2/2 Great work!

Structural Analysis NMR Jigsaw 1A.

October 2025

In a ^{1}H NMR spectrum measured in a 400 MHz spectrometer, the peak from TMS (the reference compound) is found to occur at 400.130000 MHz. Two other peaks in the spectrum are found at 400.131023 and 400.132179 MHz.

1. The shifts in ppm can be computed using the following formula, with ν_{ref} being the frequency of TMS, and ν the frequency of the peak.

   $$\delta(ppm) = 10^{6} \times \frac{\nu - \nu_{ref}}{\nu_{ref}} \tag{1}$$

   Thus, the peak at 400.131023 MHz corresponds to $\delta = 2.55ppm$ and the peak at 400.132179 MHz corresponds to $\delta = 5.45ppm$.

2. Rearranging Equation (1), we can find the expression for ν at a different frequency as a function of ν_{ref}.

   $$\nu = \nu_{ref}(10^{-6} \times \delta(ppm) + 1) \tag{2}$$

   The peak with $\delta = 2.55ppm$ can now be found at 600.131530 MHz, and the peak with $\delta = 5.45ppm$ can be found at 600.133271 MHz. The chemical shifts in *ppm* do not change, as it is a ratio.

3. We measure in *ppm* because we obtain the same values for different strength magnetic fields, since it is a ratio of values. Shifts in *ppm* are independent of the magnetic field strength, as the peaks are moved by the same amount if the magnetic field strength is changed.

4. By increasing the magnetic field strength, we increase peak separation, which increases resolution. Therefore, it is worth increasing the magnetic field strength if the analysis is more complex and requires better resolution.

5. The strength of magnetic field required depends on the molecule to be analysed. If it is a simpler molecule, without complex splitting patterns that may require to be determined, a weaker field can be used. It will also result in a cheaper NMR machine. Higher fields improve sensitivity and resolution, but may not be required for routine analyses.

2/2 Nice work!

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Jigsaw 1A

Keeler Section 2.1. NMR frequencies and chemical shifts

In a ^{1}H NMR spectrum measured in a 400 MHz spectrometer, the peak from TMS (the reference compound) is found to occur at 400.130000 MHz. Two other peaks in the spectrum are found at 400.131023 and 400.132179 MHz.

1. Compute the chemical shifts of these two peaks in ppm.

$$\delta = \frac{\nu_{sample} - \nu_{ref}}{\nu_{spectrometer}} \cdot 10^6$$

$$\delta_1 = \frac{400,131\,023 - 400,130\,000}{400} \cdot 10^6 = 2,557\,5 \text{ ppm}$$

$$\delta_2 = \frac{400,132\,179 - 400,130\,000}{400} \cdot 10^6 = 5,447\,5 \text{ ppm}$$

2. This sample is re-run on a different spectrometer which operates at 600 MHz for protons. The reference frequency for this spectrometer is 600.130000 MHz. What would be the frequency, in MHz and ppm, of the other two peaks on this spectrometer?

$$\nu_{sample} = \nu_{ref} + \frac{\delta \cdot \nu_{spectrometer}}{10^6}$$

$$\nu_1 = 600,130\,000 + \frac{2,5575 \cdot 600}{10^6} = 600,131\,535 \text{ MHz}$$

$$\nu_2 = 600,130\,000 + \frac{5,4475 \cdot 600}{10^6} = 600,133\,269 \text{ MHz}$$

The chemical shift in ppm remains the same on any spectrometer, but the frequency difference scales with the spectrometer's magnetic field strength.

3. Why do we generally report peak locations in ppm?

Chemical shifts in ppm do not depend on the spectrometer's field. They stay the same on all instruments. This makes spectra easy to compare.

4. Based on part (2), is it worth it using higher magnetic fields? Why?

Yes, using higher magnetic field is often worth it. Peaks are farther apart in Hz, so overlapping signals are easier to see. Sensitivity is better and weak signals are easier to detect. Small differences in chemical shifts are clearer. Higher fields cost more and may cause some line broadening. For complex or crowded spectra, high field is best. For simple spectra, mid-field is usually enough.

due to field inhomogeneity

5. What's one reason there are a wide range of magnetic fields used in modern spectrometers? (i.e., why don't we all just use the "best" one?) Hint: Think about the Build-A-Spectrometer activity from earlier.

