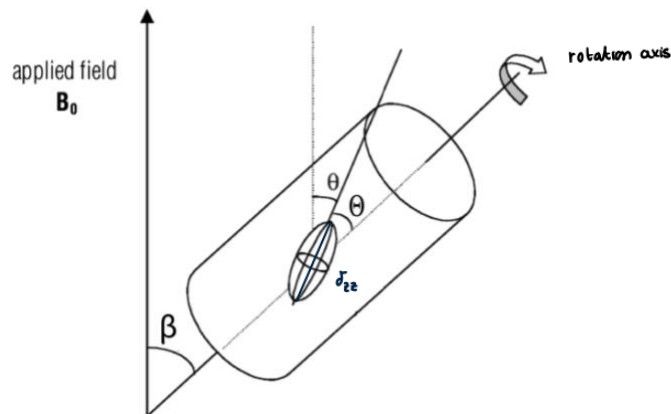


Jigsaw 5D

Solid-State NMR

1. [Week 4 Slides 13–43] The diagram shows the schematic sample setup for a magic-angle spinning experiment.



- a. Define the angles β , θ and Θ .

β = magic angle = angle between B_0 and the rotation axis

θ = angle between B_0 and σ_{zz}

Θ = angle between σ_{zz} and rotation axis

- b. Name three interactions which are averaged or partially averaged by sample spinning.

1) Dipolar coupling between nuclear spins

2) Quadrupolar interactions

3) Anisotropic part of chemical shift

- c. For a nucleus with a chemical shielding tensor with axial symmetry, we can write the chemical shift as the sum of isotropic and anisotropic terms:

$$\delta = \delta_{iso} + \underbrace{(\delta_{zz} - \delta_{iso}) \left(\frac{3 \cos^2 \beta - 1}{2} \right)}_{\text{anisotropic part}}$$

For which angle β is the anisotropic part 0?

$$\frac{3 \cos^2 \beta - 1}{2} = 0$$

$$3 \cos^2 \beta - 1 = 0$$

$$\cos^2 \beta = \frac{1}{3}$$

$$\cos \beta = \frac{1}{\sqrt{3}}$$

$$\beta = \cos^{-1} \left(\frac{1}{\sqrt{3}} \right) = 54,74^\circ \Rightarrow \text{magic angle}$$

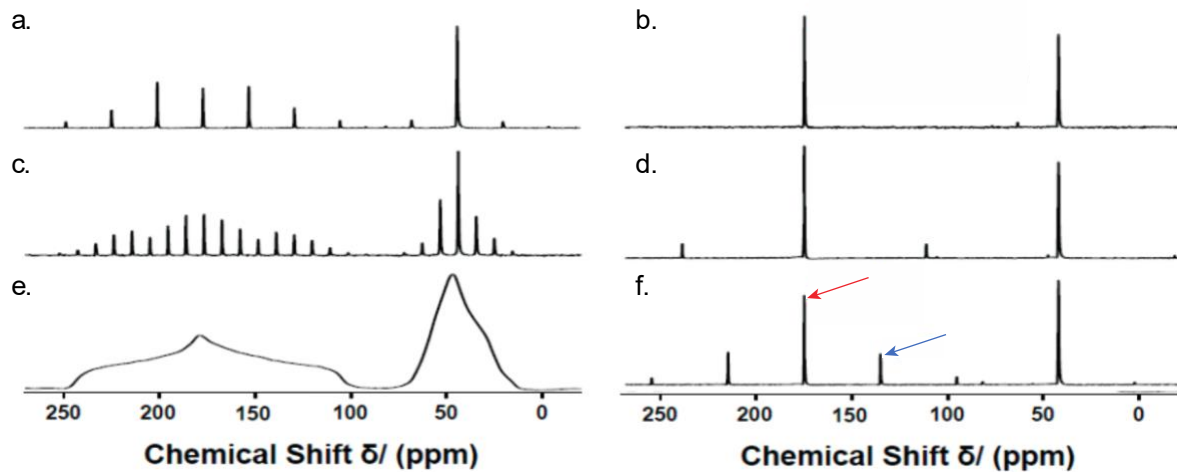
- d. What is the effect of spinning the sample around an axis oriented at $\beta = 90^\circ$?

$$\bar{\sigma} = \sigma_{iso} + (\sigma_{zz} - \sigma_{iso}) \left(\frac{3 \cos^2(90^\circ) - 1}{2} \right) \quad \cos(90^\circ) = 0$$

$$\bar{\sigma} = \sigma_{iso} - \frac{1}{2} \sigma_{zz} + \frac{1}{2} \sigma_{iso} = \frac{3}{2} \sigma_{iso} - \frac{1}{2} \sigma_{zz}$$

\Downarrow
 the anisotropic part is changed by $-\frac{1}{2}$

2. Here are six solid-state NMR spectra of the same sample recorded at different MAS spinning rates: 0kHz (static), 1kHz, 3kHz, 5kHz, 8kHz and 14kHz.



