Additional Reading Material

Tutorial Name: **Simulated NMR Spectrum using Jmol**

Link for reference: https://www.chemistrysteps.com/nmr-chemical-shift/

The basic principle of NMR spectroscopy:

When a sample is exposed to a magnetic field the nuclei distribute in two different energy levels. Some are oriented with the applied magnetic field, lower in energy **–** α Spin state and some are aligned opposite to the magnetic field, higher energy state **–** β Spin state. The electromagnetic radiation matching this energy difference (radio frequency) is applied. Each proton absorbs energy exactly matching the gap (resonance) between the α and β states causing a spin-flip. The protons relax back after releasing energy which is converted to the δ (ppm) value on the spectrum. The energy gap between the α and β states is slightly different for each type of proton depending on their environment which is the neighboring atoms.

The energy axis is called a **δ (delta)** axis and the units are given in **part per million (ppm)**. Most often the signal area for organic compounds ranges from **0-12 ppm**.

The ppm value of a given proton depends on the energy difference between α and β states which also depends on how much energy it received from the magnetic field.

The strength of the magnetic field that each proton experiences and therefore jumps to a certain energy level in the β state depends on how exposed it is to the field. The electron cloud around protons protects them from being exposed to the field 100%.

Higher the electron density, less the given nucleus experiences the magnetic field. Therefore, lower the electron density the more it is exposed to the magnetic field and more energy it absorbs.

A neighboring electronegative atom pulls the electron density thus exposing the nucleus to a stronger magnetic field.

For the protons, the electrons form the shield. The more electron-withdrawing the group, the stronger the proton feels the magnetic field. They are less shielded by the electrons and more exposed to the field.

The higher the electron density, the better the shield and thus protected the nucleus. And depending on the neighboring groups, we can predict the signal region of a given proton.

Upfield and Downfield

The terms upfield and downfield refer to the low and high energy of the signals respectively. Yes, it sounds confusing since you would expect the downfield to indicate a lower energy region and upfield as higher energy.

The wording has a historical origin. The first-generation NMR spectrometers used what is called "continuous wave field sweep". In this the frequency of rf radiation was kept constant and the magnetic field strength was slowly increased to detect which field strengths produce a signal. The more shielded protons required a stronger magnetic field to resonate and therefore the high energy was on the right side thus making it upfield and the terms upfield and downfield indicated high energy and low energy.

However, modern NMR instruments are designed to work by pulsed Fourier-transform NMR (FT-NMR) where the magnetic field is held constant and a short pulse covering the entire range of relevant radio frequencies is irradiated. So, the protons that are shielded appear to be at lower energy levels. Therefore resonate at lower frequency and the ones deshielded experience stronger magnetic field and resonate at higher energy which is opposite to what happened in older instruments. This doesn't mean that the results were different, no they produce identical data, but the wording is mixed.

Downfield means higher energy, high frequency – left side of the spectrum (higher ppm)

Upfield means lower energy, lower frequency – right side of the spectrum (lower ppm)

Chemical Shift Values

As already mentioned, the resonance frequency giving the signal in NMR, and indicating the types of protons, is shown on the x axis by δ (delta). The 0 ppm is a reference point where the protons of tetramethylsilane, $(CH3)_4Si$, also called TMS, give the signal.

There are a few reasons why TMS is used as a reference. First, it is a rare example of a carbon connected with a less electronegative element, silicon, which makes it shielded and therefore appear at lower ppm where other protons do not give signal and the peak at 0 ppm can be ignored when analyzing an NMR spectrum.

Second, it has a low boiling point which makes purifying the sample easier if needed.

The signals of all the other protons are reported in terms of how far (in Hertz) they are shifted from TMS signal and the chemical shift value (δ) is measured by the ratio of this shift in Hertz and the operational frequency of the spectrometer in MHz:

$$\delta = \frac{\text{(shift in Hz from TMS)}}{\text{(spectrometer frequency in MHz)}}$$

The operational frequency of most NMR instruments is in the MHz region and this is why the units are given in parts per million (ppm).

Now, you may ask, what is the purpose of dividing the shift by the frequency of the instrument? Why not just report the shift in Hz?

Magnetic Strength and PPM Value

The energy difference of the α and β states for different protons is very little energy wise (for example, 0 – 1200 Hz). Again, this depends on the instrument, but it is still a low energy compared to the super powerful magnets that are used. Nevertheless covering 0-1200 on a spectrum axis is not convenient when analyzing an NMR especially if the difference of two peaks is only a few Hz. However, this is rather a decorative obstacle.

The key reason here is to have a formula which allows a field-independent measure of the signals, meaning regardless what NMR is used, the chemical shift should always be the same for the given proton.

For example, ethanol, under certain conditions, gives two signals at 1.25 and 3.72 ppm with modern powerful NMR instruments and it did the same when the first instruments came about in mid last century. Having consistent results helps in many ways since research itself opens an infinite possibility of getting errors and surprises.

So, when switching to a more powerful NMR, let's say from 300 MHz to 900 MHz, the shift of the signal from TMS changes but because we divide it by the operational frequency of the instrument, the ppm value stays the same.