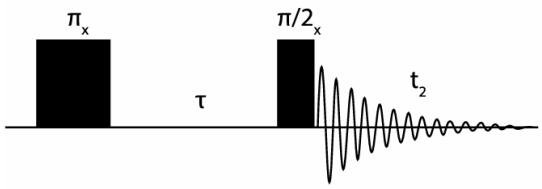
JIGSAW 2B

October 14 2024

Question 1

1. * [Keeler Section 9.5] The pulse sequence of the inversion recovery experiment is shown below.



   a. Use the vector model to explain what happens in a spectrum observed in t_2 when the delay τ, in the pulse sequence, is varied.

   b. Draw the expected signal intensity during t_2 as a function of τ.

   c. What kind of information can be extracted from a series of experiments with different τ?

a) The magnetization start at equilibrium on the z axis, then a π_x rotation is applied, aligning the vector on the $-z$ axis. During the time τ, the vector returns slowly to equilibrium (that is, goes back to z orientation). This changes the norm of the vector depending on τ. This vector norm can be measured by performing a $\frac{\pi}{2}_x$ rotation, which aligns the vectors on the y axis, as seen on the following figure.

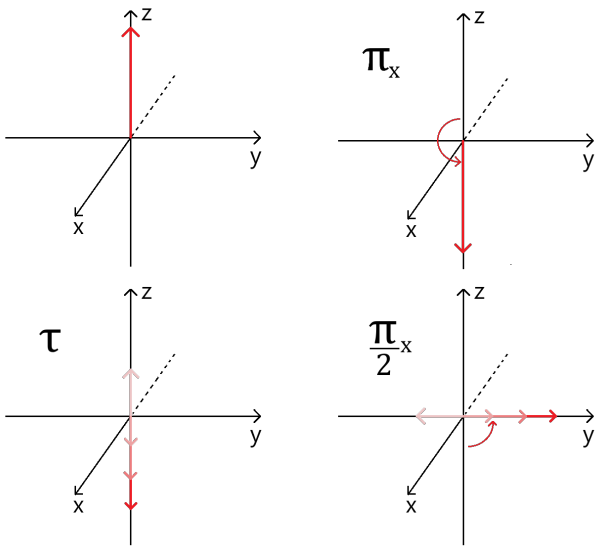


Figure 1: Vector model

b) As we can see on the previous figure, the vector length, and so the signal strength, depends on the delay time τ. By convention the signal is negative if the vector is aligned on the y axis. The signal observed as a function of τ will look as such :

