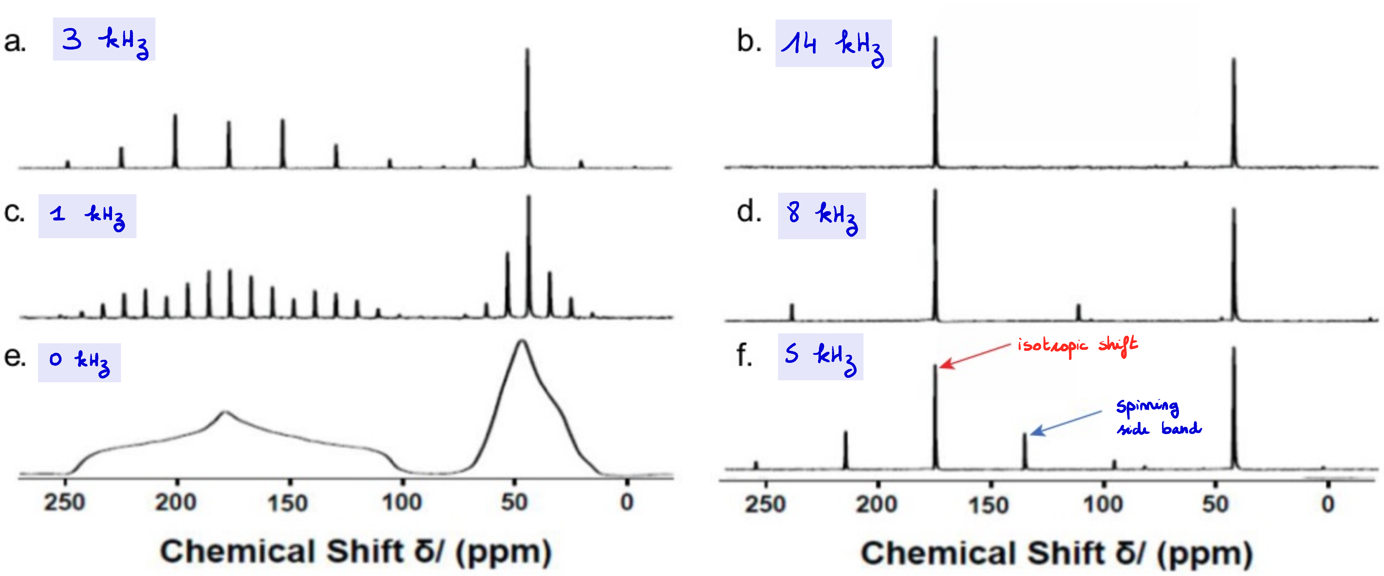
Great job!

25/11/2024

Jigsaw 5E

1. * 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?

In solid-state NMR, the chemical shift of a nucleus varies depending on the orientation of the molecule with respect to the magnetic field.

- Static sample (0 kHz): since the sample is not spinning, multiple orientations of the molecule in the sample lead to multiple chemical shifts for the same nucleus. These shifts get combined as a broad complex signal.
- Increase of spinning rate: when the sample spins, the different orientations of the molecule with respect to the magnetic field are averaged out. This averaging effect leads to narrower, sharper and fewer peaks.

Increased spinning speed pushes sidebands further away from the isotropic chemical shift, increasing the intensity of the isotropic peak

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

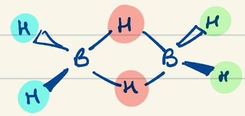
Spinning side bands are additional peaks that appear around the main isotropic peak.
They appear because the spinning does not perfectly eliminate all anisotropic effects.
The sidebands can be found symmetrically around central (isotropic) peak.

Not always symmetric, depends on the shape of the powder pattern

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

The spacing between the peaks depends on the spinning speed.
The sidebands are spaced at integer multiples of the spinning frequency: a lower spinning speed results in smaller spacing while a higher spinning speed results in larger spacing between the sidebands.

Exercice 2:



Good! Make sure to state that the J-couplings to all other spins in the system are equivalent

a) Both bridging H (here in red) atoms are equivalently related to each nucleus of the molecule.
=> they are magnetically independent

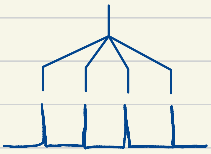
By taking a pair of H which are not attached to the same B atom, they are chemically equivalent but not magnetically equivalent

By taking a pair of H which are attached to the same B atom, they are magnetically equivalent.

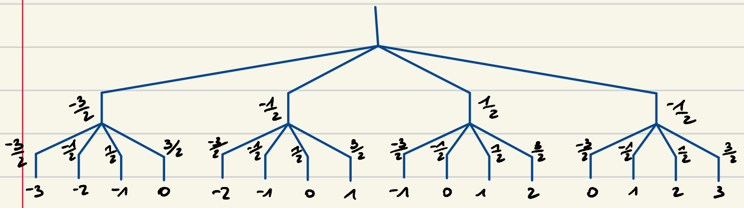
By comparing the bridging hydrogen and the extrem hydrogen, they are not chemically and not magnetically equivalent.

b) for the terminal proton, the majoritory J coupling is with the B atom they are directly bonded to. B has a spin of $\frac{3}{2}$, so it has $2J+1 = 4$ spin states.

