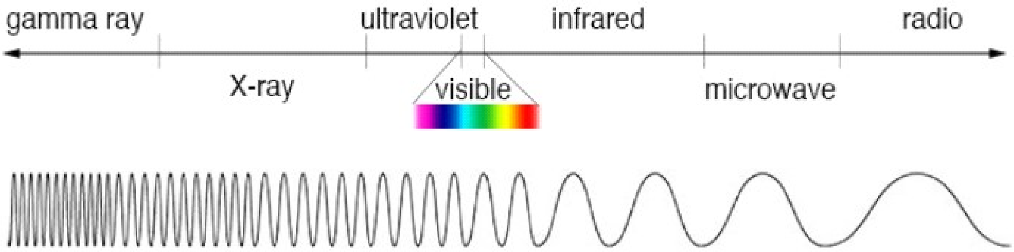
Organic Chemistry I, CHM 3140, Dr. Laurie S. Starkey, Cal Poly Pomona

Nuclear Magnetic Resonance (NMR) Spectroscopy - Chapter 15 (Klein)

The Electromagnetic Spectrum

wavelength:
longer/shorter
Energy:
higher/lower
frequency:
higher/lower

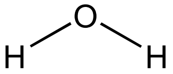


(Image Credit: NASA's Imagine the Universe)

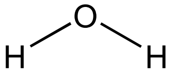
wavelength:
longer/shorter
Energy:
higher/lower
frequency:
higher/lower

Infrared (IR) spectroscopy reveals which **functional groups** are present in a molecule. When certain wavelengths of IR light are absorbed, specific bonds are vibrationally excited: they stretch or bend. For example, ~1700 cm^{-1} light will cause a carbonyl (C=O) bond to stretch, so an absorption in that region indicates the presence of a ketone or aldehyde functional group.

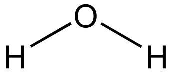
bending:



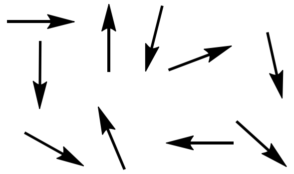
symmetric stretching:



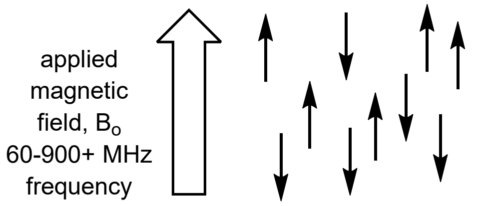
asymmetric stretching:



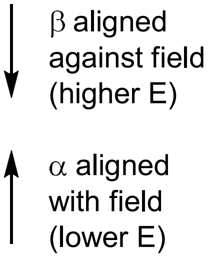
Acquiring an NMR spectrum (15.1, 15.2) Like all spectroscopic methods, NMR involves the use of electromagnetic energy to excite a molecule. By observing this interaction, we can learn something about the structure of the sample. In NMR spectroscopy, radio frequency waves are used (60,000,000 Hz or 60 MHz, also 200, 360, 500, etc.) and the result is a change in the spin of a nucleus. The nuclei which can be observed include ^{1}H "proton NMR," ^{13}C "C-13 NMR," ^{15}N, ^{19}F, ^{31}P. These all have magnetic moments (like tiny magnets) and will interact with an applied magnetic field. Each of these nuclei has a spin quantum number I=1/2 and has two spin states of equal energy. When a magnetic field is applied, these spin states will align **with** (α) or **against** (β) the field. Those aligned with the field are lower in energy than those aligned against the field; the difference in energy between α and β is proportional to the strength of the magnet used. Application of radio waves at just the right frequency will cause certain nuclei to absorb energy and "flip" from the α to the β spin state. As the excited nucleus relaxes back to the ground state, a signal is recorded and an NMR spectrum can be obtained. The frequency of this energy transition depends on the electronic environment of the nucleus.

