# Σειρά 3 C

## Problem 1

a) + c)

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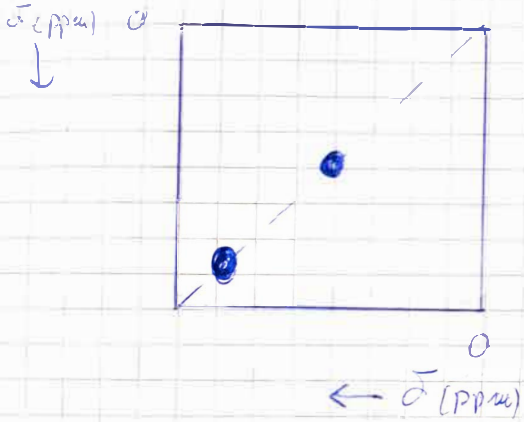
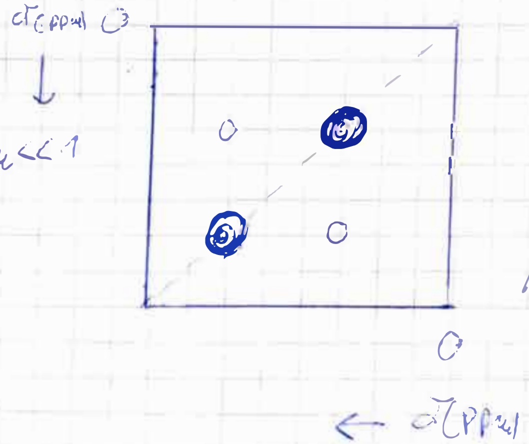
i) $k\tau_m = 0$



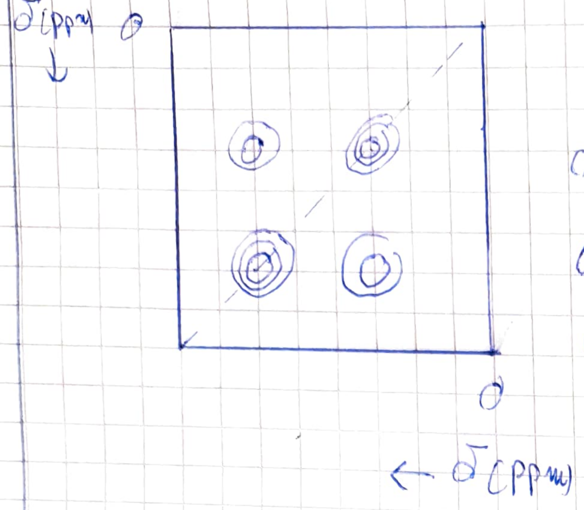

No mixing period is allowed ($\tau_m = 0$) ⇒ spins don't exchange ⇒ only diagonal peaks

ii) $k\tau_m << 1$



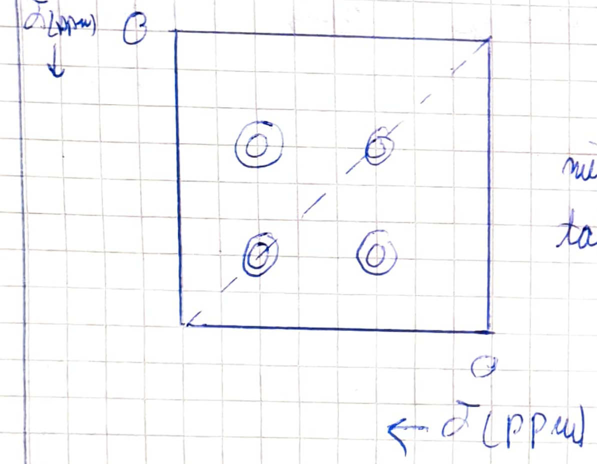

Exchange is slow compared to mixing period allowed ⇒ only few exchanges take place ⇒ diagonal peaks much more intense than cross peaks

