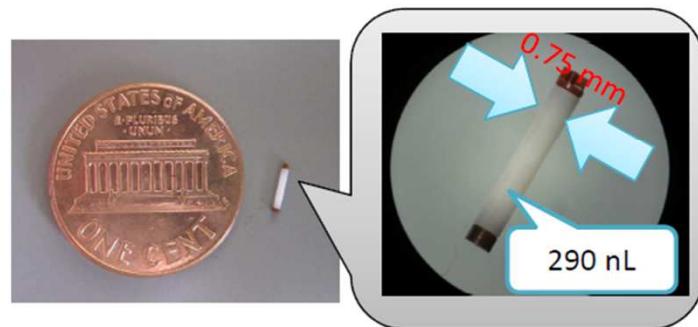
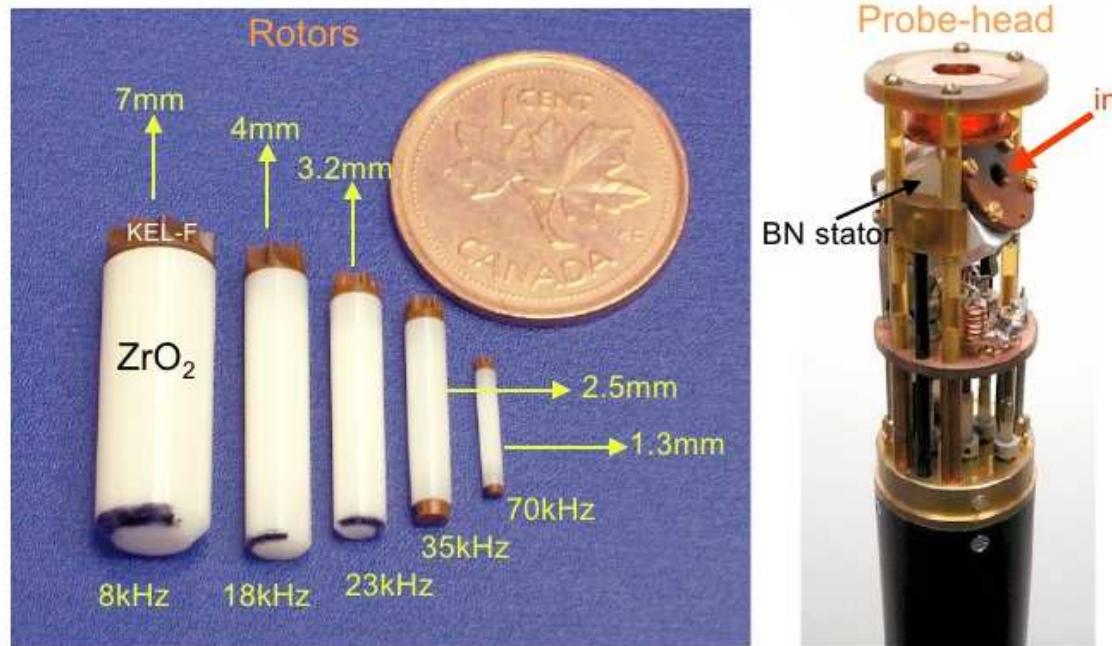
# Chemical shift anisotropy – powder



# Magic angle spinning (MAS)



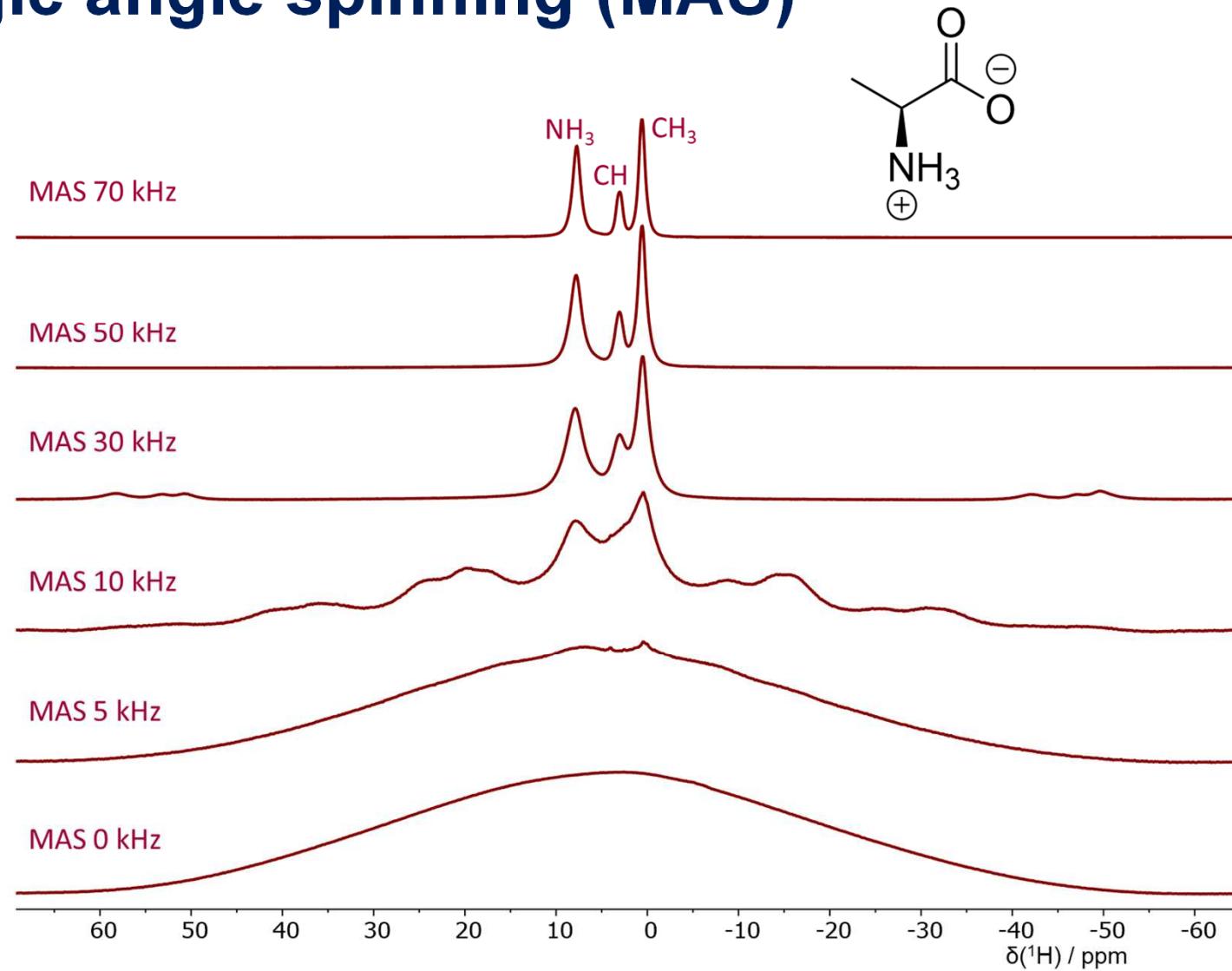
# Magic angle spinning (MAS)