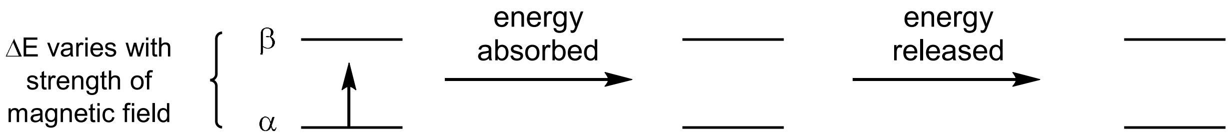


nuclear spins random
(all have equal energy)

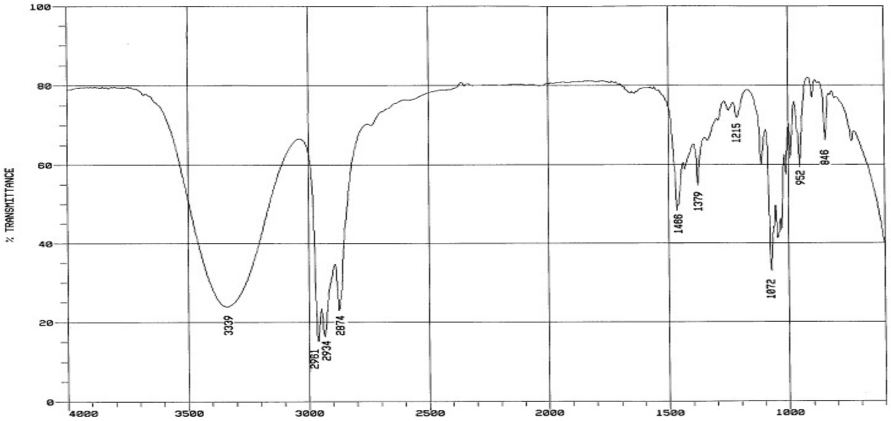


nuclear spins aligned with or against the field
(these two states have different energy)

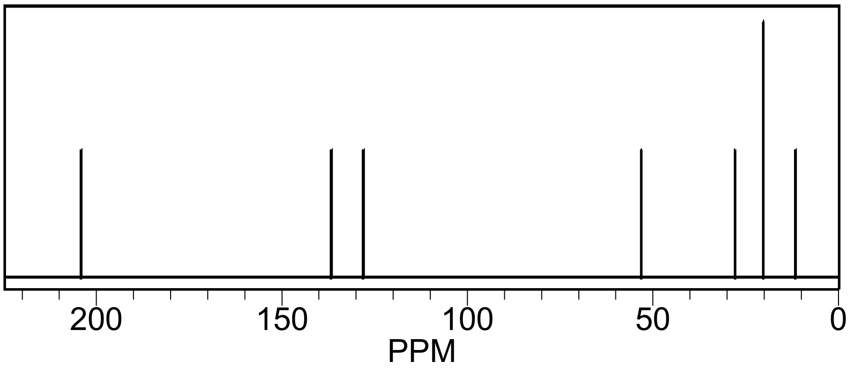




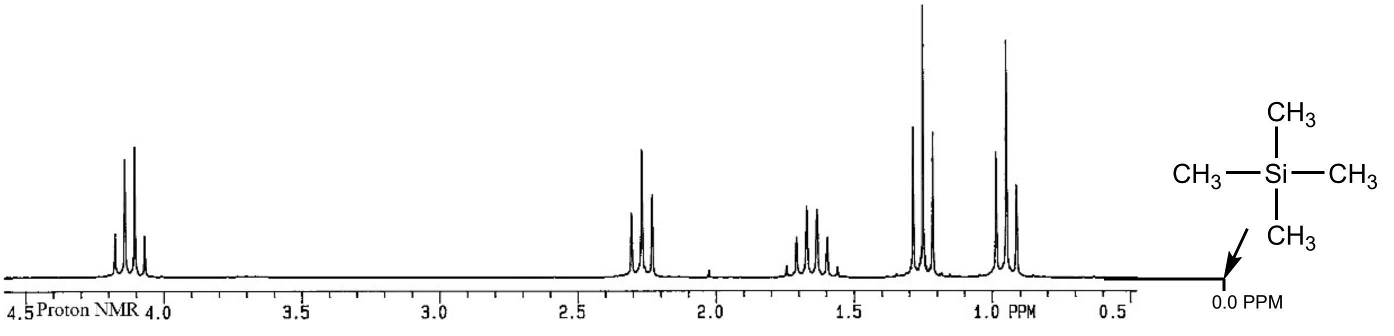
IR spectrum shows **functional groups** *(see Klein Chapter 14 & CHM 3140L lab)*



^{13}C NMR spectrum shows how many different types of carbons are in a molecule, and whether each carbon is in an electron-rich or electron-deficient environment.



