2/2 Very nice!

CH-314 Structural Analysis
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Jigsaw 3E

General

1. True or false. Justify your answer.

   a) Fourier transformation converts time domain to the frequency domain.

   True, the measurement was recorded "in time" so the aim is to convert this signal into frequencies to get the spectrum

   b) Fourier transformation converts frequency domain to the time domain.

   ~~False, see question a)~~

   True, the Fourier transform goes both ways

   c) Multiplet splitting patterns are caused by scalar couplings.

   True, by definition

   d) Reducing the magnetic field results in smaller separation of peaks within multiplets in ppm.

   ~~False, in ppm reducing the magnetic field will increase the separation as it is proportional to $\frac{1}{B}$ However, in Hz, the magnetic field has no influence on the separation~~

   (d) True, the coupling stays the same in Hz; but since it gets divided by a smaller magnetic field (in MHz), the value in ppm increases

2. The international reference compound used in NMR to set up the chemical shift scale is tetramethylsilane, $Si(CH_3)_4$, commonly known as TMS. Consider a sample containing pure liquid TMS for analysis.

Isotope	Nuclear Spin	Natural Abundance	γ / rad·s^{-1}·T^{-1}
^1H	½	~100%	2.675×10^8
^{12}C	0	98.9 %	0
^{13}C	1/2	1.1 %	$6.728 \cdot 10^7$
^{28}Si	0	92.23 %	0
^{29}Si	1/2	4.68 %	$-5.315 \cdot 10^7$
^{30}Si	0	3.09 %	0

a. Complete the table above by filling in the most common isotope(s) present in the sample (list all isotopes with ≥ 1% natural abundance), the nuclear spin, the natural abundance, and the gyromagnetic ratio of each isotope. Which isotopes are NMR-active? Why?

The active isotopes NMR-active are ^1H, ^{13}C and ^{29}Si. Indeed, the gyromagnetic should be non-zero

(and spin)

b. Consider a magnetic field strength (B_0) of 11.7467 T. What are the resonance frequencies of the active nuclei (in MHz)?

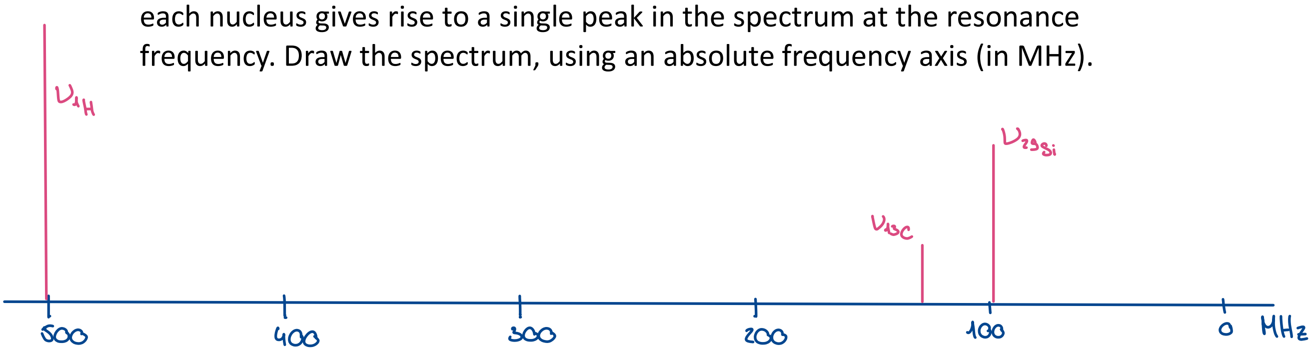
Using NMR frequency : $\nu_{NMR} = \frac{|\gamma| B_0}{2\pi}$

^1H : $\nu_{NMR} = \frac{|2.675 \cdot 10^8| \cdot 11.7467}{2\pi} = 5.0001 \cdot 10^8 \ s^{-1} = 500.01 \ MHz$

^{13}C : $\nu_{NMR} = \frac{|6.728 \cdot 10^7| \cdot 11.7467}{2\pi} = 125.78 \ MHz$

^{29}Si : $\nu_{NMR} = \frac{|-5.315 \cdot 10^7| \cdot 11.7467}{2\pi} = 99.366 \ MHz$

c. Considering the high symmetry of the molecule and neglecting all couplings, each nucleus gives rise to a single peak in the spectrum at the resonance frequency. Draw the spectrum, using an absolute frequency axis (in MHz).



d. Why is it not possible to detect this theoretical spectrum, i.e. to detect heteronuclei in one single experiment?

The range of frequency is huge which means that we will need a very large energy to cover the whole spectra. This can be considered as experimental limitations. This explains why we usually do each atom/species at a time.

2/2 Well done!

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Jigsaw 3E

General

1. True or false. Justify your answer.

   a) Fourier transformation converts time domain to the frequency domain.

