

Introduction to NMR - Proton NMR

The different kinds of information one can obtain from an NMR spectrum can be classified in the following four ways: the number of different kinds of magnetically **different nuclei** in the compound, the **chemical shift** of the nuclei, the **coupling** of the nuclei to **neighboring** nuclei, and the number of absorbing nuclei via the **integration** of the peaks. Each of these will be discussed in turn.

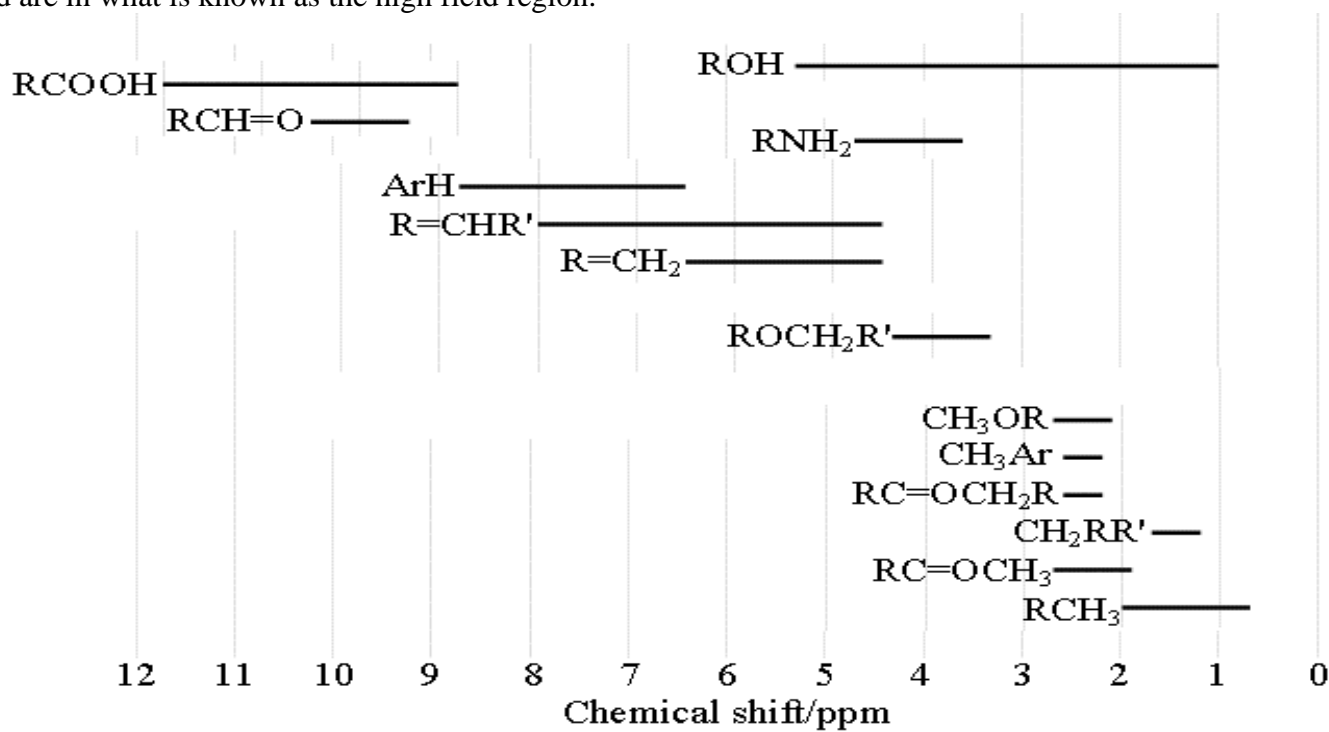
The **number of magnetically different nuclei** in a molecule will determine the number of peaks in the spectrum. For example, in the C1 to C4 alcohols a spectrum that contains just two peaks in the proton spectrum must either be methanol CH_3OH or *t*-butyl alcohol, $(\text{CH}_3)_3\text{COH}$. Because all three hydrogens in the methyl group of methanol and all nine hydrogens in the methyl groups of *t*-butyl alcohol are equivalent, they will each show as a single peak in the proton (^1H) spectrum. How many different peaks will there be in the carbon spectra of methanol and *t*-butyl alcohol?

