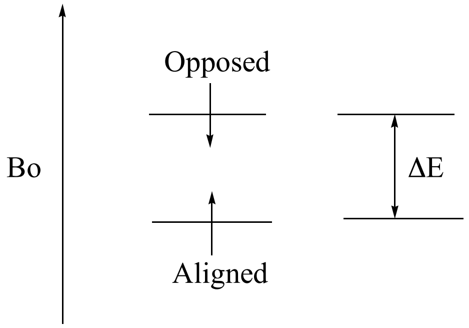
NMR Continued (focusing on ^{1}H NMR)

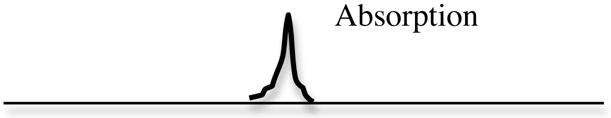
An NMR experiment requires a magnet (e.g., 14 Tesla), and a radio freq. transmitter. A tube containing the sample is placed inside the magnet - there are many sources that diagram this.

If you apply a magnetic field (B_O) to an isolated ^{1}H nucleus, there are two possible energy states: one with the nuclear spin **aligned** with the field and the other with it **opposed**.



Note: $\Delta E = h\nu$ (ν is in the radio frequency range)

Absorption from the lower energy state to the higher one becomes possible, which allows a spectrum to be observed:

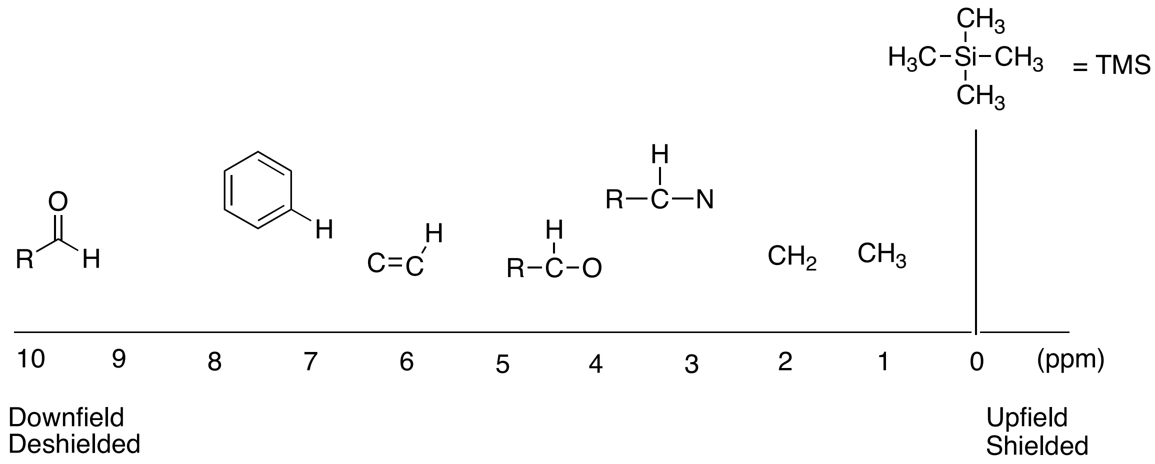


Chemical Shift

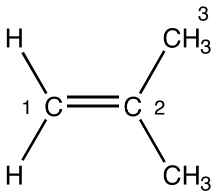
Chemical shift measures the change in the frequency of absorption. The chemical shift is typically shown in units of parts per million (ppm), and is compared to a reference. For ^{1}H NMR, this reference is usually tetramethylsilane (TMS).

The hydrogen atoms in TMS are highly shielded, and the signal for TMS is set at 0 ppm.