# Magic angle spinning (MAS)



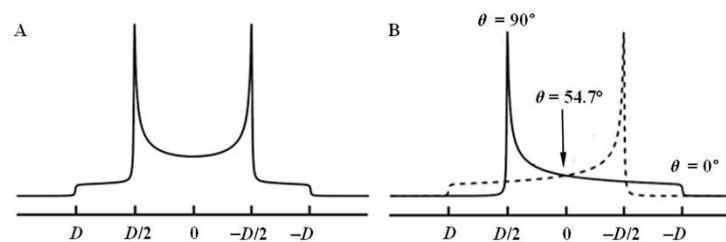
# Magic angle spinning (MAS)



# Dipolar and quadrupolar coupling

Direct spin-spin interaction (dipolar coupling)

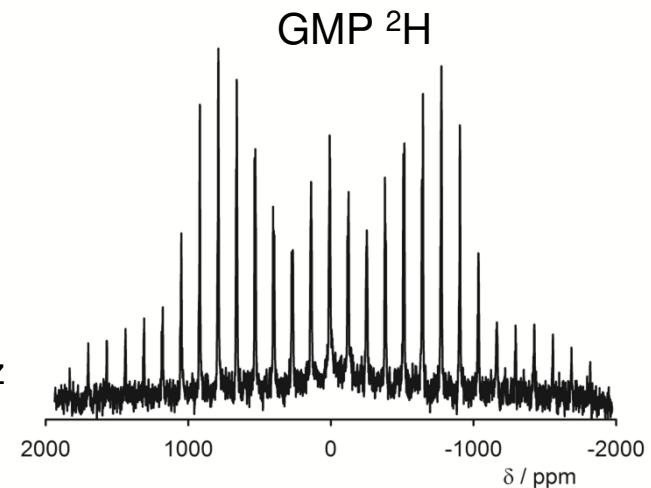
- Depends on gyromagnetic ratio  $\gamma$  and internuclear distance
- C-H  $\approx$  25 kHz
- High power decoupling



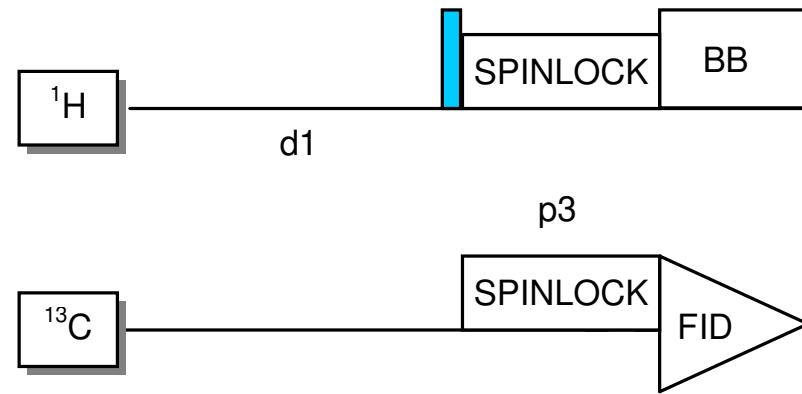
Quadrupolar coupling

- Nuclei with  $I > 1/2$  (e.g.  $^2\text{H}$ ,  $^{14}\text{N}$ ,  $^{17}\text{O}$ ,  $^{23}\text{Na}$ ,  $^{35}\text{Cl}$ )
- $\approx$  MHz

Quadrupolar coupling  $C_Q \sim 200$  kHz  
(typical value for O-D groups)