Chemical Shift (δ) is the property of the absorbing nuclei that results from the electronic environment around the atom. Measured in parts per million, with **high** chemical shift numbers being associated with nuclei with **low** electron density. Below, “B” is field strength, and “v” is frequency.

$$\delta = (1,000,000) \frac{(\text{ref B} - \text{sample B})}{\text{ref B}} \text{ in ppm} \quad \delta = (-1,000,000) \frac{(\text{ref v} - \text{sample v})}{\text{ref v}} \text{ in ppm}$$

Proton chemical shifts (<http://chem.ch.huji.ac.il/nmr/techniques/1d/row1/h.html>):

Proton chemical shifts generally range from 0 to 12 ppm and are referenced from tetramethylsilane (TMS, $(\text{CH}_3)_4\text{Si}$). The lower chemical shifts are associated with protons that have a high electron density and are in what is known as the high field region.



As the picture above shows, each functional group carbon has associated with it a range of chemical shift values. The functional groups are discussed in the “Notes” under “Organic Chemistry Information” on the course website. While some are quite narrow (e.g. the methyl group attached to a benzene ring (CH_3Ar)), others like alcohols are very wide. Beyond this, there are always several functional groups whose range overlap. For this reason, H-1 spectra such are more helpful in **excluding** possible functional groups from an

unknown, rather than identifying a prospective group. Thus, the position of an absorption (peak) limits the possible functional groups to choose from, **but will not identify it**. One final caveat is that the effects of functional groups are largely additive. That is, having two chlorine atoms attached to a carbon will roughly double the shift change from having only one attached.

Coupling is the interaction of a nucleus with neighboring nuclei and results in a pattern of peaks. For the simplest and common spectra, number of peaks is $n+1$ where n is the number of neighboring, equivalent $I = \frac{1}{2}$ nuclei (I is the nuclear spin quantum number). For nuclei with spins other than $\frac{1}{2}$ (e.g. deuterium or boron), this rule does not work.

Coupling in proton spectra primarily arises from coupling of the protons on one nucleus (usually carbon) to the protons on an adjacent nucleus that is magnetically different (also usually carbon). If the protons doing the splitting have the same coupling constant, splitting will result in $n+1$ peaks where n is the number of neighboring protons. The intensity of the peaks will follow Pascal's triangle:

			1		
		1		1	
	1		2		1
1		3		3	
	1		3		1

Thus, a **triplet** will indicate **two** neighboring protons, a **quartet** will indicate **three** neighboring protons, etc. The coupling constant associated with this splitting is denoted as an H-H coupling through three bonds: $^3J_{H-H}$. **Coupling constants** are the separation between peaks (in Hz) caused by coupling. The magnitude of the constant is about 5-15 Hz and is independent of the magnetic field of the spectrometer.

Decoupling is removing the coupling information (by irradiating the molecule at the neighboring nuclei's absorbing frequency) from a spectrum. Carbon spectra are usually obtained with hydrogen decoupling turned on. The reason for this will be gone into detail in the next lecture. As a result, peaks in a "normal" C-13 spectrum do not show coupling. Similarly, protons on an oxygen usually rapidly exchange with other -OH protons and are "exchange decoupled" and usually (but not always) show up as single (decoupled) peaks.

Integration is the area under an NMR peak or set of peaks. The integration is proportional to the number of nuclei involved in the absorption. Thus, if there are two peaks in a spectrum, one with twice the integration of the other, the first indicates twice as many protons as the second.

1. Solve the following structures from their proton spectra:

Molecular Formula	chemical shifts (multiplicity, integration) multiplicity: d-doublet, t-triplet, q-quartet, m-multiplet
a) C ₇ H ₈ O	2.43 (s, 1), 4.58 (s, 2), 7.28 (m, 5)
b) C ₄ H ₈ Br ₂	1.9 (s, 6), 3.9(s, 2)
c) C ₃ H ₇ Br	1.1 (t, 3), 1.9 (m, 2), 3.4(t, 2)
d) C ₁₁ H ₁₆	1.2 (s, 9), 2.3 (s, 3), 7.2 (m, 4)
e) C ₄ H ₁₀ O	1.2 (t, 3), 3.5(q, 2)
f) C ₄ H ₈ O ₂	1.3 (t, 3), 2.0(s, 3), 4.1 (q, 2)
g) C ₄ H ₈ O ₂	1.0 (t, 3), 1.7(m, 2), 2.3 (t, 2), 11.5 (s, 1)