- i. Which spectrum corresponds to each spinning rate?

a) 3 kHz b) 14 kHz
 c) 1 kHz d) 8 kHz
 e) 0 kHz f) 5 kHz

- ii. The red arrow indicates the isotropic shift, but what does the second arrow correspond to?

It corresponds to a spinning side band as spinning doesn't perfectly eliminate all anisotropic effects

- iii. What does the spacing between the peaks in part (ii) depend on?

*It depends on the spinning speed [higher speed \Rightarrow larger spacing
 lower speed \Rightarrow smaller spacing
 side bands are spaced at integer multiples of the spinning frequency .*

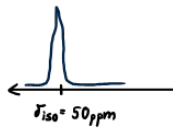
3. [From past exam] Consider the principal values for the following ^{13}C chemical shift anisotropy (CSA) tensors:

- a. $\delta_{11} = \delta_{22} = \delta_{33} = 50$ ppm
 b. $\delta_{11} = 30$ ppm, $\delta_{22} = 10$ ppm, $\delta_{33} = 0$ ppm

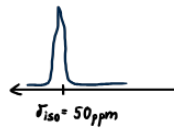
Sketch the powder pattern of the ^{13}C spectra for **both static and Magic Angle Spinning (MAS)** conditions for each CSA tensor. Of the two static spectra, which has a larger value of span (Ω)?

$$\delta_{iso} = \frac{\delta_{11} + \delta_{22} + \delta_{33}}{3}$$

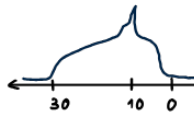
a) static



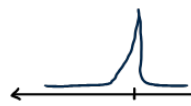
MAS



b) static



MAS



$$\delta_{iso} = \frac{30 + 10 + 0}{3} = 13,3 \text{ ppm}$$

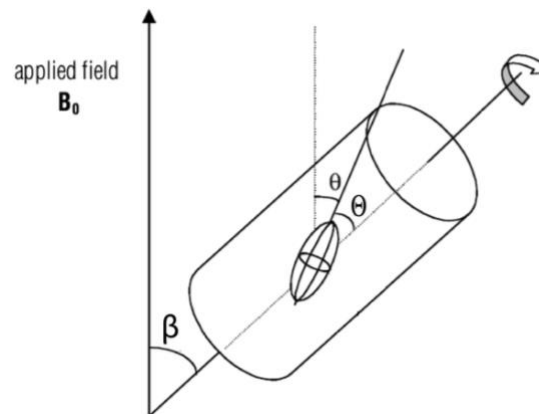
↓

larger span

Jigsaw 5D

Solid-State NMR

1. [Week 4 Slides 13–43] The diagram shows the schematic sample setup for a magic-angle spinning experiment.



- a. Define the angles β , θ and Θ .

β : angle along the spinning axis that appears when spinning the sample / angle between the spinning axis of the rotor and the external magnetic field B_0 .

θ : angle between the rotor axis and a molecular principal axis or interaction tensor.

Θ : angle between the molecular tensor axis and the external magnetic field B_0 .

- b. Name three interactions which are averaged or partially averaged by sample spinning.

1. Chemical Shift Anisotropy (CSA): Under MAS of angle $54,7^\circ$ the anisotropic part of the chemical shift is averaged to its isotropic value.
 2. Dipolar Coupling: heteronuclear and homonuclear dipolar interactions. MAS averages the orientation-dependant dipolar term.
↳ high MAS speeds are effective for suppressing strong ^1H - ^1H couplings.
 3. Quadrupolar Interactions: MAS averages the 1st order quadrupolar interaction. However, the 2nd order term is only partially averaged, not fully removed.
- c. For a nucleus with a chemical shielding tensor with axial symmetry, we can write the chemical shift as the sum of isotropic and anisotropic terms:

$$\delta = \delta_{iso} + (\delta_{zz} - \delta_{iso}) \left(\frac{3 \cos^2 \beta - 1}{2} \right)$$

For which angle β is the anisotropic part 0?

