CH-314 Structural Analysis
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Jigsaw 1C

Introduction to Nuclear Magnetic Resonance

1.75/2

1. * [Keeler Sections 2.1 and 3.2] 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. *See also: Jigsaw 1B.1*

Isotope	Nuclear Spin	Natural Abundance	γ / rad·s^{-1}·T^{-1}
^{1}H	½	~100%	2.675×10^{8}
^{12}C	0	98,89%	0
^{13}C	1/2	1,11%	$6,728\cdot10^{7}$
^{28}Si	0	92,2%	0
^{29}Si	1/2	4,7%	$-5,319\ 10^{7}$
^{30}Si	0	3,1%	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?

All isotopes with a nuclear spin are NMR-active. So ^{1}H, ^{13}C and ^{29}Si have a nuclear spin of 1/2, which makes them energetically active and therefore visible in NMR.

all isotopes with a nuclear spin **different than 0!**

b. [Keeler Section 3.3] Consider a magnetic field strength (B_0) of 11.7467 T. What are the resonance frequencies of the active nuclei (in MHz)?

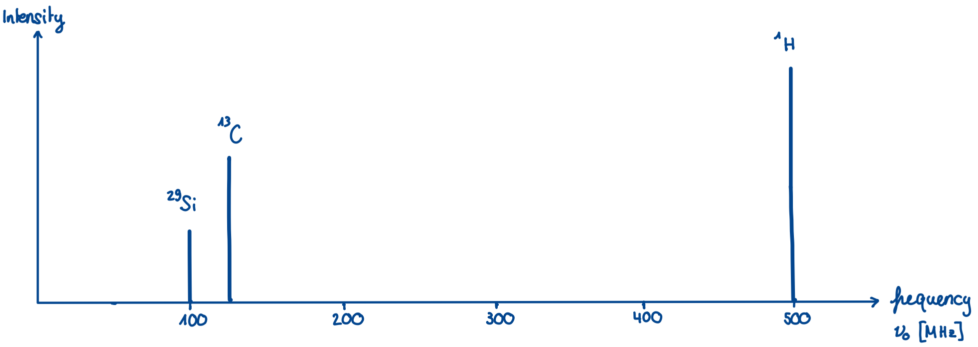
To calculate the resonance frequencies, we used this formula :

$\nu_0 = \frac{-\gamma B_0}{2\pi}$ where B_0 is the magnetic field strenght and γ the gyromagnetic ratio in rad·s^{-1}·T^{-1}

we only calculated the resonance frequency for the NMR-active isotops.

- ^{1}H : $\nu_0 = \frac{-2,675\cdot10^{8}\cdot11,7467}{2\pi} \simeq -500,1\ MHz$
- ^{13}C : $\nu_0 = \frac{-6,728\cdot10^{7}\cdot11,7467}{2\pi} \simeq -125,8\ MHz$
- ^{29}Si : $\nu_0 = \frac{5,319\cdot10^{7}\cdot11,7467}{2\pi} \simeq 99,4\ MHz$

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).



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^{28}Si	0	92,232	0
^{29}Si	½	4,699	$-5,319\cdot10^7$
^{30}Si	0	3,092	0

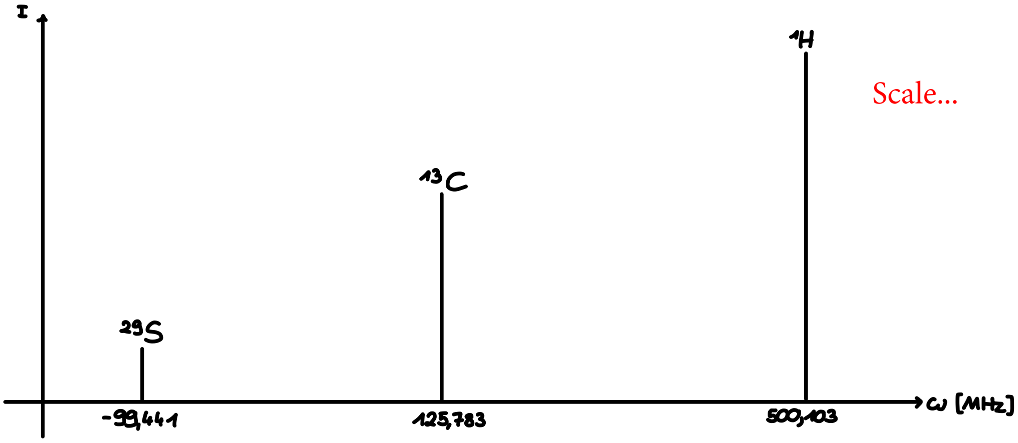
a. Complete the table above by filling in the most common isotope(s) present in the sample (list all isotopes with ≥ 1% natural abundance), the nuclear spin, the natural abundance, and the gyromagnetic ratio of each isotope. Which isotopes are NMR-active? Why?