iii) $k\tau_m \simeq 2$




Exchange time is comparable to the mixing period $\Rightarrow$ considerable amount of exchanges take place $\Rightarrow$ comparable intensity of diagonal and cross peaks

iv) $k\tau_m >> 2$




Exchange time is much lower than mixing period $\Rightarrow$ infinitely many exchanges take place $\Rightarrow$ both diagonal and cross peaks have the same intensity

c) In order to have cross peaks of considerable intensity, the exchange time needs to be on the same timescale as the mixing period $\tau_m$. As $\tau_m$ is in the order of 100 ms, the corresponding motion regime is the slow regime.

## Problem 2

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**Really good!!**

The pulse is applied to the proton nuclei $\Rightarrow$ it oscillates at Larmor frequency of the protons $\Rightarrow$ it introduces an offset frequency for the carbons:

$$\nu_{offset} = \nu_{^{13}C}^{Larmor} - \nu_{^{1}H}^{Larmor} = \left[(-125) - (-500)\right] MHz =$$

$$= 375 \; MHz$$

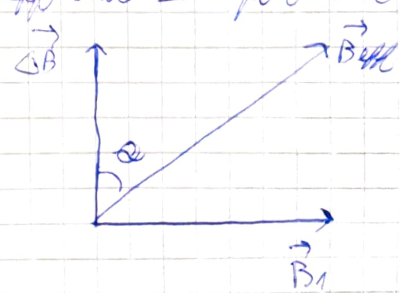
The precession frequency around the field ~~of the pulse~~ $B_1$ of the pulse is $\omega_1 = 2\pi\nu_1$

$t_p = 8 \mu s$ ~~rea~~, $\beta = \frac{\pi}{2}$ and $\beta = \omega_1 \cdot t_p \Leftrightarrow$

$\Leftrightarrow \beta = 2\pi \nu_1 \cdot t_p \Leftrightarrow \frac{\pi}{2} = 2\pi \cdot \nu_1 \cdot 8 \cdot 10^{-6} s \Rightarrow$

$\Rightarrow \nu_1 = 31250 \; Hz = 0.03125 \; MHz$

Let $\theta$ be the tilt angle between $B_{eff}$ and $\Delta B$ for the carbon nuclei




$$\tan\theta = \frac{B_1}{\Delta B} = \frac{\nu_1}{\nu_{offset}}$$

$$\Rightarrow \tan\theta = \frac{0.03125}{375} = 8.33 \cdot 10^{-5}$$

$\Rightarrow \theta = 0.005° \Rightarrow$ no significant effect on the $^{13}C$ nuclei

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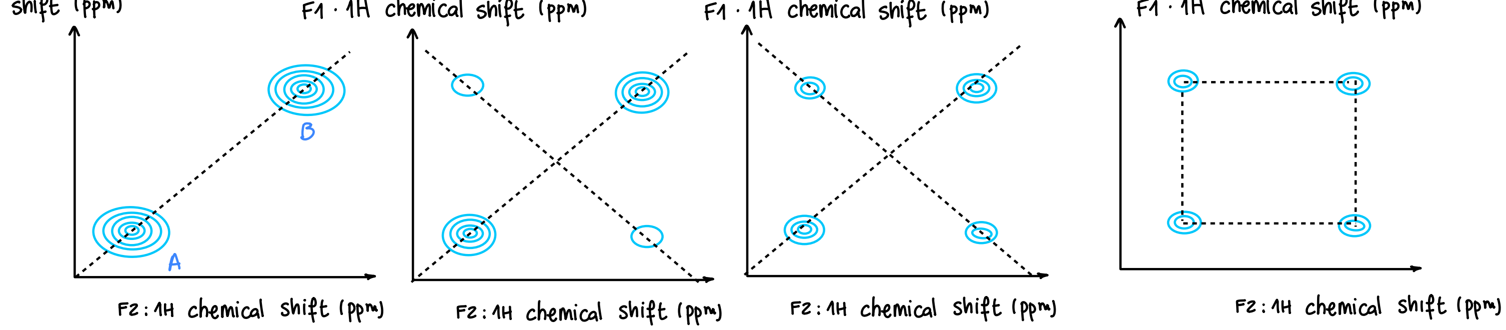
# Jigsaw 3C