# Cross polarisation (CP)

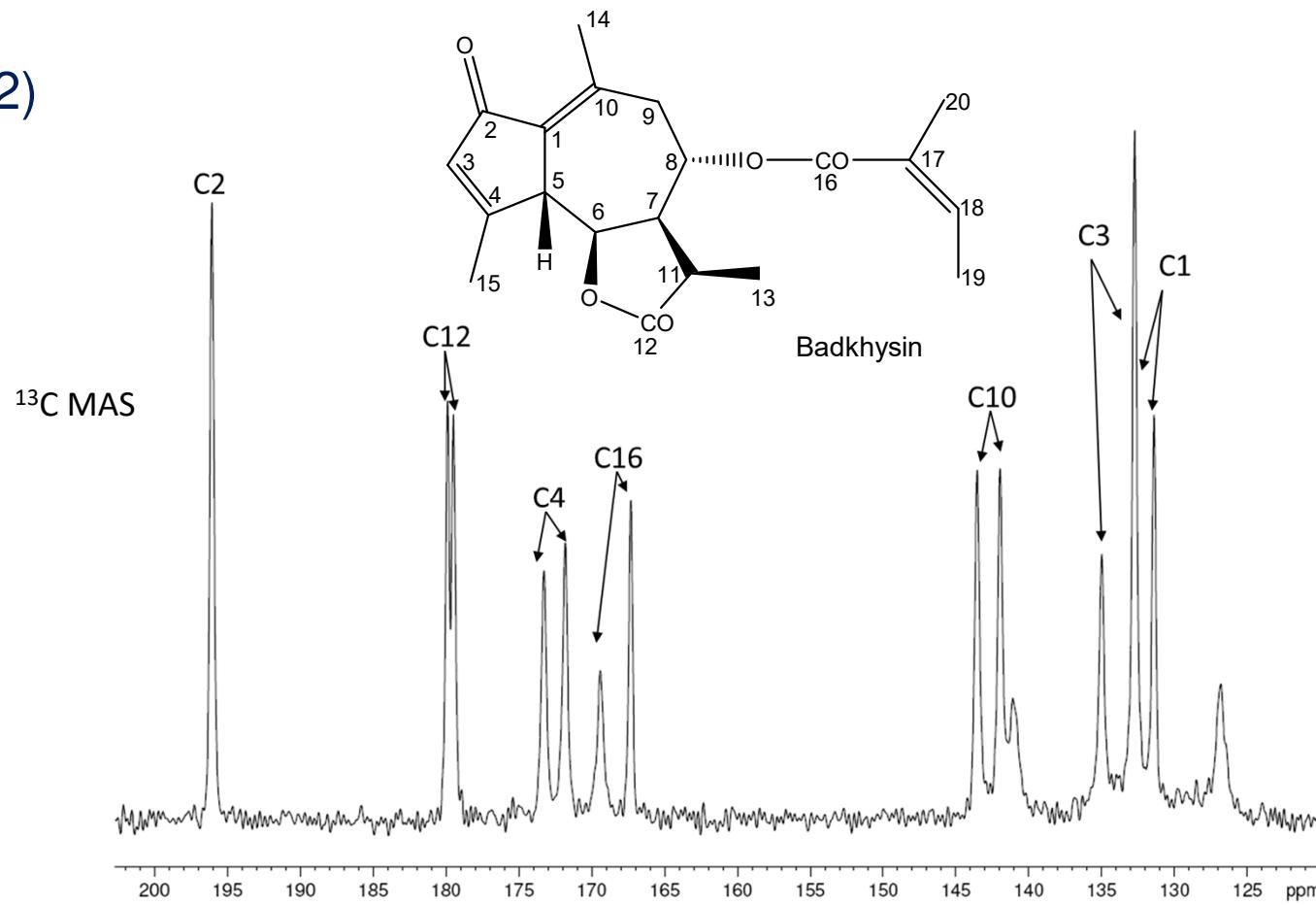


Sensitivity gain

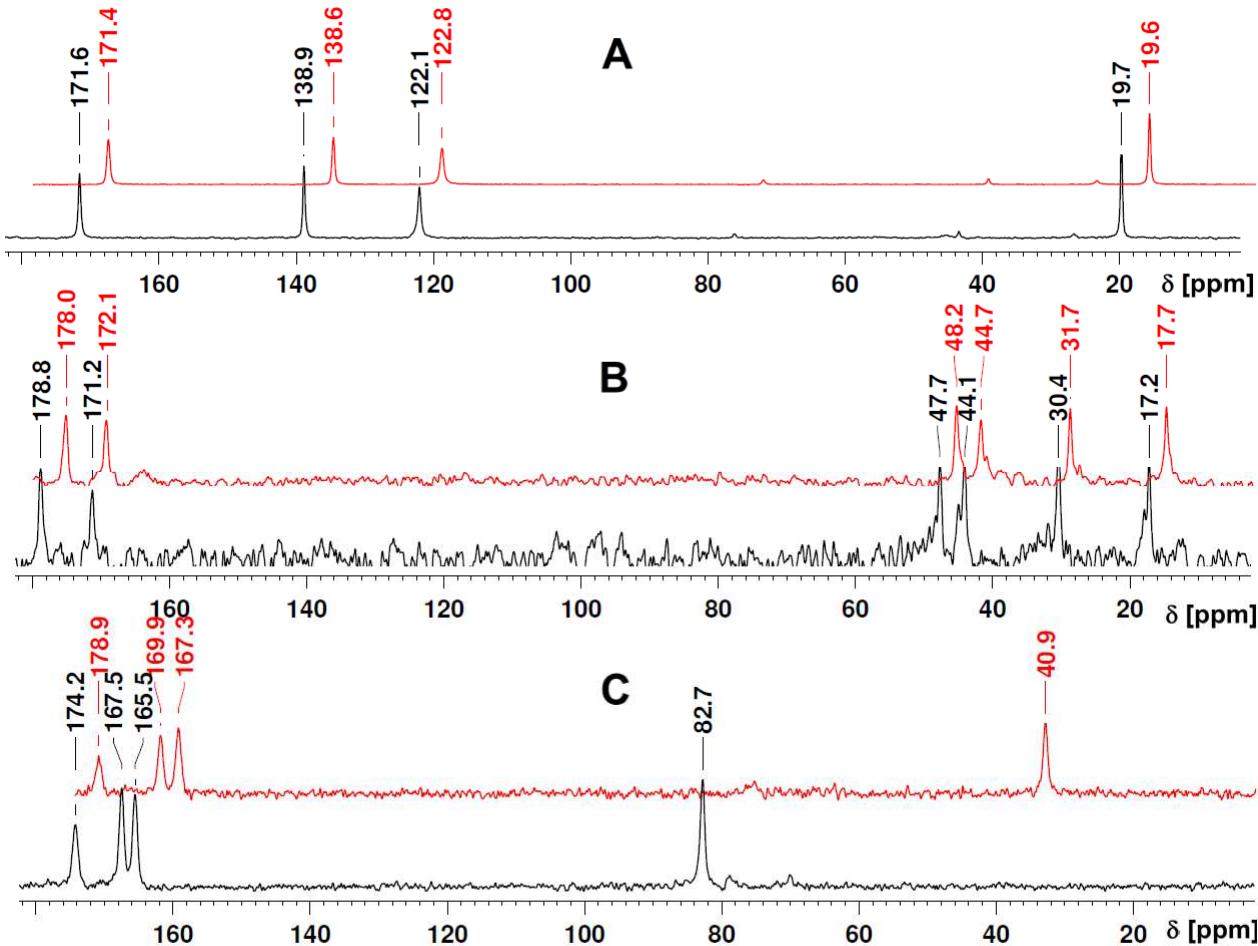
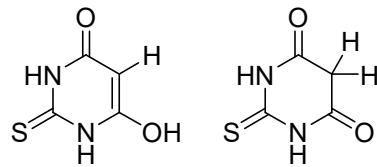
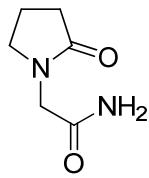