^1H, ^{13}C and ^{29}Si are NMR active as their spin is non zero.

b. [Keeler Section 3.3] Consider a magnetic field strength (B_0) of 11.7467 T. What are the resonance frequencies of the active nuclei (in MHz)?

$\omega=\gamma B_0$
$\omega(^1H)=500,103$ MHz
$\omega(^{13}C)=125,783$ MHz
$\omega(^{29}Si)=-99,441$ 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).



Scale...

d. * [Keeler Section 2.4] Why is it not possible to detect this theoretical spectrum, i.e. to detect heteronuclei in one single experiment?

Different nuclei have different γ, meaning that they resonate at different frequency for a given B field strength

Within the same nuclei the differences in frequency are really small so we need to focus on one region to observe their difference.

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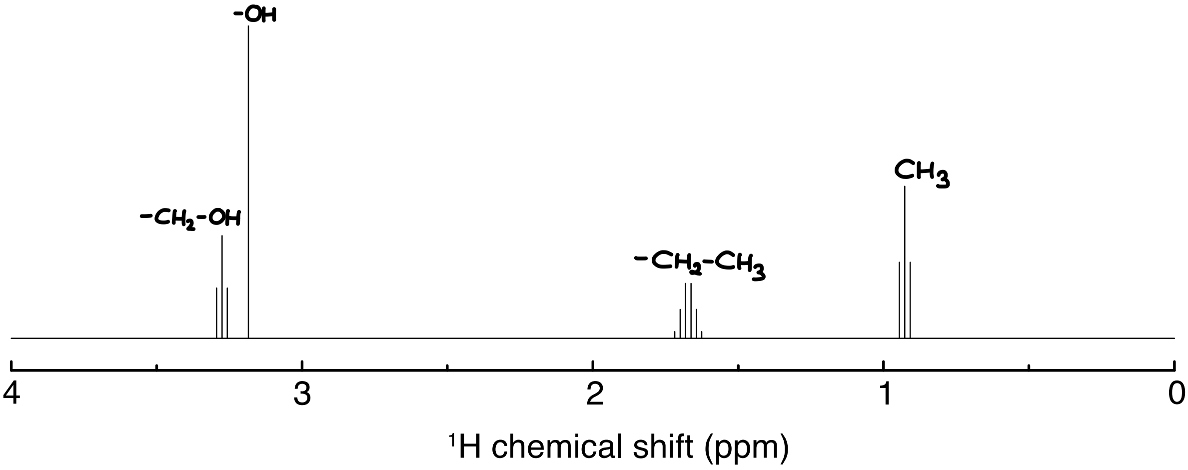
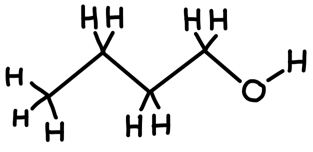
2. * [Keeler Section 2.3] The following ^1H spectrum is of a molecule with the chemical formula $C_4H_{10}O$. Predict the structure of the molecule, assign the spectrum, and give the relative intensities of the signals.





butan-1-ol

No. CH3CH2CH2OCH3

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Jigsaw 1C

Introduction to Nuclear Magnetic Resonance

2/2

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   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?

   ^{1}H, ^{13}C, ^{29}Si are NMR-active as they have non-zero nuclear spin, i.e. a non-zero magnetic moment, which is detected by NMR

   b. [Keeler Section 3.3] Consider a magnetic field strength (B_0) of 11.7467 T. What are the resonance frequencies of the active nuclei (in MHz)?