Great! Note that the initial recovery is fairly quick

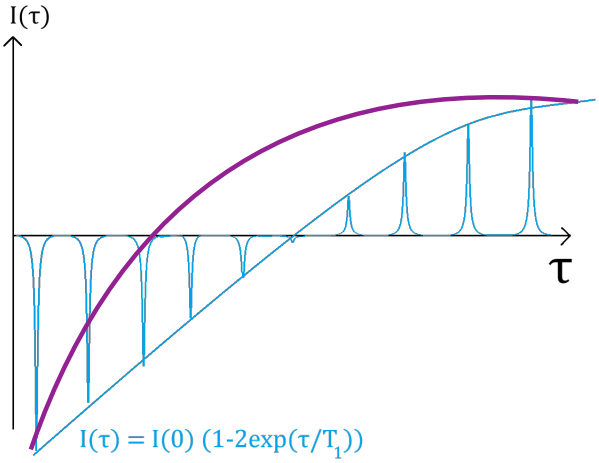
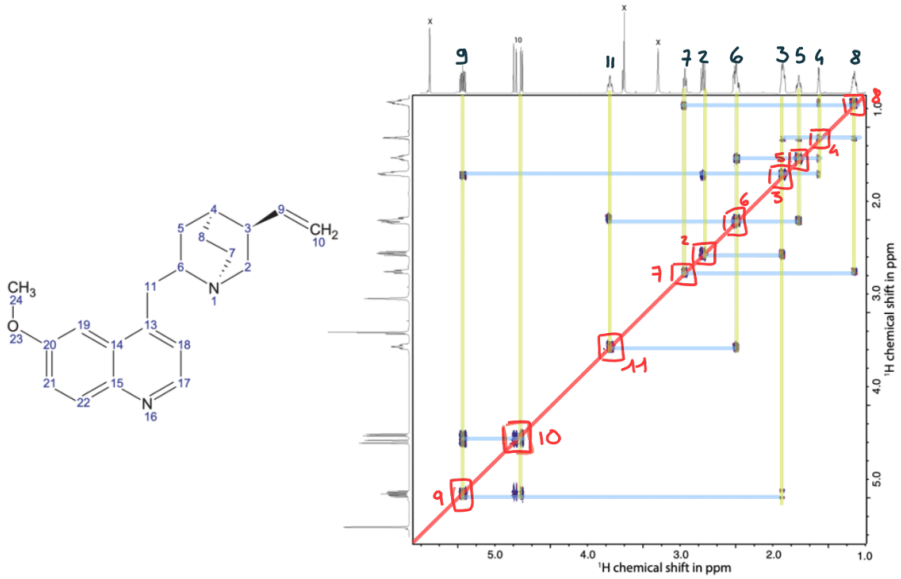


Figure 2: Signal intensity as a function of tau

c) This method is called Inversion-Recovery, and is used to determine the longitudinal relaxation time T_1. This is because: $\alpha(\tau) = \alpha_0(1 - exp(\frac{\tau}{T_1}))$
We can extract T_1 from this equation by analyzing the signal as a function of τ

2. [From Past Exam] [Keeler Section 8.4] By looking at the DQF-COSY spectra below and by knowing the assignment of proton 10, assign what you can. Why is not possible to assign all the peaks?



- Each signals on the real diagonal matches a proton of the above molecule

- If signals are alligned along a same horizontal or vertical line, the corresponding protons are interacting with each other.

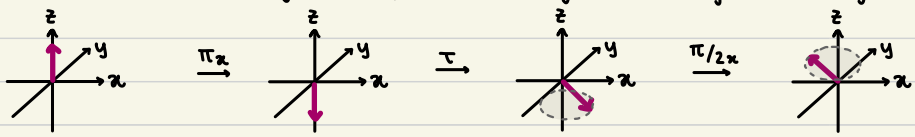
- One cannot assign all the peaks because DQF-COSY filters them out: signals that only couple with themselves are suppressed. Moreover the maximal chemical shift is $\delta_{max} = 6$ ppm which is too low to percieve aromatic protons usually around 7 ppm.

Good! Signals like the methoxy group (24) don't couple to anything else, so they won't show up on a DQF-COSY

Nice work!

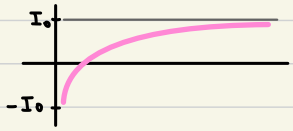
Question 1

a. As τ varies, the intensity of each peak (or the length of the magnetizat° longitudinal component) changes



Mostly correct! However, the angle of the magnetization with the z-axis will stay constant. Rather than precessing with some magnetization projected into the xy-plane, the magnetization will remain (anti-)parallel to z during τ. The π/2 pulse then pushes whatever magnetization has recovered onto the y-axis.

b. $I(t) = I_0(1 - 2\exp(\tau/T_1))$



c. T_1, the longitudinal relaxat° time

Question 2

see the graph: DQF-COSY give 3-bond and 4-bond interaction

What about the methoxy group (24)? It should show up in this chemical shift range. (Hint: what would it be coupled to? How would this show up on the plot/would it show up on the plot?)

we see that x is likely the solvent

not all peaks are able to be assigned because aromatics happen at 7ppm, and the chemical shift here doesn't go further than 6ppm

peaks 13-24 can therefore not be assigned