^{1}H NMR (Proton NMR) spectrum



tetramethylsilane (TMS) serves as a reference, $\delta = 0$

Information obtained from a ^{1}H "Proton" NMR spectrum (15.3):

1) **# of signals** indicates the number of different types of hydrogens (chemical equivalence).

2) **Integration** or peak area indicates how many hydrogens are in each signal. It is given as a ratio.

3) **Chemical shifts** are given as δ (delta) values, in ppm (~0-10). The chemical shift indicates the electronic environment of the hydrogens (electron-rich/shielded or electron-poor/deshielded).

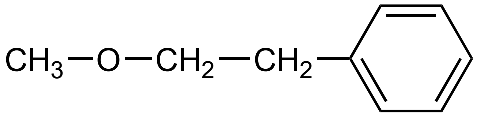
4) **Splitting patterns** indicate the # of *neighboring* hydrogens. The magnitude of the coupling constants (given as *J* values) depend on the spatial relationship (dihedral angle) of the two protons.

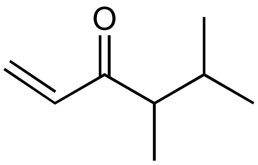
1) Number of NMR Signals: chemical equivalence of protons (or carbons) (15.4)

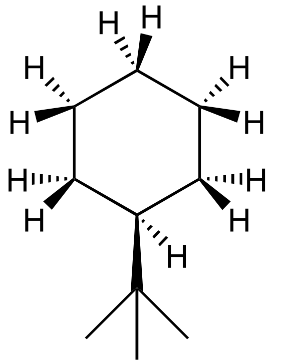
How many unique H's (label a, b, c...) and C's (label 1, 2, 3...) are on each compound?

8 H atoms, so 8 signals?

$CH_3-CH_2-CH_3$





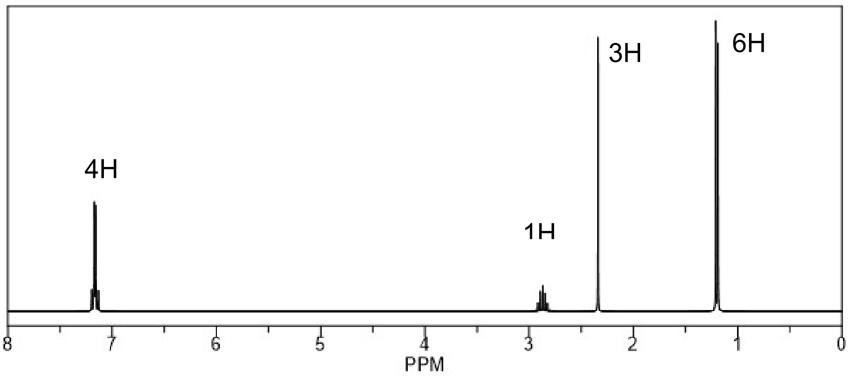


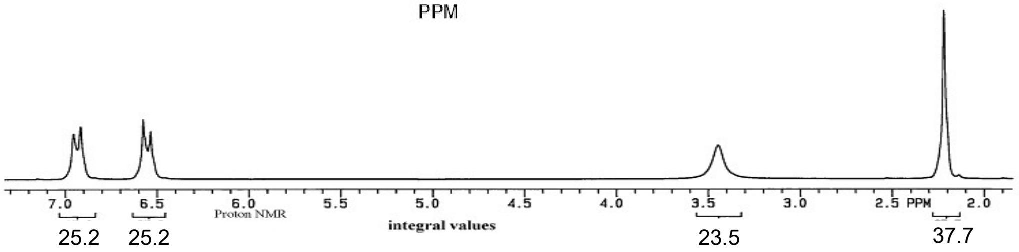
homotopic H's: equivalent in NMR (same chemical shift/δ value)

enantiotopic H's: equivalent in NMR (same chemical shift/δ value)

diastereotopic H's: not equivalent in NMR (different δ values, *J* values, split each other, etc.)