   True : $I(\omega) = \int S(t) \exp\{-i\omega t\} dt$

   ↑to frequency ↳from time

   b) Fourier transformation converts frequency domain to the time domain.

   ~~False, it's the other way around. See a).~~

   True, the Fourier transform goes both ways

   c) Multiplet splitting patterns are caused by scalar couplings.

   True, scalar coupling is also known as spin-spin coupling and multiplet are caused by the interactions of different spins in neighbouring nuclei in liquid state NMR.

   d) Reducing the magnetic field results in smaller separation of peaks within multiplets in ppm.

   ~~False, it doesn't reduce it increases.~~

   (d) True, the coupling stays the same in Hz; but since it gets divided by a smaller magnetic field (in MHz), the value in ppm increases

2. The international reference compound used in NMR to set up the chemical shift scale is tetramethylsilane, $Si(CH_3)_4$, commonly known as TMS. Consider a sample containing pure liquid TMS for analysis.

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^{28}Si	0	~92.23%	0
^{29}Si	1/2	~4.67%	$-5.315\cdot10^7$
^{30}Si	0	~3.10%	0

   a. Complete the table above by filling in the most common isotope(s) present in the sample (list all isotopes with ≥ 1% natural abundance), the nuclear spin, the natural abundance, and the gyromagnetic ratio of each isotope. Which isotopes are NMR-active? Why?

   ^{13}C, ^1H, and ^{29}Si are NMR-active because they have non-zero nuclear spin.

   b. Consider a magnetic field strength (B_0) of 11.7467 T. What are the resonance frequencies of the active nuclei (in MHz)?

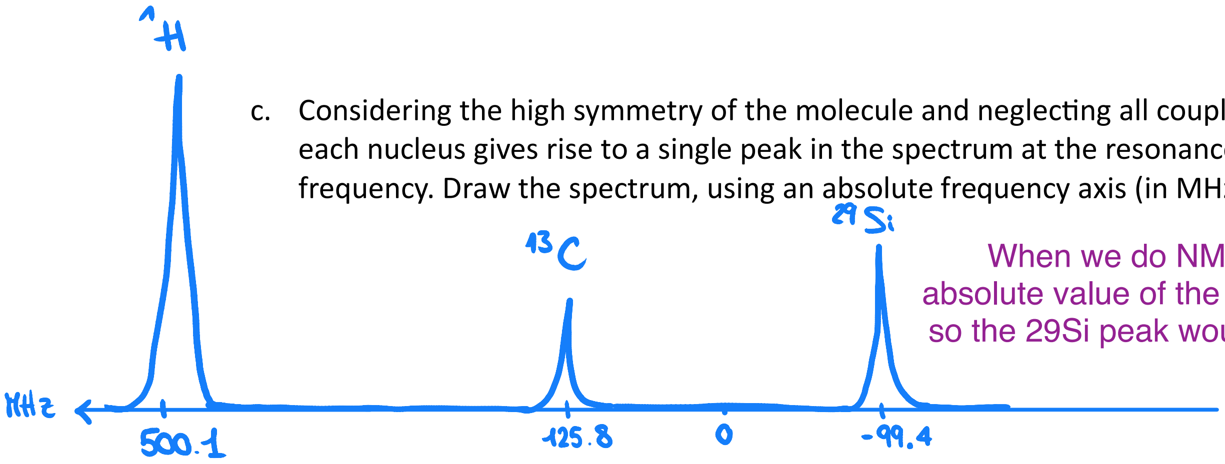
$$f = \frac{\gamma B_0}{2\pi}$$

$^1H \Rightarrow 5{,}0\cdot10^8$ Hz 500,1 MHz

$^{13}C \Rightarrow 1{,}26\cdot10^8$ Hz 125,8 MHz

$^{29}Si \Rightarrow -9{,}94\cdot10^7$ Hz - 99,4 MHz

c. Considering the high symmetry of the molecule and neglecting all couplings, each nucleus gives rise to a single peak in the spectrum at the resonance frequency. Draw the spectrum, using an absolute frequency axis (in MHz).



When we do NMR, we take the absolute value of the Larmor frequency, so the 29Si peak would be at +99 MHz

d. Why is it not possible to detect this theoretical spectrum, i.e. to detect heteronuclei in one single experiment?

The natural abundance of hetero nuclei being lower than that of proton, their signals are weaker. The signal sensitivities also depend on the values of the gyromagnetic ratios.

These don't really stop us, since the issues don't go away when you look at just one nucleus (13C still has a low abundance and lower gyromagnetic ratio when you measure only that spectrum)

It would be too expensive energetically to perform the experiment over all frequencies.

This is the key thing; in order to excite spins more than ~100kHz apart, we would need VERY VERY high power pulses, which is just not practical. It would also severely limit the peak resolution