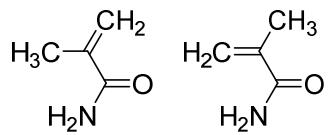
Repetition time shortening

# Nonequivalent molecules in asymmetric unit

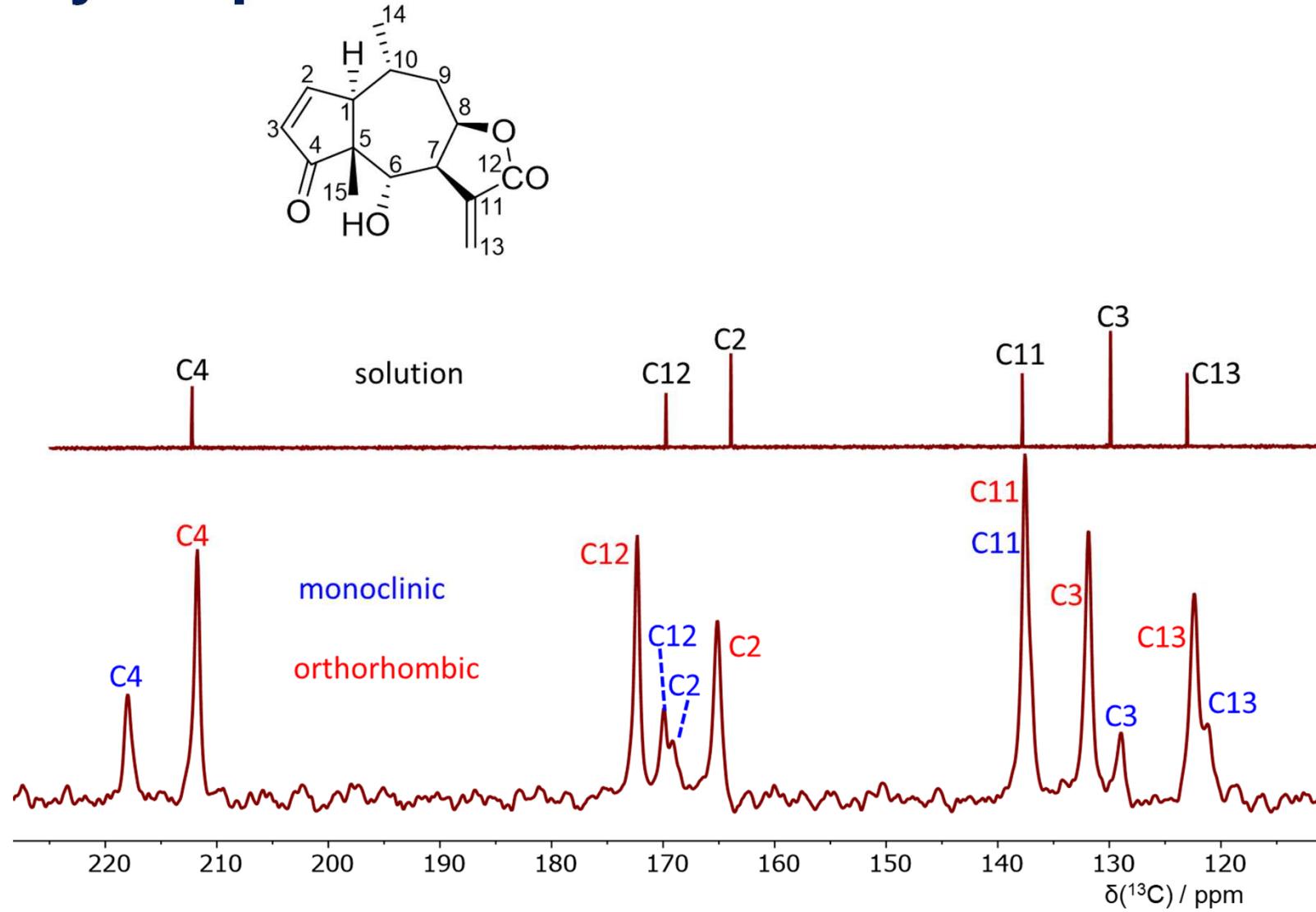
( $Z' = 2$ )



