Introduction to NMR-Proton NMR

The different kinds of information one can get from an NMR spectrum can be classified in the following 4 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-butanol, $(CH_3)_3COH$. Because all three H in the methyl group of methanol and all nine H in the methyl groups of t-buthanol are equivalent they will each show as a single peak in the proton spectrum. How many different peaks will there be in the carbon spectra of methanol and t-butanol?

Chemical Shift- the property of the absorbing nuclei that results from the electronic environment around the atom. Measured in parts per million and **high** chemical shift numbers are associated with nuclei **low** electron density.

$$\delta = 1000000\frac{(\text{ref B- sample B})}{(\text{ref B})} \text{ in ppm} \qquad = -1000000\frac{(\text{ref } \nu\text{- sample } \nu)}{(\text{ref } \nu)} \text{ in ppm}$$

Proton chemical shifts (http://drx.ch.huji.ac.il/nmr/techniques/1d/h.html):

Proton chemical shifts generally run from 0 to 12 ppm and are referenced from TMS (tetra methyl silane). 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.

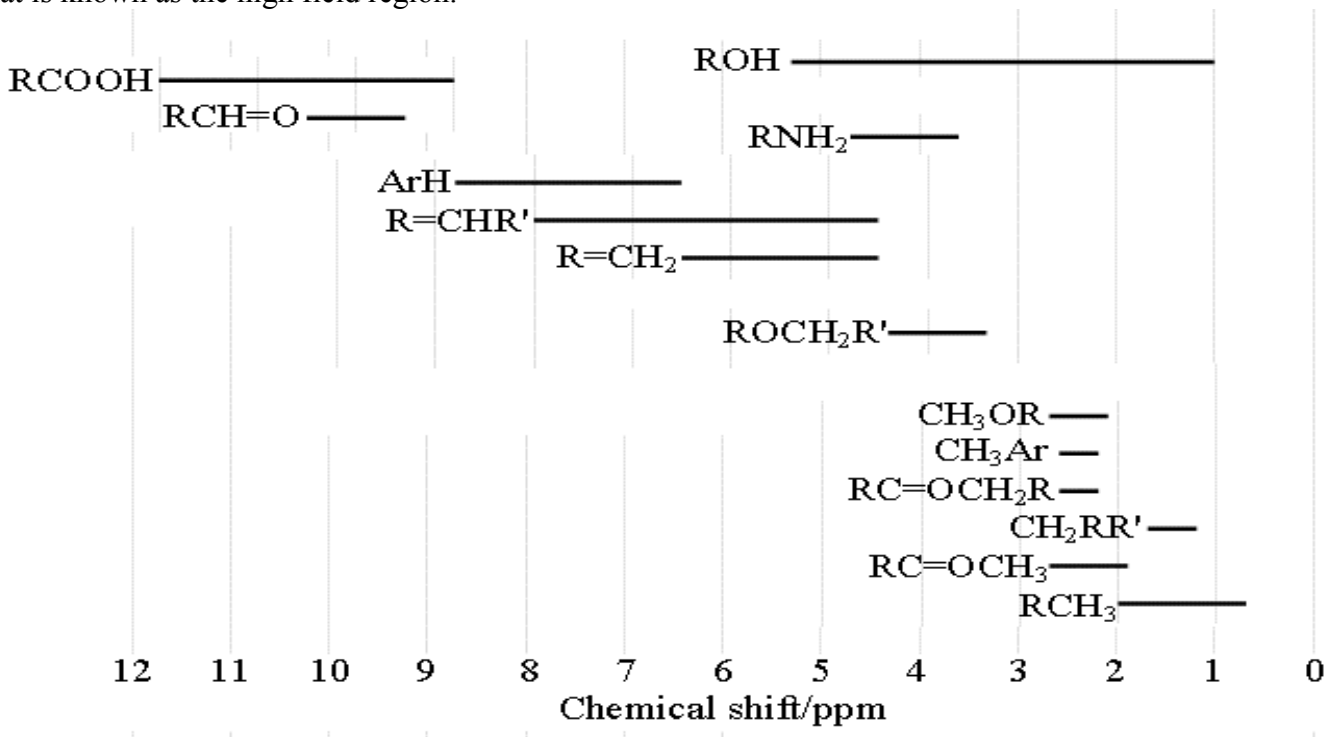

Table of H1 Substituent parameters on tetrahedral C (methane shift =.23 ppm)

Group	α	β	Group	α	β
-R	0.62	.01	-Cl	2.80	0.70
-C(=0)OR	1.77	.33	-OR or -OH	2.97	0.35
-C(=O)R	1.87	.33	-OC(=O)(R/H)	3.40	.45
-I	1.94	.90	-OPh	3.60	0.80
-Ph	2.00	.33	-NO2	3.82	.75
-Br	2.47	.95	-F	4.00	0.70

Sample Calculation. Predict the chemical shifts in ethanol: CH_3CH_2OH.

predicted shifts = .23 +2.97+.62 = 3.82 (exp 3.69)
= .23 + .62+.35 = 1.20 (exp 1.23)
the chemical shift of the -OH depends on concentration, solvent, H-bonding and can appear any where from.5 to 5.

Coupling-Interaction of the nucleus with neighboring nuclei. 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=1/2 nuclei. NOTE the restriction on the use of this rule.

Coupling Constants-The separation between peaks (in Hz) caused by coupling.

Coupling in proton spectra is primarily due to coupling of the protons to neighboring protons with different chemical shifts. If the protons doing the splitting have the same coupling constant, splitting will result in 2n+1 peaks where n is the number of neighboring protons. The intensity of the peaks will follow Pascal triangle:

1
1 1
1 2 1
1 3 3 1
etc

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 a H-H coupling through three bonds: $^3J_{H-H}$. The magnitude of the constant is about 5-15 Hz and independent of the magnetic field of the spectrometer.

Decoupling-Removing the coupling information (by irradiating the molecule at the neighboring nuclei's frequency). Carbon spectra are usually run with hydrogen decoupling on. The reason for this will be gone into in detail in the next lecture. But 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- the area under a NMR peaks or a set of peaks. The integration is proportional to the number of nuclei involved in the absorption.

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_7H_8O	2.43(s,1) 4.58 (s,2) 7.28 (m, 5)
b) $C_4H_8Br_2$	1.9(s,6) 3.9(s,2)
c) C_3H_7Br	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) $C_4H_{10}O$	1.2(t,3) 3.5(q,2)
f) $C_4H_8O_2$	1.3(t,3) 2.0(s,3) 4.1(q,2)
g) $C_4H_8O_2$	1.0(t,3) 1.7(m,2) 2.3(t,2) 11.5(s,1)