$$3 \cos^2 \beta - 1 = 0 \Rightarrow \cos^2 \beta = \frac{1}{3}$$

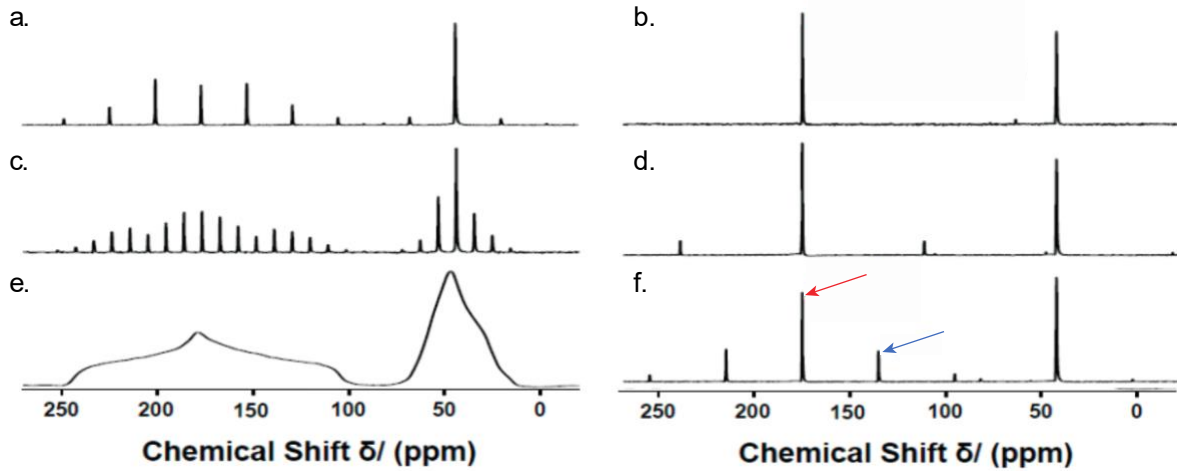
$$\hookrightarrow \beta = \arccos \left(\sqrt{\frac{1}{3}} \right) = 54,74^\circ$$

- d. What is the effect of spinning the sample around an axis oriented at $\beta = 90^\circ$?

At $\beta = 90$, $\cos \beta = 0$, so we will have an anisotropic factor of $-\frac{1}{2} \Rightarrow \delta = \delta_{iso} - \frac{1}{2} (\delta_{zz} - \delta_{iso})$

→ Answered on last page

2. Here are six solid-state NMR spectra of the same sample recorded at different MAS spinning rates: 0kHz (static), 1kHz, 3kHz, 5kHz, 8kHz and 14kHz.



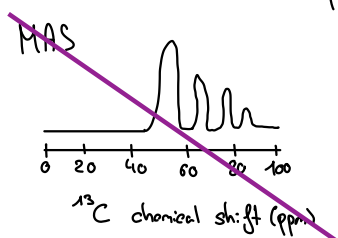
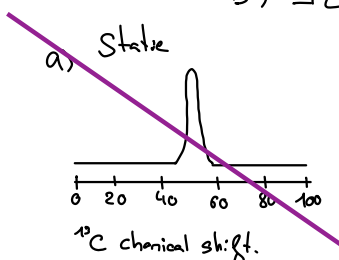
- i. Which spectrum corresponds to each spinning rate?
- ii. The red arrow indicates the isotropic shift, but what does the second arrow correspond to?
- iii. What does the spacing between the peaks in part (ii) depend on?

3. [From past exam] Consider the principal values for the following ^{13}C chemical shift anisotropy (CSA) tensors:

- a. $\delta_{11} = \delta_{22} = \delta_{33} = 50$ ppm
- b. $\delta_{11} = 30$ ppm, $\delta_{22} = 10$ ppm, $\delta_{33} = 0$ ppm

Sketch the powder pattern of the ^{13}C spectra for **both static and Magic Angle Spinning (MAS)** conditions for each CSA tensor. Of the two static spectra, which has a larger value of span (Ω)?

• Span (Ω):
 a) $\Omega = \delta_{11} - \delta_{33} = 50 - 50 = 0$ ppm
 b) $\Omega = \delta_{11} - \delta_{33} = 30 - 0 = 30$ ppm
 } Spectre b) as a bigger span.



Should have four plots.... see other group's answers - for MAS spectra we only see one peak at the isotropic chemical shift; for the static spectrum of b, we would see a broader spectrum with a distinctive "powder pattern"

Question 2:

- (i)
- a: 3 kHz \rightarrow fewer sidebands, more separated
 - b: 14 kHz \rightarrow essentially only the isotropic peaks left (fast MAS)
 - c: 1 kHz \rightarrow lots of very closely-spaced sidebands, still looks almost like the static pattern
 - d: 8 kHz \rightarrow mainly isotropic peaks, only weak sidebands
 - e: 0 kHz (static) \rightarrow broad powder pattern, no MAS sidebands
 - f: 5 kHz \rightarrow clear isotropic peaks with several sidebands
- (ii) The blue arrow points to a MAS spinning sideband of that resonance, produced by chemical-shift anisotropy under MAS
- (iii) The spacing between the sidebands is equal to the MAS spinning (the rotor speed). In other words, sidebands are separated by ν_r (in Hz), so their spacing depends on the MAS rate.