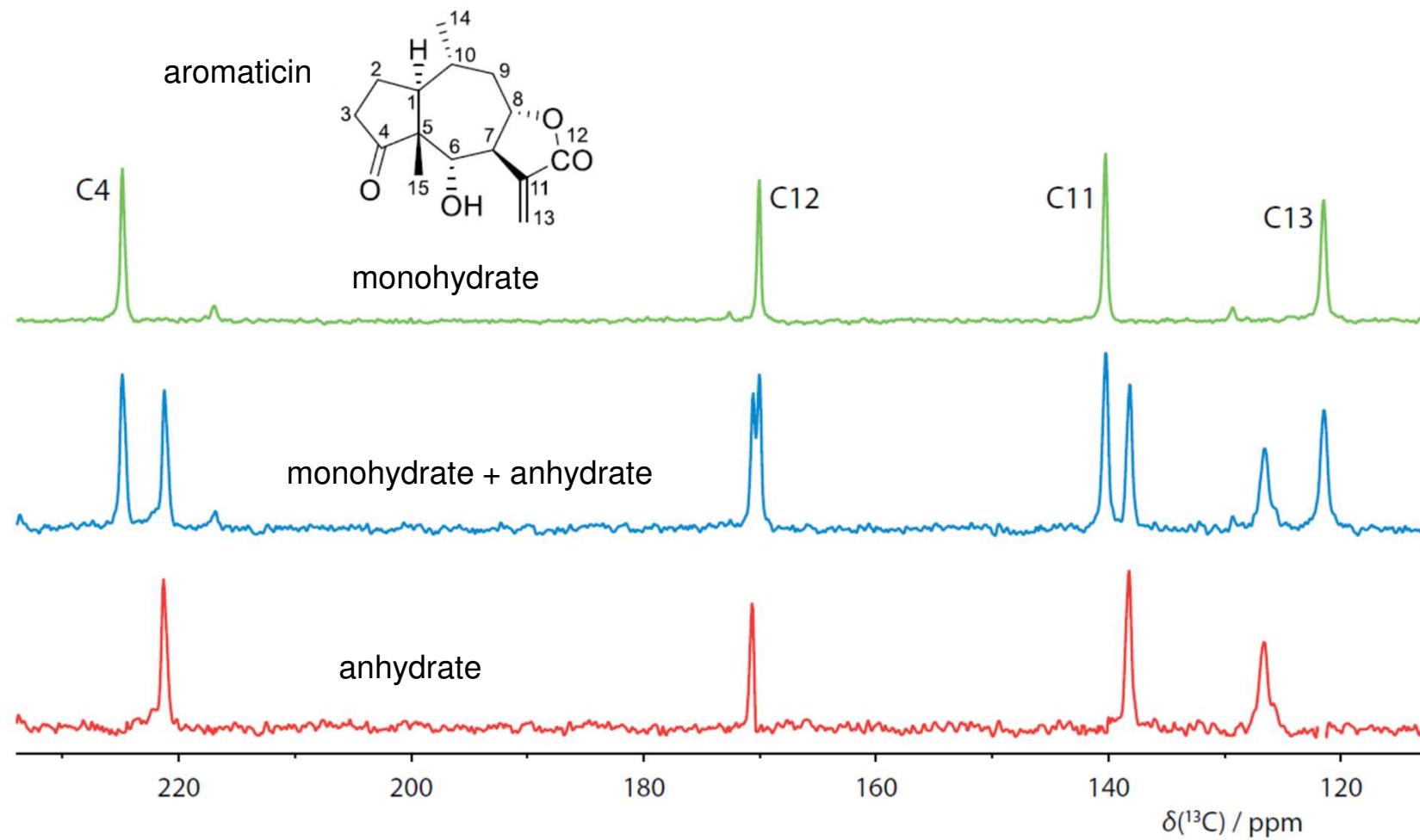
# Polymorphism



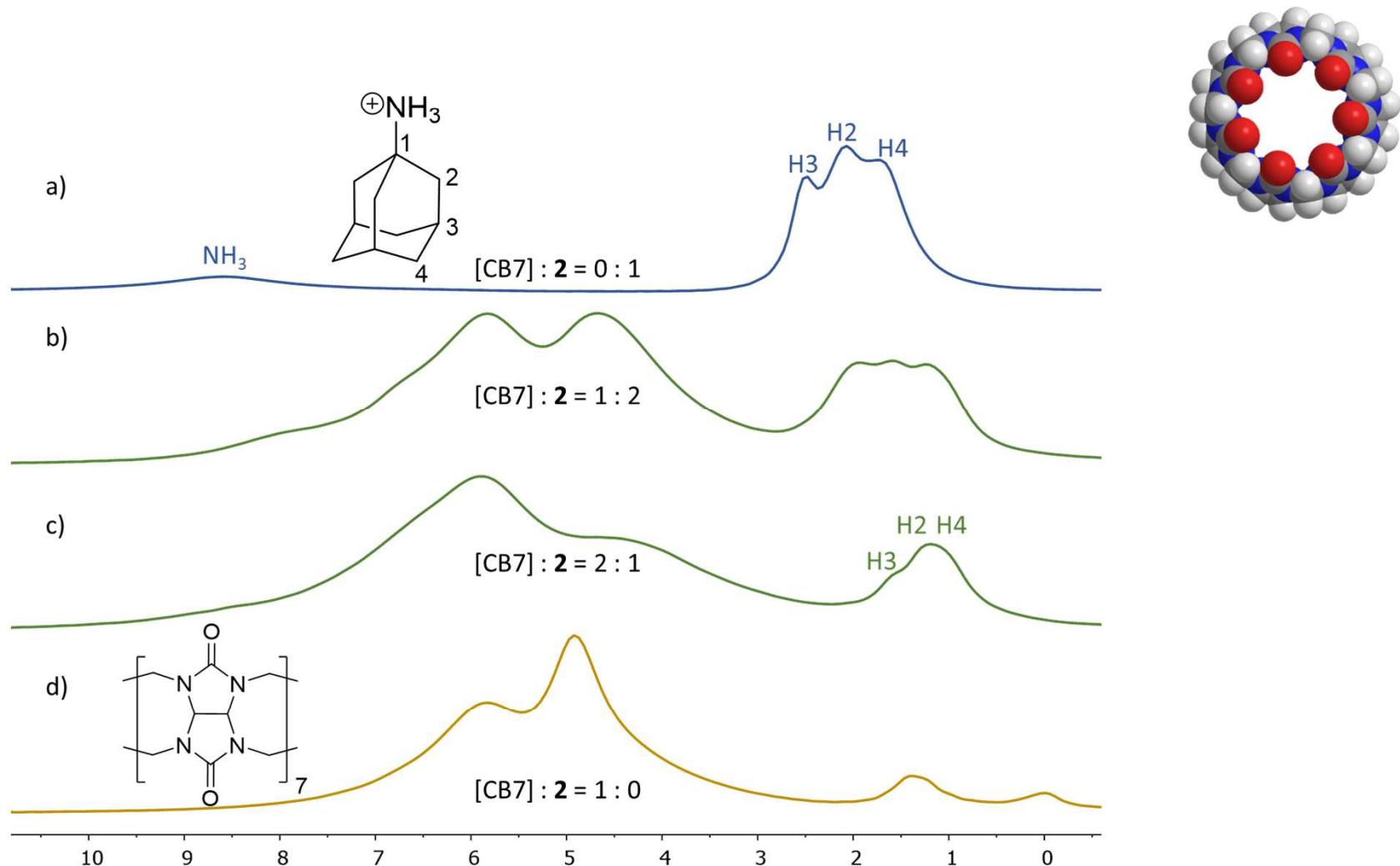