2) Peak Integration: number of protons giving rise to signal (15.6)

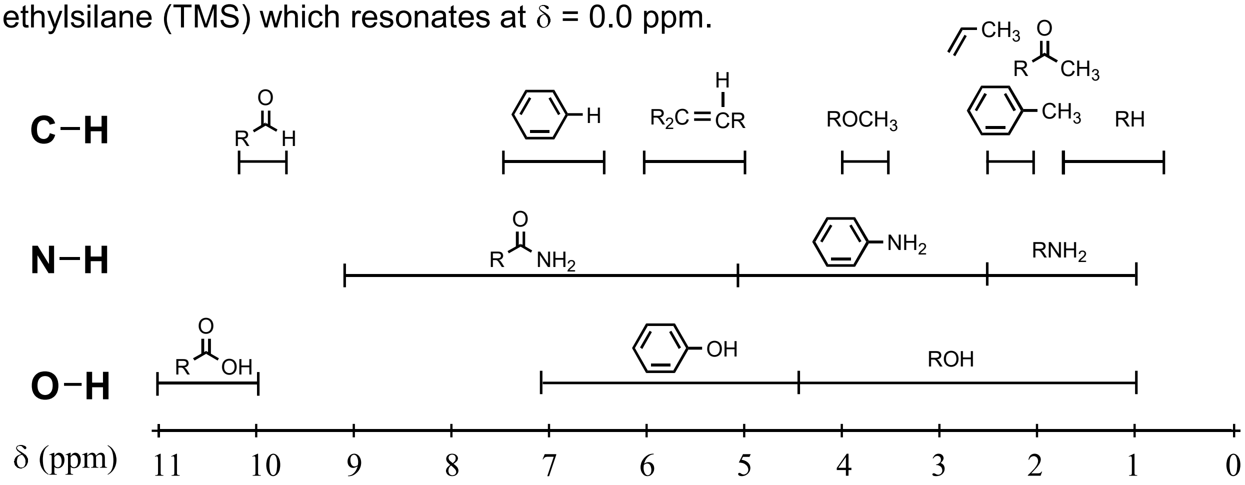




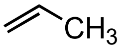
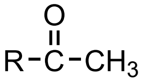
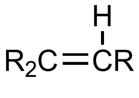
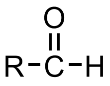
see SkillBuilders 15.1, 15.2, 15.4

3) Chemical Shift (δ value): where signal occurs on spectrum (15.5)

Delta values are given in parts per million (ppm) relative to the reference compound tetramethylsilane (TMS) which resonates at δ = 0.0 ppm.

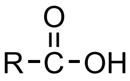
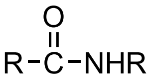


Protons on Carbon

Type of C-H	δ (ppm)	Description of Proton
$R-CH_3$	0.9	alkyl (methyl)
$R-CH_2-R$	1.3	alkyl (methylene)
R_3C-H	1.5-2	alkyl (methine)
	1.8	allylic (C is next to a pi bond)
 $R-\overset{O}{\overset{\parallel}{C}}-CH_3$	2-2.3	α to carbonyl (C is next to C=O)
$Ar-CH_3$	2.3	benzylic (C is next to a benzene ring)
$RC\equiv C-H$	2.5	alkynyl
R_2N-CH_3	2-3	α to nitrogen (C is attached to N)
$R-CH_2-X$	3-3.5	α to halogen (C attached to Cl/Br/I)
$RO-CH_3$	3.8	α to oxygen (C is attached to O)
$R-CH_2-F$	4.5	α to fluorine (C is attached to F)
 $R_2C=\overset{H}{\overset{\vert}{C}}R$	5-5.3	vinylic (H is attached to alkene C)
$Ar-H$	7.3	aromatic (H is on a benzene ring)
 $R-\overset{O}{\overset{\parallel}{C}}-H$	9.7	aldehyde (H is on C=O)

Note: aldehyde proton (-CHO) has small coupling with neighboring H's, so it usually appears as a ***singlet***

Protons on Oxygen/Nitrogen*

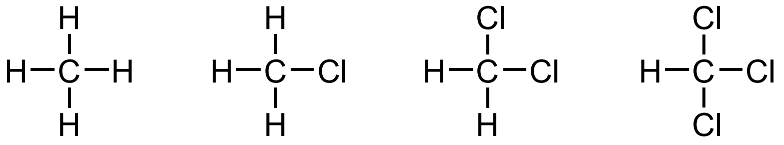
Type of H	δ (ppm)	Description
ROH	0.5-5	alcohol
ArOH	4-7	phenol
 $R-\overset{O}{\overset{\parallel}{C}}-OH$	10-13	carb. acid
RNH_2	0.5-5	amine
$ArNH_2$	3-5	aniline
 $R-\overset{O}{\overset{\parallel}{C}}-NHR$	5-9	amide