1. [Week 3 Slides 65-74] Consider the EXSY spectrum of a symmetrical 2 spin (A and B) system. The intensity of the four peaks are given by the following equations:

$$I_{AA}(\tau_m) = \frac{1}{2}[1 + \exp(-2k\tau_m)]\exp(-\tau_m/T_1)M_{A0}$$
$$I_{BB}(\tau_m) = \frac{1}{2}[1 + \exp(-2k\tau_m)]\exp(-\tau_m/T_1)M_{B0}$$
$$I_{AB}(\tau_m) = \frac{1}{2}[1 - \exp(-2k\tau_m)]\exp(-\tau_m/T_1)M_{B0}$$
$$I_{BA}(\tau_m) = \frac{1}{2}[1 - \exp(-2k\tau_m)]\exp(-\tau_m/T_1)M_{A0}$$

   a. Draw the 2D EXSY spectrum, taking into account the relative intensity of diagonal and cross peaks, at the following values of $k\tau_m$:

i. $k\tau_m = 0$ ii. $k\tau_m \ll 1$ iii. $k\tau_m \approx 2$ iiv. $k\tau_m \gg 2$




   b. For each plot in (a), explain what is happening to the peak intensity and why.

At $t=0$, let's say the protons 1 are in A and the protons 2 are in B, as they are all in the same spot the intensity is higher. As time flies, exchange happen, so some of the protons 1 go in B and protons 2 go in A. As a result, the intensity of the initial pics decrease and 2 new pics appears. More the time past more they are exchanged and the intensity of the new pics increases (i.e. original pic intensities decreases). At $t \to \infty$, we reach a certain equilibrium and results four pics of the same NRJ.

   c. 2D exchange spectroscopy is used to determine exchange in which motion regime? Explain why.

2D spectroscopy is used to determine slow motion regime because we have a better separation.

**There might be some cases where the separation between the protons that exchange might be close to each other and the separations would still be a problem. The reason why it determines slow motion regime is because the timescale this exchange occurs is within the relaxation timescale and hence, measurable by NMR.**

2. [Keeler Section 4.5] A spectrometer operates at a Larmor frequency of 500 MHz for $^1H$ and hence 125 MHz for $^{13}C$. Suppose that a 90° pulse of length 8 µs is applied to the proton nuclei. Does this have a significant effect on the $^{13}C$ nuclei?

$w \cdot \tau = \frac{\pi}{2} \iff 2\pi\nu\tau = \frac{\pi}{2} \Rightarrow \nu = \frac{1}{4\tau} = \frac{1}{4 \times 8 \times 10^{-6}} = 31\,250$ Hz

Transmitted setted to $^1H$ : $\frac{1}{2}$ range of possible frequencies

Then for $^1H$, $\tan\theta = \frac{31\,250}{\underbrace{2500}_{\frac{1}{2}\text{ of the transmittor's frequency}}} \to \theta = 1{,}48$ rad $\to 85.3°$ Shifted enough to have a great intensity

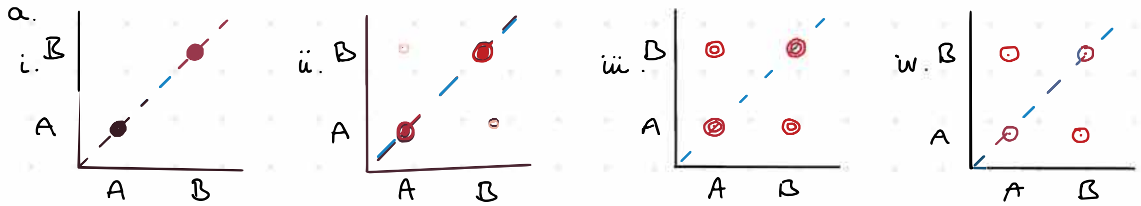
For $^{13}C$, $\tan\theta = \frac{31\,250}{12\,500} = 1{,}19$ rad $\to 68{,}2°$ Not impacted because not shifted enough to have a great intensity. Will come back to soon to the equilibrium.