# Polymorphism



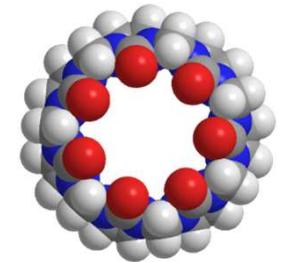
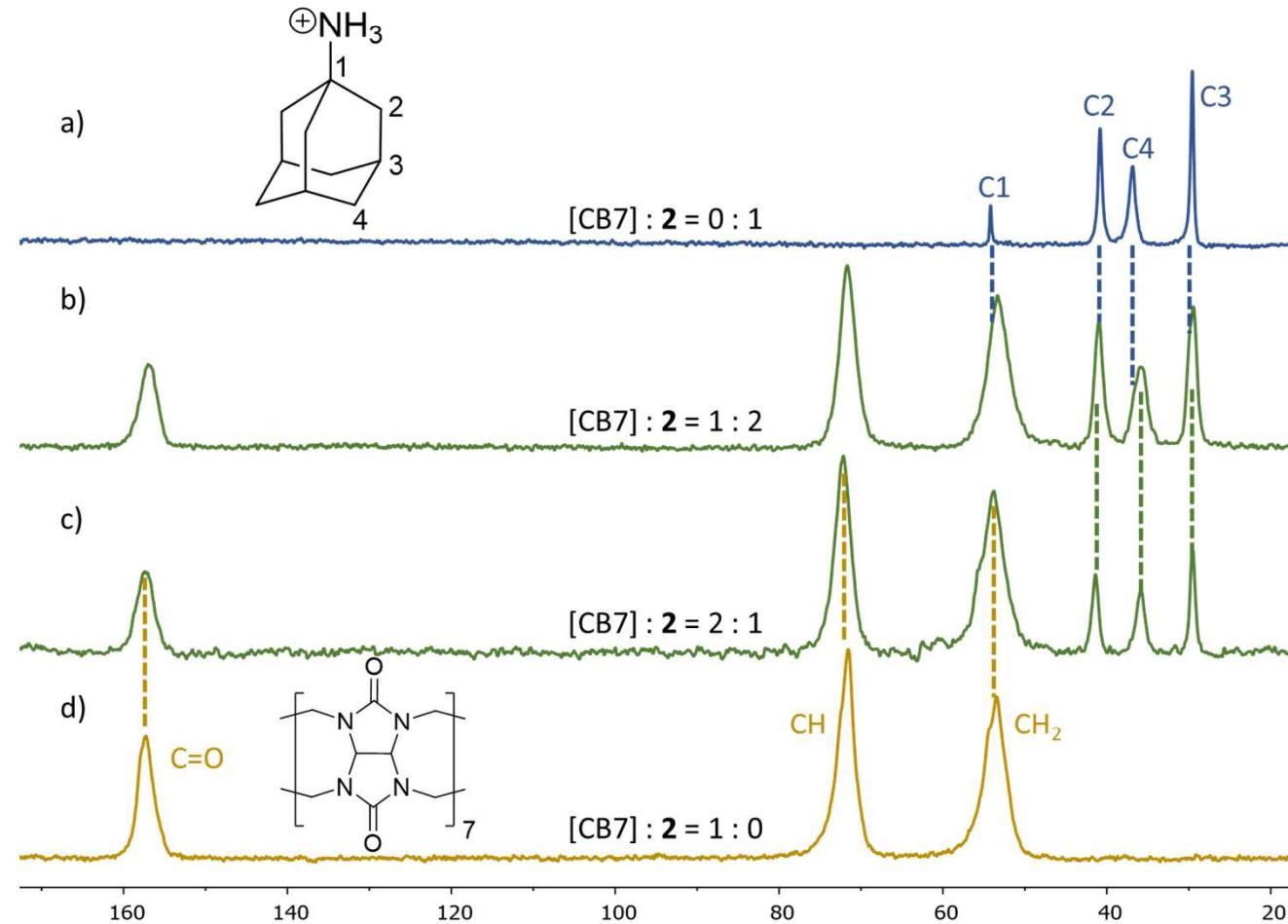
# Polymorphism