Protons on N or O typically have wide ranges of expected chemical shifts; the actual δ value depends on the solvent used, the concentration, etc. Because these protons are acidic and therefore, exchangeable, they may be broad peaks and usually have no splitting (they don't couple with neighboring protons.* ***Typically, OH and NH appear as broad singlets**. If a deuterated protic solvent is used (e.g., D_2O or CD_3OD), then the NH and OH protons will exchange with deuterium and the peaks shrink or disappear entirely, because D (^2H) does not show up in the ^1H NMR spectrum.*

R = alkyl group

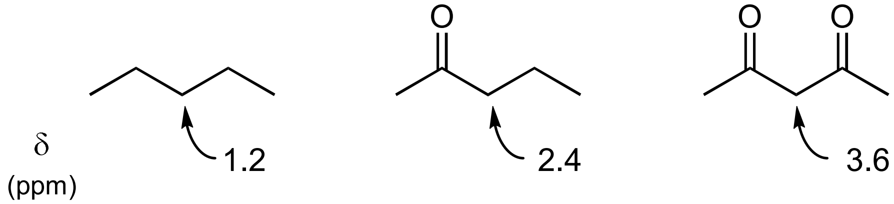
Ar = aromatic ring, such as benzene

Electron-withdrawing effects are additive

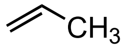


δ (ppm)	0.9	3.1	5.5	7.3

(Why no CCl_4 listed?)

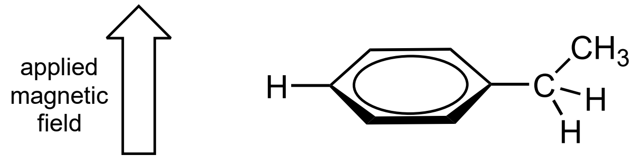


Effects of pi electrons on chemical shift (anisotropy)

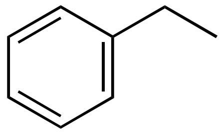
Type of C-H	δ (ppm)	Description of Proton
	1.8	allylic (C is next to a pi bond)
Ar−CH_3	2.3	benzylic (C is next to benzene ring)
$R_2C=\overset{H}{C}R$	5-5.3	vinylic (H is attached to alkene C)
Ar−H	7.3	aromatic (H is on a benzene ring)

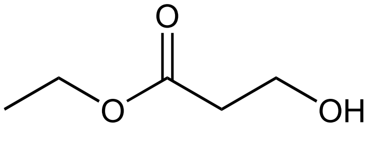
Why are protons that are on pi bonds or adjacent to pi bonds shifted downfield?

The external magnetic field causes the circulation of pi electrons which generates a ring current. These **anisotropic effects** cause **deshielding**, so protons attached to the benzene ring ~7 ppm.



Estimate the **integration** and **chemical shift** for each unique proton:





see SkillBuilder 15.3

4) Shape of the Signal: splitting patterns and the n+1 rule (15.7)

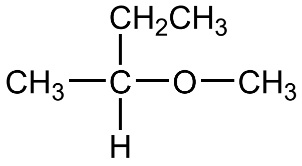
Each proton acts like a tiny magnet, causing a splitting of its neighbors' signals. Neighboring protons are said to be "coupled" and the size of the splitting is described by the coupling constant, *J*.

Exceptions: OH, NH and aldehyde (-CHO) protons typically do not couple with neighboring protons and typically appear as a singlet (no splitting).

see SkillBuilder 15.5

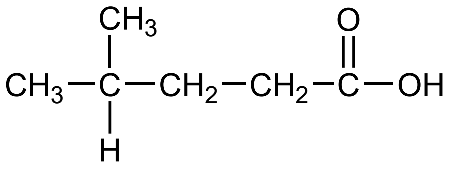
# of nonequivalent neighboring H's (**n**)	# peaks (**n+1**)	ratio of peaks
0		
1		
2		
3		
4		
5		
6		

Putting it all together: predicting a ^{1}H NMR spectrum (15.8, 15.9)



$CH_3-CH(CH_2CH_3)-O-CH_3$

proton	#H, split	δ (ppm)



$CH_3-CH(CH_3)-CH_2-CH_2-C(=O)-OH$

proton	#H, split	δ (ppm)

see SkillBuilders 15.6, 15.7

Match the labeled peaks in the NMR with the protons on the given structure.