   $$\nu_0 = \frac{\gamma B_0}{2\pi}$$

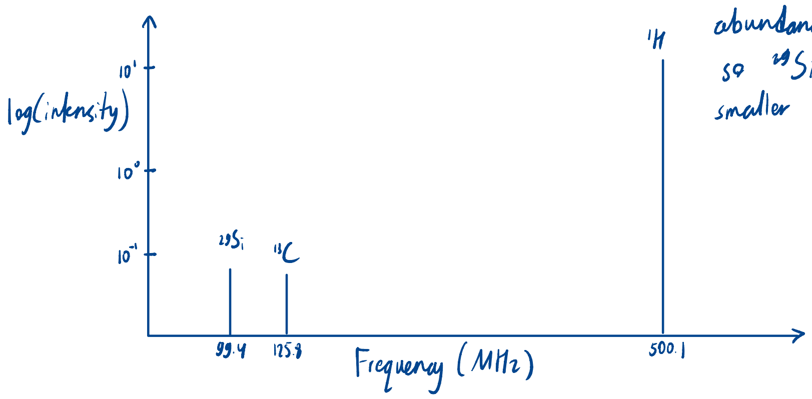
   $$^{1}H: \nu_0 = \frac{2.675\times10^{8}\times 11.7467}{2\pi} \approx 500.1\ MHz$$

   $$^{13}C: \nu_0 = \frac{6.728\times10^{7}\times 11.7467}{2\pi} \approx 125.8\ MHz$$

   $$^{29}Si: \nu_0 = \frac{5.319\times10^{7}\times 11.7467}{2\pi} \approx -99.4\ MHz$$

   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).

   ^{29}Si and ^{13}C have low natural abundance, and there are 12 H atoms, so ^{29}Si and ^{13}C peaks are smaller than ^{1}H peak

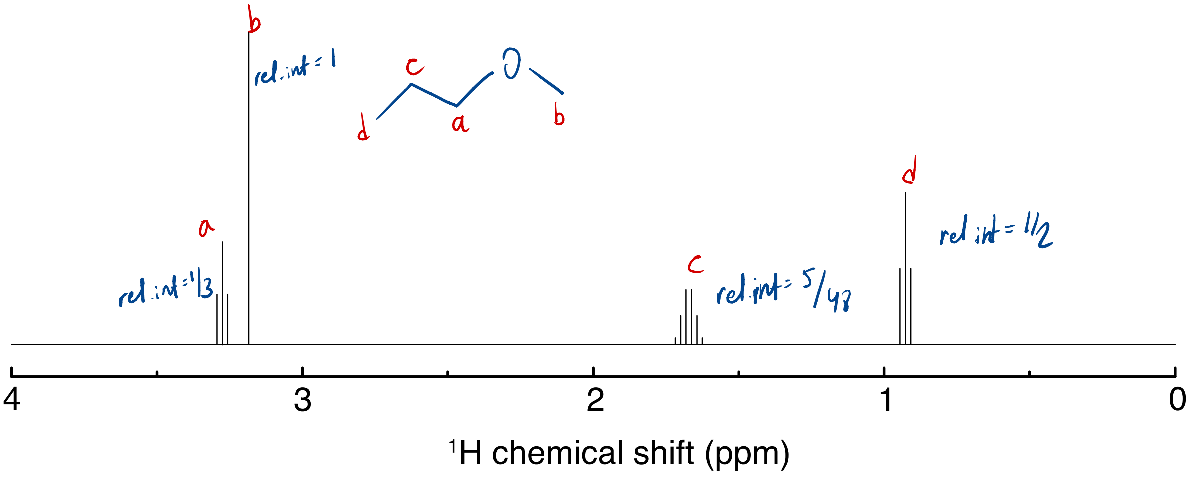


d. * [Keeler Section 2.4] Why is it not possible to detect this theoretical spectrum, i.e. to detect heteronuclei in one single experiment?

NMR machines are tuned for 1 specific frequency range at a time as the nuclei resonate at very different frequencies. Also, as some peaks (^1H in our case) are much stronger than others (^{13}C and ^{29}Si), signal-to-noise ratio becomes problematic.

2. * [Keeler Section 2.3] The following ^1H spectrum is of a molecule with the chemical formula $C_4H_{10}O$. Predict the structure of the molecule, assign the spectrum, and give the relative intensities of the signals.

2/2



Let's consider relative intensity of b to be 1

As b corresponds to 3H, then the sum of intensities of peak a will be 2/3. As a triplet splits by ratio 1:2:1, the intensity of peak a will be $2/3 \times 2/4 = 1/3$

Peak c also corresponds to 2H, and as a sixtet, it splits by the ratio 1:5:10:10:5:1, so the intensity will be $2/3 \times 5/32 = 5/48$

Peak d corresponds to 3H, and as a triplet, it splits by ratio 1:2:1, so the relative intensity will be $1 \times 2/4 = 1/2$