NMR Spectroscopy

- Some nuclei posses **spin** (ie: behave as if they have angular momentum), and, as a result, have **very weak magnetic fields** associated with them. When placed in a **strong magnetic field**, there is an interaction between both fields which gives rise to a set of **nuclear spin energy levels** [note: in the absence of an applied field, all spins have the same energy]. **Radiowaves** of appropriate frequency cause **transitions** between these energy levels and this gives rise to the **NMR signal**.
- The nuclear spin is specified by the **nuclear spin quantum number, *I***. It may takes values that are **multiples** of ½. A nucleus with spin ***I*** gives rise to ***2I + 1*** different energy levels when placed in a field.
- A few rules that help predict *I* for different nuclei:
    - Nuclei with **even numbers of protons** *and* **even number of neutrons** have $I = 0$.
    - Nuclei with **odd numbers of protons** *and* **odd number of neutrons** have integral spins.
    - Nuclei with **odd atomic masses** have **half-integral** spins.
- And a few spins to learn:

Nucleus	% Natural abundance	*I*
^{1}H	99.985	½
^{2}H (D)	0.015	1
^{10}B	20	7
^{11}B	80	3/2
^{12}C	98.9	0
^{13}C	1.1	½
^{14}N	99.6	1
^{16}O	99.8	0
^{19}F	100	½
^{31}P	100	½

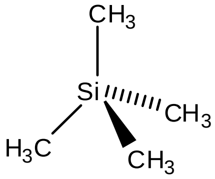
- The different in energy between the spin states depends on the **strength of the applied field** and on the **nucleus itself**. However, it also depends on the **electron density** around the nucleus. The **denser** the electron cloud around the nucleus, the **more shielded** the nucleus is from the external field and the **smaller** the **energy difference**.

This results in a **lower frequency** of the NMR peak. These difference are tiny – just hundreds of Hz. This is in contrast to the different frequencies that different nuclei vibrate at – typically **hundreds** of **MHz** apart.

- Nuclei that are in the same **symmetrical** or **rotational symmetrical** place in a molecule are in **equivalent environments** are only give rise to **one peak**.
- Since shifts are also affected by the applied field, we use a **normalised scale** based on a **reference compound**, as:

  $$\text{Chemical shift } (\delta) \text{ in ppm} = \frac{\text{Frequency of resonance} - \text{Frequency of reference}}{\text{Frequency of reference}} \times 10^6$$

  The reference compound used is **trimethylsilane** (TMS):

  This is advantageous for various reasons. **(a)** it gives only one signal, both in ^{13}C and ^{1}H NMR **(b)** S is slightly electron donating with respect to C, and so the Cs in TMS are slightly more shielded than most Cs in organic compounds. The TMS peak is therefore over to the right, out of the way **(c)** TMS is chemically inert.
- Absorption peaks can be affected by **nearby nuclei**. If a nearby nucleus is pointing **in the direction** of the external field, then the external field felt by our nucleus will be ***more***, and vice-versa. When this happens with more than one nucleus, the number of ways we can permute these nuclei in a given configuration determines the intensity of each of the peaks.
  - Note, of course, that coupling only occurs to nuclei with a non-zero spin.
  - If the nucleus couples to ***n*** **equivalent nuclei** with **spin** ***I***, the resonance signal is **split** into ***2nI + 1*** **lines**. If $I = ½$, the intensities of each of the peaks can be worked out using Pascal's Triangle.
  - When coupling non-equivalent nuclei (either different nuclei, or identical nuclei through more bonds), we get things like *triplets of doublets* or the like. In that case, the number of peaks and their intensities must be worked out using a tree diagram.
  - The distance between each of the new peaks is called the **coupling constant** and is measured in **Hz**. If nuclei Y and Z are coupling through x bonds, we denote

the coupling constant ${}^{x}J_{Y\text{-}Z}$. The more bonds there are between coupling nuclei, the weaker the interaction gets and the smaller the coupling constant becomes.

- In fact, *J* is basically a rough measure of the *s* character of atoms in a molecule, because coupling is a nuclear effect mediated by electrons, and *s* orbitals are the only ones with a significant density near the nucleus.
- Certain splitting are *not* seen:
    - C–H coupling is **not usually seen**, because spectra are **broadband proton decoupled**; while the ^{13}C spectrum is being recorded, the sample is **irradiated** in such a way that the protons' spin move rapidly between "up" and "down". If this is done **fast enough**, the **couplings** to ^{13}C average to **0**, and **all coupling disappears**. We do this over a large range of frequencies so that *all* protons are rapidly interconverting (hence "broadband").

      This is usually done, despite the fact the coupled spectra carry more information, because (a) the signal strength becomes weaker, and signals could easily become lost in the background noise (b) in most compounds, the multiplets will overlap, and it would be hard to say which go together as a multiplet and which are caused by other nuclei.

      The **attached proton test** (APT) experiment (run on an NMR spectrometer) allows us to get the best of both worlds – the peaks from carbon atoms with an **even** number of **hydrogens** point one way, and those with an **odd** number point the other way. Which way is which can easily be identified by checking what way the $CDCl_3$ (with **0** hydrogens – an even number) peak is pointing.
    - **C–C coupling** is not usually seen, because of the low abundance of ^{13}C in naturally occurring carbon. For splitting to be seen, *both* carbons concerned must be ^{13}C, and since the natural abundance of ^{13}C is 1%, only 0.01% of molecules are in that situation. Coupling can be seen, however, if the sample is **artificially ^{13}C enriched**.
    - **Splittings** due to **coupling between *equivalent* nuclei** are not seen. They do interact, but the effect is never seen.

        - Splittings due to coupling with atoms with $\boldsymbol{I} > \frac{1}{2}$ are often not seen. This is because **relaxation** (a process which causes spin states rapidly interconvert) is very rapid for most nuclei with $\boldsymbol{I} > \frac{1}{2}$. As a result, all the couplings to that nucleus average to 0. However, there are a few examples of nuclei with $\boldsymbol{I} > \frac{1}{2}$ which do relax sufficiently slowly for coupling to be seen, and a common example is **deuterium**, with $\boldsymbol{I = 1}$.
    - Some elements exist as several isotopes, only some of which are spin active. These will results in one peak in its "normal" position, due to the $I = 0$ nuclei, but also some "satellites" around the main peak, due to the spin active nuclei. A common example is **platinum**, of which there are 6 naturally occurring isotopes. Only **^{195}Pt**, which is **34%** abundant, is spin active with $\boldsymbol{I} = \frac{1}{2}$.
- Proton NMR gets much more complicated. The same reference compound provides the 0, but protons resonate between 0 and 14ppm [note that the actual frequencies are significantly different – this is not the start of the carbon 0-200ppm scale!]. The approximate regions are as follows:

0 – 3	Saturated CH$_3$, CH$_2$, CH, not next to oxygen.
3 – 4.5	Saturated CH$_3$, CH$_2$, CH, next to oxygen.
4.5 – 6.5	Protons on unsaturated carbons in alkenes.
6.5 – 8.5	Protons on unsaturated carbons in benzene and aromatic hydrocarbons.
8.5 – 10.5	Protons on unsaturated carbons next to oxygen (anhydrides).