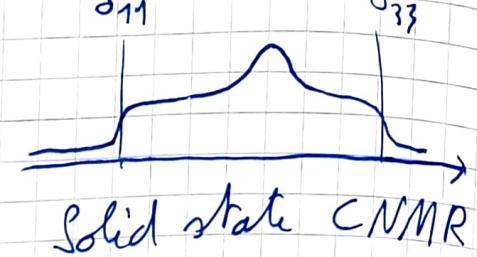
Jigsaw 5A



Solid state CNMR

Good! 2/2

1.) a.), b.) Span(Ω): $\Omega = \delta_{11} - \delta_{33} \geq 0$

↑ ↑

2 of the chemical shift principal values

→ Its the anisotropy of the molecule. Its the max. width of the system. ↳ How dif. the shielding is in dif. directions

Skew(κ): $\kappa = 3(\delta_{22} - \delta_{iso})/\Omega$ where $\delta_{iso} = \frac{\delta_{11} + \delta_{22} + \delta_{33}}{3}$

↳ How far from axial symetry

$-1 < \kappa < 1$

→ It is the asymetry parameter, how symetric the spectra is

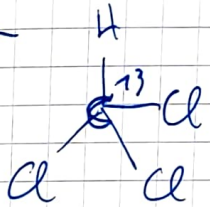
c.) i High axial symetry

Prolate

Ω is medium sized

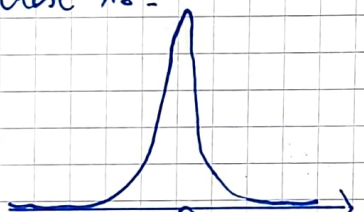
κ = medium → close to ±1

Sign depends on the molecule



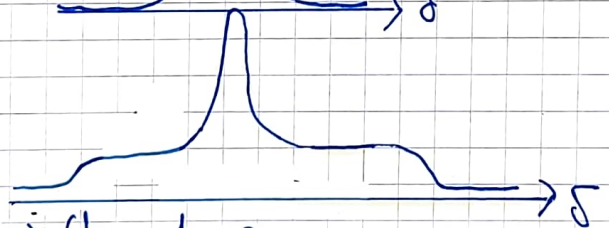
ii. Ω is small

$\kappa = 0$

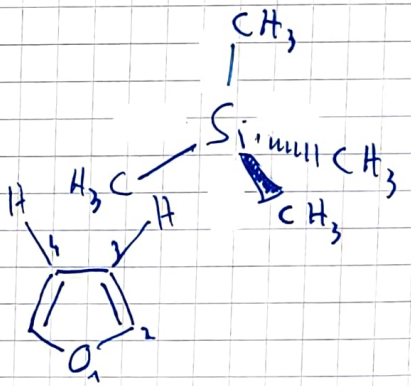


iii. Ω is big

κ = small



→ close to 0



2.) The spray-dried tablets show a ^{1}HNMR spectrum of an amorphous sample since the peakes are very broad and round. This is due to the many different magnitudes of interactions causing various different but similar chemical shifts. The tablet lactose is the one required for the experiment as its in crystaline form. This can be seen from the sharp and narrow peakes.

CH-314 Structural Analysis
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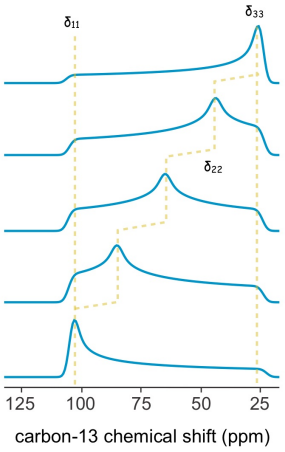
Jigsaw 5A

1.75/2

1. [Week 4 Slides 38-41] Two useful parameters in static solid-state NMR are the span, Ω, and skew, κ.



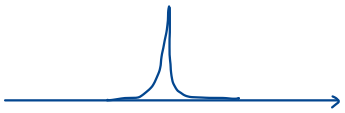
a. What do Ω and κ represent? I.e., what information do they tell you about the molecule?
Ω represents the measurement of overall extent of anisotropy and κ is the measurement of the deviation from axial symmetry.

b. How can we determine Ω and κ from a static spectrum?
By those formulas: $\Omega = \delta_{11} - \delta_{33}$
$\kappa = 3(\delta_{22} - \delta_{iso})/\Omega$ with $\delta_{iso} = \frac{\delta_{11}+\delta_{22}+\delta_{33}}{3}$

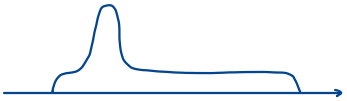
c. For the specified nucleus of each of the following molecules, predict the values of Ω and κ and draw the expected powder pattern. For Ω, you do not need to give a precise value, just a qualitative estimate (small, moderate, large). Assume the samples are all in a solid powder and measured in static conditions.

i. The ^{13}C in chloroform
Ω = large
κ = 1 because it's an oblate

ii. The ^{29}Si in tetramethylsilane
Ω ≈ 0
κ ≈ 0

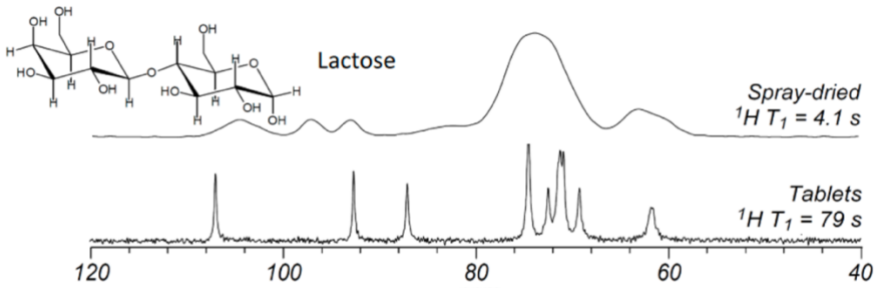


iii. The 3,4 protons in furan
asymmetric environment
Ω = large
κ ≈ 1/0 because it's a prolate



2/2

2. Solid-state NMR can be useful to determine if a sample is amorphous or crystalline. Imagine you need to buy lactose for your experiments, but you need it to be crystalline. A laboratory offers two types of lactose: spray-dried and in tablets, the spectra of which you can see below. Which of these two is appropriate for your experiments and why?



Amorpheous state → badly resolved because the molecules are in random orientations.

Cristalline state → resolved because the number of orientations is limited, which implies a limited number of interactions with the magnetic field.

We actually have many orientations, and the sum of all orientationsis observed leading to broadening due to CSA. However, this broadening can be averaged by spinning the sample at MAS.

=> The tablets is appropriate because it is crystalline.