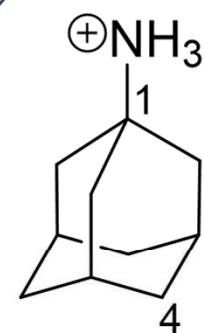
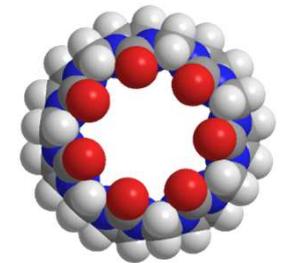
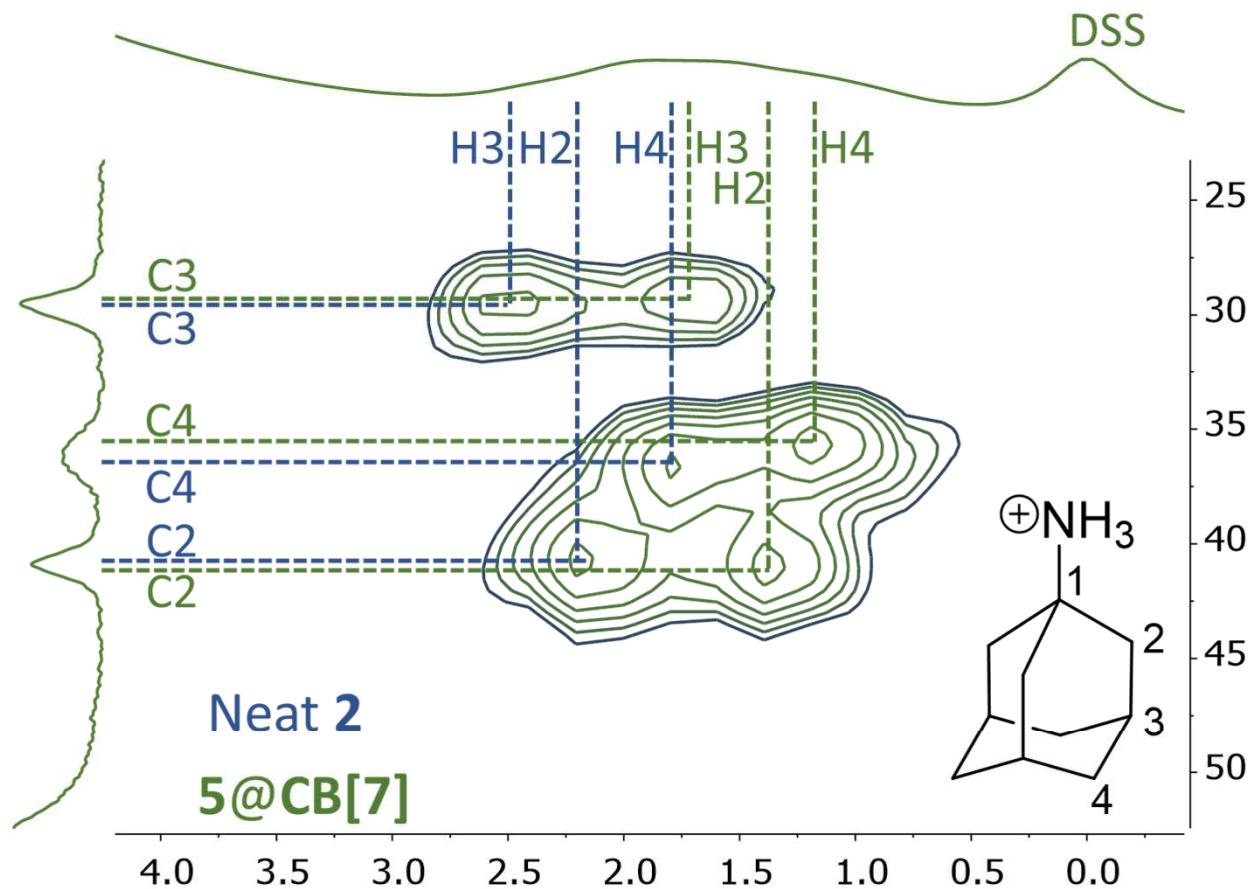
# Host-Guest Complexes with Cucurbit[7]uril