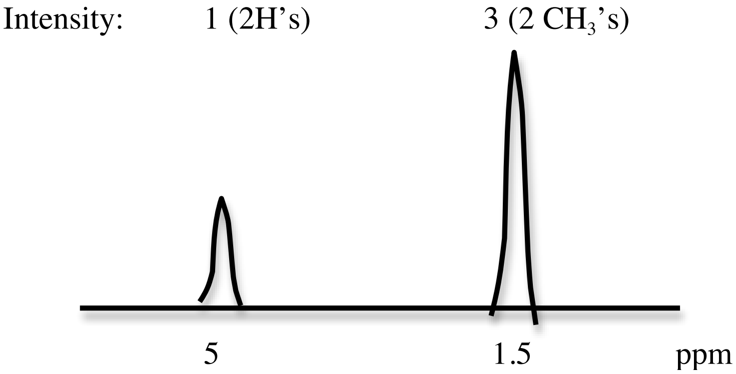
Deshielding occurs when electrons are pulled away from a hydrogen atom, which can be caused by the presence of an electron withdrawing group (e.g., a carbonyl). When the electrons are pulled away, the nucleus is more exposed to the magnetic field, resulting in a **downfield** chemical shift.



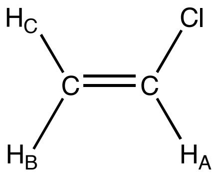
Examples:



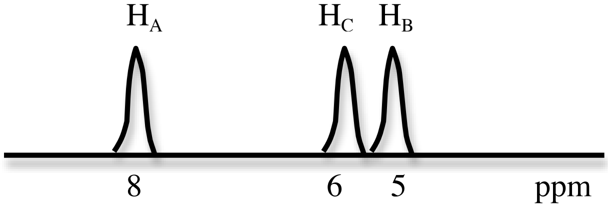
2-methylpropene



The intensity (and the peak area) depends on the number of hydrogen atoms. In this case, the intensity ratio is 2 : 6, which is the same as 1 : 3. Note that the two methyl groups are in the same chemical environment, as are the two hydrogen atoms on C1.

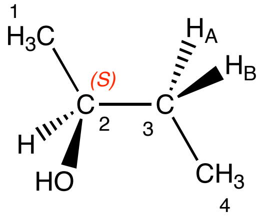


1-chloroethene aka
chloroethylene
vinyl chloride



H_B and H_C are different due to the distance from the Cl.
H_B is trans to the Cl, while H_C is cis.

Diastereotopic Protons

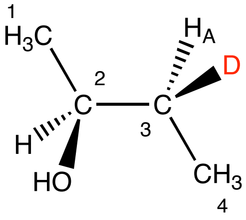


(S)-2-butanol
butan-2-ol

C-2 is a stereogenic centre, and there is no plane of symmetry in the molecule. H_A and H_B are in different chemical environments and have different chemical shifts, therefore they are **diastereotopic.**

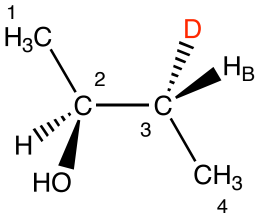
The methyl group shows only one signal because the C-C bond can freely rotate and NMR cannot distinguish between the H's. The barrier to bond rotation is only a few kilocalories per mole and about 15 to 20 kilocalories per mole of energy are available at room temperature. Hence rotation is very rapid.

If you substitute H_A or H_B with deuterium (labeled as D; an isotope of hydrogen with one proton and one neutron) you get diastereomers; therefore, these two hydrogens are diastereotopic. The chemical shifts of two diastereotopic protons may not always be very different.



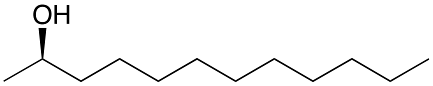
SS isomer

diastereomers



SR isomer

Example:

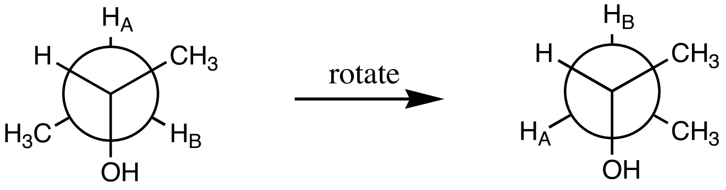


(R)-2-dodecanol

Every CH_2 group in this molecule has two diastereotopic protons.

Newman Projections

The round circle in the structure below is the back carbon (C-3 of 2-butanol) – carbon 2 is directly attached to it and is represented as the dot (point) where the bonds meet in front.