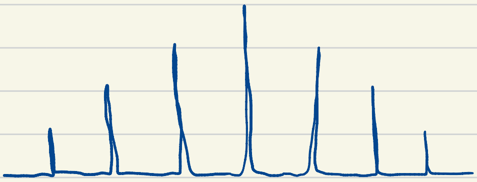
The spectra of the proton will look like:



For the bridging H, we used the same concept, but they are bridging to two B atoms. So we can do the tree method to find the number and intensity of the peak:



Which gives us the following spectra:



NMR Jigsaw 5E

October 2024

1 Exercise 1

1.1

We assign spectra using the following logic:

- 0 khz is e: static, null spinning rate gives us a continuous chemical shift sampling
- 1 khz is c: slightly faster spinning but still slower than other values, giving us a higher resolution rate
- We proceed w/ similar logic iteratively to deduce that the remaining are, in order: 3:A
- 5: F
- 8: D
- 14: B

1.2

The blue arrow corresponds to a shift that is no longer fully isotropic due to the MAS effect: it is what's called a MAS sideband.

1.3

The spacing between the peaks will depend on the exact value of the Magic Angle spinning rate.

2 Exercise 2

2.1

The bridging protons are chemically equivalent as they have identical chemical shifts, and are symmetric w.r.t to the two borons: thus they are also magnetically equivalent.
Each pair of terminal protons, are symmetric relative to the boron atom that the are attached to, meaning that they have both identical chemical shifts and J-couplings: they are thus magnetically equivalent. Note however that the protons from one pair aren't magnetically equivalent to the protons from another.

2.2

The terminal protons are linked to one boron atom each, so they exhibit a quartets structure since boron has a spin of $I = 3/2$ (thus 4 states)
The bridging protons are linked to 2 Boron atoms at once: so they exhibit a double quartet structure. Note also that the fact that they're connected to two Boron atoms means that they are more strongly shielded, hence giving them a weaker chemical shift. Relative intensity of the peaks is 4:2, or 2:1, since there's two briding protons andd 4 terminal ones.
A model of the PPM intensities of the NMR spectrum can be found in Hore:

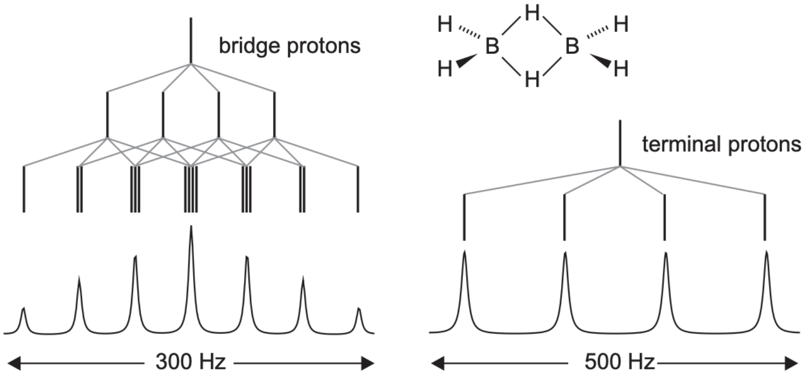
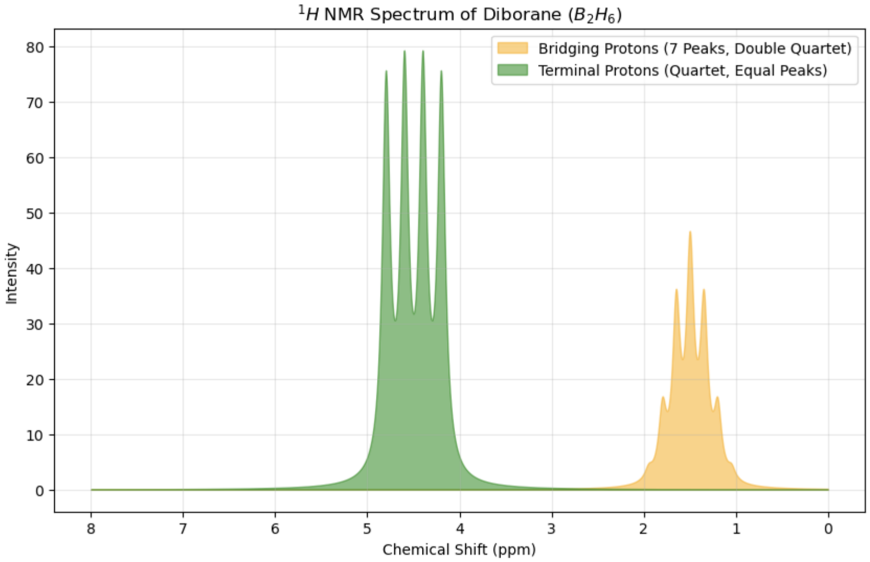


Fig. 3.8 ^{1}H NMR spectra of the terminal and bridge protons in diborane, $^{11}B_2H_6$.

We model all the information found above into a single graph below:


^1H NMR Spectrum of Diborane (B_2H_6)
Bridging Protons (7 Peaks, Double Quartet)
Terminal Protons (Quartet, Equal Peaks)
Intensity
80
70
60
50
40
30
20
10
0
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)