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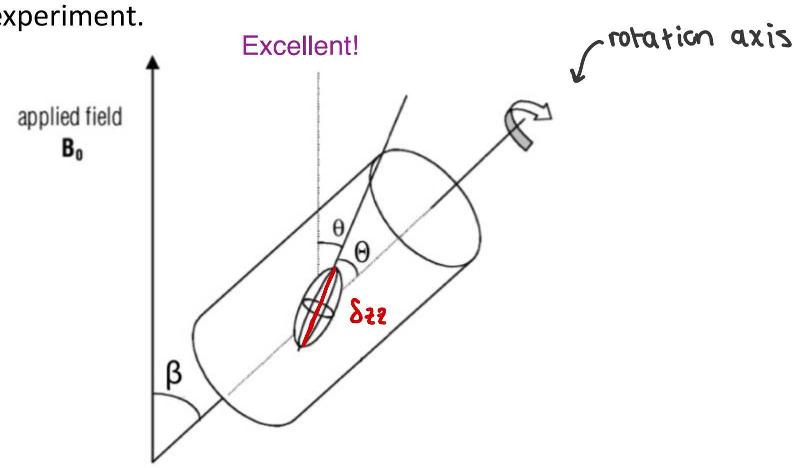
Jigsaw 5D

1. [Week 4 Slides 47-50] The diagram shows the schematic sample setup for a magic-angle spinning experiment.

Excellent!



a. Define the angles β, θ and Θ.

β: angle between Bo and the rotation axis → magic angle
θ: angle between Bo and δzz
Θ: angle between δzz and rotation axis

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

- dipolar coupling between nuclear spins
- quadrupolar interactions
- anisotropic part of chemical shift

↳ Zeeman effect, scalar coupling and isotropic part of chem shift stay the same

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 does the anisotropic part average to 0?

$$\Rightarrow \left(\frac{3\cos^2\beta - 1}{2}\right) = 0 \Rightarrow 3\cos^2\beta - 1 = 0$$

$$\cos^2\beta = 1/3$$

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

$$\Rightarrow \beta = \cos^{-1}\left(\sqrt{1/3}\right)$$

$$\beta = 54.74°$$

d. What is the effect of spinning at β = 90°?

$$\delta = \delta_{iso} + (\delta_{zz} - \delta_{iso})\left(\frac{\overbrace{3\cos^2(90)}^{=0} - 1}{2}\right)$$

$$\delta = \delta_{iso} - \tfrac{1}{2}\delta_{zz} + \tfrac{1}{2}\delta_{iso}$$

$$\delta = \tfrac{3}{2}\delta_{iso} - \tfrac{1}{2}\delta_{zz}$$

⟶ the anisotropic part is changed by 1/2 conversion: $\delta v = 1\,ppm = 400\,Hz$

2. [From Past Exam] [Keeler Section 9.8] The rate constant (in s^{-1}) for a symmetrical two-site exchange has the temperature dependence $k = 10^{13}\exp[-2500/T]$. The rate constant in Hz for which the two peaks merge together is $k_{merge} = \frac{\pi \delta v}{\sqrt{2}}$, where δv is the chemical shift difference in Hz. Consider a chemical shift difference of 1.0 ppm. Determine the number of peaks in the 400 MHz spectra at the following temperatures:

$$k_{merge} = \frac{\pi \delta v}{\sqrt{2}} = \frac{\pi \cdot 400}{\sqrt{2}} = 888.58\ Hz$$

a. 98 K

$$k(98K) = 10^{13} \exp(-2500/98) = 83.38\ Hz < k_{merge}$$

We observe only 1 peak when $k(T) > k_{merge}$

For T = 98 K we observe 2 peaks

b. 108 K

$$k(108) = 10^{3} \exp(-2500/108) = 884.89\ Hz < k_{merge}$$

For T = 108 K we observe 2 peaks

But k(108) and kmerge are close which means that this 2 peaks are starting to overlap

c. 150 K

$$k(150) = 10^{3} \exp(-2500/150) = 577\,774.85\ Hz > k_{merge}$$

For T = 150 K we observe 1 peak

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Nice work!

CH-314 Structural Analysis
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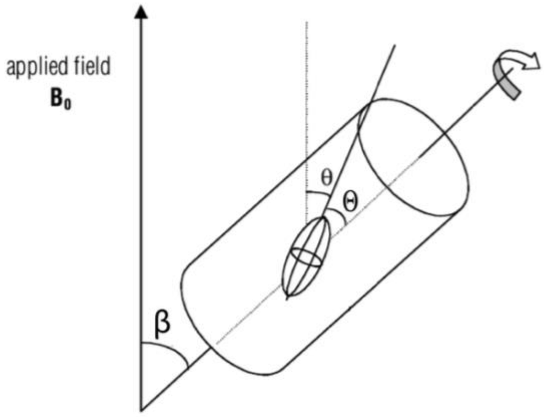
Jigsaw 5D

1. [Week 4 Slides 47-50] The diagram shows the schematic sample setup for a magic-angle spinning experiment.



   a. Define the angles β, θ and Θ.

   β = magic angle spinning
   θ = angle BTW δ_{zz} axis and magnetic field
   Θ = angle BTW δ_{zz} and magic angle spinning.

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

   be more specific:
   1. anisotropic interactions
   2. dipole - dipole coupling (dipolar couplings depend on orientation)
   3. quadruple coupling, for chemicals with spin quantum number > 1/2

   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:

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

   anisotropic

   For which angle β does the anisotropic part average to 0?

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

$$\Leftrightarrow 3\cos^2\beta = 1 \Leftrightarrow \cos\beta = \pm\frac{1}{\sqrt{3}} \Leftrightarrow \begin{cases} \beta = 0{,}96 \text{ rad} \\ \beta = 2.19 \text{ rad} \end{cases}$$

   = 54.74° (the "magic angle")

   d. What is the effect of spinning at β = 90°?

$$\delta = \frac{3}{2}\delta_{iso} - \frac{\delta_{zz}}{2}$$

   the chemical shift δ will be shifted by $+\frac{3}{2}\delta_{iso}$ and $-\frac{1}{2}\delta_{zz}$

2. [From Past Exam] [Keeler Section 9.8] The rate constant (in s^{-1}) for a symmetrical two-site exchange has the temperature dependence $k = 10^{13}\exp[-2500/T]$. The rate constant in Hz for which the two peaks merge together is $k_{merge} = \frac{\pi\delta\nu}{\sqrt{2}}$, where δv is the chemical shift difference in Hz. Consider a chemical shift difference of 1.0 ppm. Determine the number of peaks in the 400 MHz spectra at the following temperatures:

a. 98 K $k = 84.4$
$k_{merge} = 888$ Hz } $k < k_{merge}$ <=> 2 peaks

b. 108 K $k = 884.9 \longrightarrow k < k_{merge}$ 2 peaks

Very close to k_merge, so you would see two peaks in the process of merging

c. 150 K $k = 5.8 \cdot 10^5 \longrightarrow k > k_{merge}$ 1 peak.