# Host-Guest Complexes with Cucurbit[7]uril



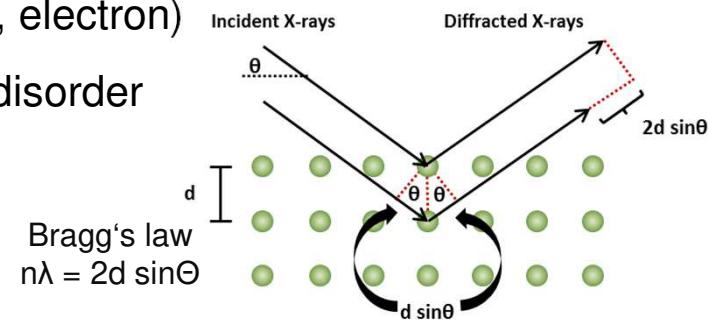
# Host-Guest Complexes with Cucurbit[7]uril



# NMR crystallography

Crystallography: diffraction experiments (X-ray, neutron, electron)

X-ray crystallography – weaknesses: hydrogen atoms, disorder

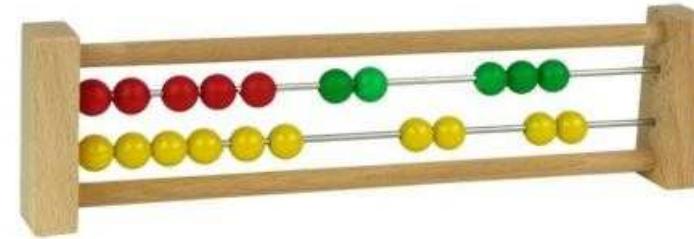
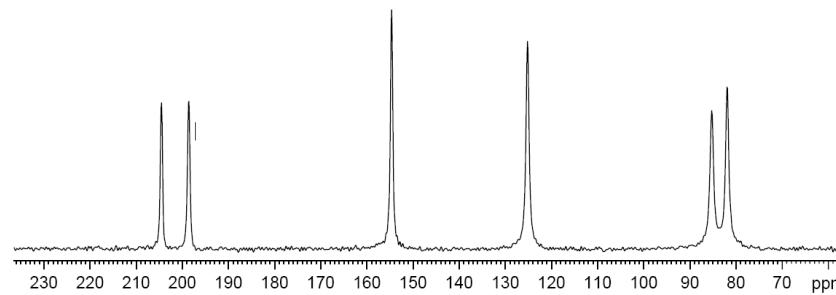


NMR spectroscopy – solution, solid

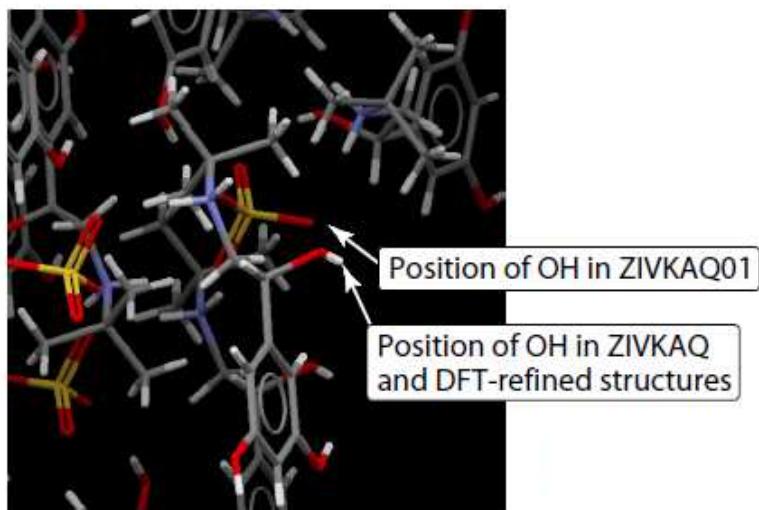
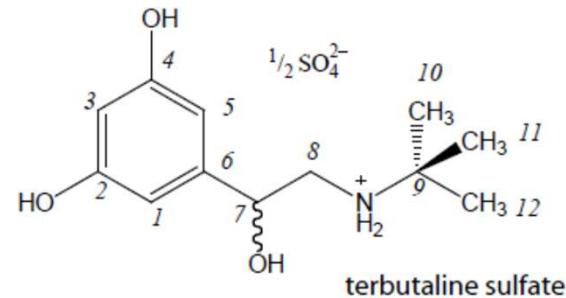
– strengths: hydrogen atoms, local information, dynamics

NMR crystallography:

Solid-state NMR spectroscopy + quantum-chemical calculations



# Correcting diffraction structures



<sup>13</sup>C NMR shows clearly that H is incorrectly positioned in ZIVKAQ01

Harris et al. *Magn. Reson. Chem.* **2010**, *48*, S103.

