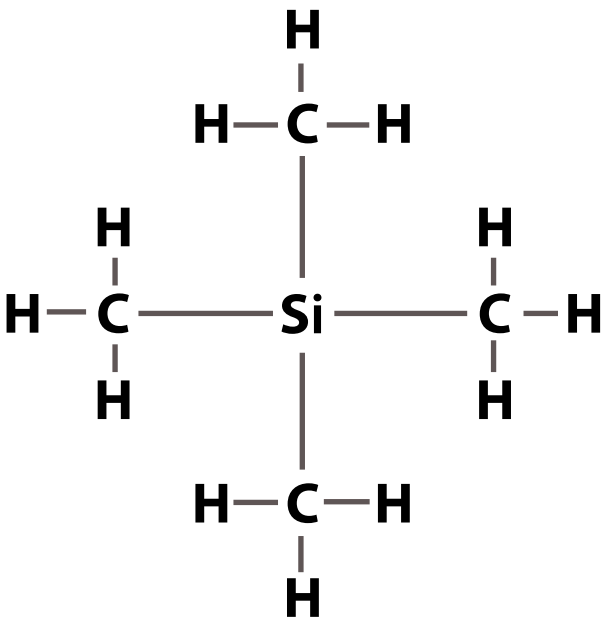
Chemical shift and TMS

Although the resonance frequencies of protons in different environments are different, they are very close together. Since it is very difficult to measure frequencies with enough precision to make out these small differences a reference compound is added to the sample. The reference compound is tetramethylsilane, TMS.

TMS



TMS is chosen for many reasons. The most important are:

- The hydrogen nuclei in TMS are highly shielded because silicon has a low electronegativity. As a result you would have to increase the magnetic field by the greatest amount to bring the hydrogen back into resonance.
- It gives one strong sharp peak because it is caused by the combined effect of 12 equivalent hydrogen atoms. (They are joined on exactly the same things in exactly the same way.)

The resonance frequencies of the protons in the sample are measured relative to the resonance frequency of TMS (which is given the value 0) and are described in terms of how far they are shifted from those of TMS.

The value of the external magnetic field that causes a particular proton to resonate depends on the radio frequency that the NMR spectrometer uses. To enable data from different instruments to be compared, chemical shift has been defined to be independent of applied magnetic field strength.

$$\text{Chemical shift, } \delta = \frac{\text{shift from TMS in Hz}}{\text{spectrometer frequency in Hz}} \times 100$$

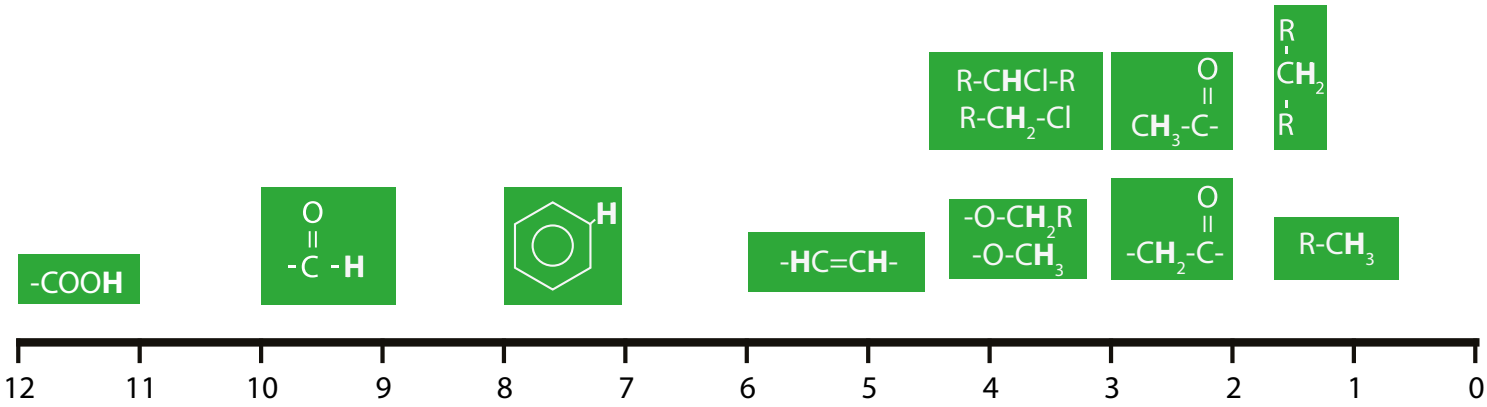
The unit of chemical shift, δ is ppm (parts per million).

In an NMR spectrum a peak at a chemical shift of 1.0 means that the hydrogen atoms which caused that peak need a magnetic field of one millionth less than the field needed by TMS to produce a resonance.

3. Chemical shift and TMS

The sample tested is usually measured in solution. It is important that the solvent used does not contain any simple hydrogen atoms because they would resonate and interfere with the NMR spectrum. For this reason tetrachloromethane, CCl_4, or deuterated trichloromethane, $CDCl_3$, are used since they are powerful solvents for organic compounds and do not contain ordinary hydrogen atoms. In $CDCl_3$ the hydrogen atoms have been replaced by its isotope deuterium.

Proton chemical shifts in aliphatic and aromatic environments



R represents an alkyl group.

The shifts are shown as ranges of values. The exact position varies depending on what else is near the particular group in the molecule.