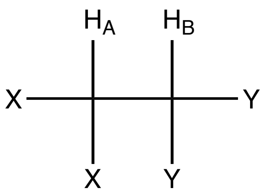
(H$_A$ is pro R, and H$_B$ is pro S)

Anti or Staggered conformation

Gauche conformation

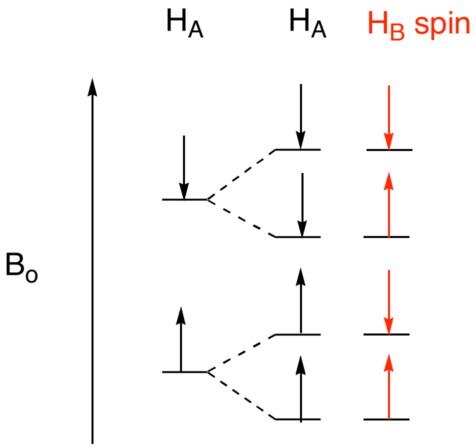
When there is a stereogenic center present, the two hydrogens, H_A and H_B, of the methylene (CH_2) group cannot be brought into the same chemical environment. Bond rotation can bring H_B to the position where H_A was before, as represented by the above Newman projections of the two conformations, but the CH_3 groups are occupying different positions and therefore the two methylene H's are not in the same chemical environment.

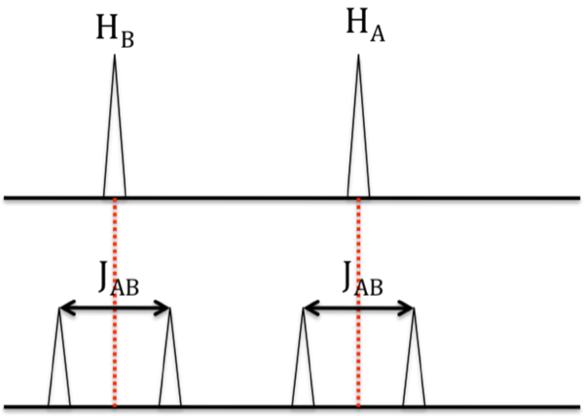
Spin-Spin Splitting (Coupling)



$X \neq Y$

H_A is not a singlet due to the influence of H_B on its spin, and vice versa. This diagram shows the energy for H_A, and the spins for H_B are shown (in red) only to show the effect on H_A





J_{AB} = **coupling constant** between atoms A and B, measured in Hertz (Hz)

The H_A coupling constant corresponds to the energy differences caused by the H_B proton in alignment with and in opposition to the field. This energy difference is equal to the effect that the H_A proton has on H_B, so both of these coupling constants are equal.

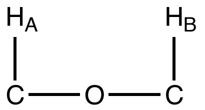
The coupled signal is centered around the same chemical shift value that the signal would have if there were no coupling.

Limitations of Coupling

1. 2 to 3 bonds separating nuclei (coupling is typically not seen between nuclei that are further apart than 3 bonds)
2. Usually no coupling across O, N, S, C=O

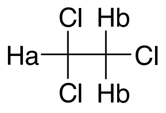
Note: there are exceptions to these rules

Example: In the following structure, H_A and H_B would not couple due to the oxygen

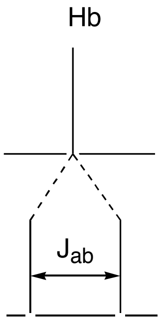


$\overset{H_A}{\overset{|}{C}}-O-\overset{H_B}{\overset{|}{C}}$

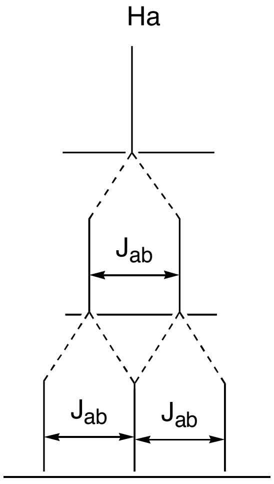
Example of coupling:



1,1,2-trichloroethane
achiral (not chiral)



doublet



triplet