One reason is cost. Higher-field spectrometers are much more expensive to build and maintain. Lower-field instruments are cheaper, easier to use and still good enough for many experiments.

2/2 Good job!

Jigsaw 1A

Question 1 :

$$\delta(\text{ppm}) = 10^6 \cdot \frac{\nu - \nu_{ref}}{\nu_{rx}}$$

peak 1: $\delta_1 = 10^6 \cdot \frac{400.131023 - 400.130000}{400} = 2.5575$ ppm

peak 2: $\delta_2 = 10^6 \cdot \frac{400.132179 - 400.130000}{400} = 5.4475$ ppm

Question 2 :

Chemical shifts don't change with field. From the 400 MHz run, the two peaks are at $\delta_1 = 2.5575$ ppm and $\delta_2 = 5.4475$ ppm .

At 600 MHz, 1ppm = 600 Hz, so the frequency offsets are :

$\Delta\nu_1 = 2.5575 \times 600$ Hz $= 1534.5$ Hz $= 0.0015345$ MHz.

$\Delta\nu_2 = 5.4475 \times 600$ Hz $= 3268.5$ Hz $= 0.0032685$ MHz.

With TMS at 600.130000 MHz, the peak positions are :
600.131535 MHz ($\approx$ 2.5575 ppm) and 600.133268 MHz ($\approx$ 5.4475 ppm)

Question 3 :

ppm is used because it expresses chemical shifts as dimensionless, field-independent ratio ($\delta \cdot 10^6$)

Question 4

Using a larger magnetic field allows for better sensitivity and resolution on the frequency spectrum without changing the ppm values of the peaks.

Question 5 :

One reason why modern spectrometers use a wide range of magnetic field strengths is that the choice of field depends on a balance between performance, cost, and the specific application.
A stronger magnetic field usually improves the spectrometer's resolution and sensitivity.
…but is more expensive

2/2 Well done!

Jigsaw 1A

Keeler Section 2.1. NMR frequencies and chemical shifts

In a ^{1}H NMR spectrum measured in a 400 MHz spectrometer, the peak from TMS (the reference compound) is found to occur at 400.130000 MHz . Two other peaks in the spectrum are found at 400.131023 and 400.132179 MHz .

1. Compute the chemical shifts of these two peaks in ppm.
   The chemical shifts can be calculated using the following formula:
   $$\delta(ppm) = 10^{6} \times \frac{\upsilon - \upsilon_{ref}}{\upsilon_{ref}}$$
   The peak at 400.131023 MHz has a chemical shift of 2.56 ppm and the peak at 400.132179 MHz has a chemical shift of 5.45 ppm.
2. This sample is re-run on a different spectrometer which operates at 600 MHz for protons. The reference frequency for this spectrometer is 600.130000 MHz . What would be the frequency, in MHz and ppm, of the other two peaks on this spectrometer?
   The chemical shifts will be the same since the same reference compound is used. The frequencies in MHz can be calculated using the following formula:
   $$\upsilon = 10^{-6} \times (\delta) \times \upsilon_{ref} + \upsilon_{ref}$$
   The peak at 2.56 ppm will now have a frequency of 600.131536 MHz and the peak at 5.45 ppm will now have a frequency of 600.133271 MHz .
3. Why do we generally report peak locations in ppm?
   When converting to ppm, the field dependence cancels out. This way positions of peaks can be expressed independent of the field strength of a specific NMR spectrometer. This makes it easier to compare and share data.
4. Based on part (2), is it worth it using higher magnetic fields? Why?
   The difference in frequency between the peaks was 0.001156 MHz for the 400 MHz spectrometer and 0.001734 for the 600 MHz spectrometer. The second difference is slightly larger, this gives a better resolution. However, this difference is pretty small.
5. What's one reason there are a wide range of magnetic fields used in modern spectrometers? (i.e., why don't we all just use the "best" one?) Hint: Think about the Build-A-Spectrometer activity from earlier.
   Because higher magnetic fields are much more expensive and complex to maintain, and not every experiment or application needs them.