A 1D range goes from 0 to 20 ppm. If we add the transmitter frequency in the middle of the spectra, the offset frequency of the edges will be 10 ppm * 500MHz = 5000 Hz. In the formula of tan(\theta)=(transmitter freq RF)/(offset freq) we see that we tilt the proton spin by 80.9 °. But keeping the same transmitter frequency we see that the offset resonance of the carbons will be at (500-125)MHz = 375*10^6 Hz. Knowing that the strength of the RF field is the same (since we are looking wether the pulse in protons will affect carbons). Adding this offset frequency to the formula we obtained that the carbons will be tilted \theta = 0.005° ... so they will barely affect them.

# Jigsaw 3C

**2/2**

1. a.




b. i. $k\tau_m = 0$ , diagonal peaks $I_{AA}$, $I_{BB}$ are at their maximum intensity

$$I_{AA} = \frac{1}{2}(1 + \exp(0))\exp(-\tau_M / T_1) M_{A0} = \exp(-\tau / T_1) M_{A0}$$

cross-peaks $I_{AB}$, $I_{BA}$ indicate no exchange between spins

$$I_{AB} = \frac{1}{2}(1 - \exp(0))\exp(-\tau_m / T_1) M_{B0} = 0$$

ii. $k\tau_m \ll 1$ , diagonal peaks still pretty intense
cross peaks are very weak, but non-zero

iii. $k\tau_m \approx 2$, $I_{AA} = \frac{1}{2}(1 + \exp(-4))\exp(-\tau_m / T_1) M_{A0}$

$$I_{AB} = \frac{1}{2}(1 - \exp(-4))\exp(-\tau_m / T_1) M_{A0}$$

$\exp(-4)$ quite small, which means intensity diagonal peaks only slighty higher than the cross peak intensities

iv. $k\tau \gg 2$ , the diagonal and crosspeaks become around the same intensity.

c. EXSY is best suited for studying molecular motions in the intermediate-to-slow exchange regime because it provides both distinct peaks along the diagonal and cross-peaks.

What you have mentiones it is true but I would add: The reason why it determines slow motion regime is because the timescale this exchange occurs is within the relaxation timescale and hence, measurable by NMR.

2. Larmor frequency seperation : $\Delta\nu = 500 - 125 = 375$ MHz

pulse bandwidth : $\Delta\nu_{pulse} = \frac{1}{8 \cdot 10^{-6}} = 125$ kHz

So, as the bandwidth is small compared to the seperation of $^1H$ and $^{13}C$, the $8\,\mu s$ $90°$ pulse at 500 MHz will not have a significant effect on the $^{13}C$ nuclei. It is not big enough to impact the 125 MHz Larmor frequency.

**A 1D range goes from 0 to 20 ppm. If we add the transmitter frequency in the middle of the spectra, the offset frequency of the edges will be 10 ppm * 500MHz = 5000 Hz. In the formula of tan(\theta)=(transmitter freq RF)/(offset freq) we see that we tilt the proton spin by 80.9 °. But keeping the same transmitter frequency we see that the offset resonance of the carbons will be at (500-125)MHz = 375*10^6 Hz. Knowing that the strength of the RF field is the same (since we are looking wether the pulse in protons will affect carbons). Adding this offset frequency to the formula we obtained that the carbons will be tilted \theta = 0.005° ... so they will barely affect them.**