6. SPECTROSCOPY: How do we know what organic molecules look like?

There are 3 main tools that you will use/see/encounter as budding young chemists that will help you determine the structures of organic molecules. These tools are Infrared Spectroscopy (IR), Mass Spectrometry (MS) and Nuclear Magnetic Resonance Spectroscopy (NMR). There are entire courses that deal with these instrumental techniques. They are constantly evolving as technology and software improve. So, I will just give you the basics here…just enough to make you dangerous…just enough to carefully think through every problem and get it wrong (let's hope not).

So, I give you an unknown compound (pure) and I ask you "what is it". You look back with a blank stare. There are three basic things you would like to know in order to begin to answer the question. They would be, in no particular order,…

a. What functional groups are present
b. The molecular weight
c. How the functional groups are assembled

…that would about cover it…Right?…Ok, maybe the molecular formula too.

6.1. InfraRed: Dance Hall Days.

Molecules dance. Yes they do. They dance. Ok, they vibrate, they bend, they stretch, they rotate…they do a lot of gymnastics. They tend to do these gymnastics when excited by light of particular energy.

Organic molecules absorb light (infrared, ultraviolet, etc.) at particular wavelengths based on different vibrational modes unique to the specific functional groups and structural features. The energy of an infrared photon can be calculated from the Planck energy equation…

$$E = h\nu$$

where $h = 6.6 \times 10^{-34}$ joule*second and ν = frequency of the photon. The frequency, ν, and speed of light, c, are related through the relation…

$$c = \lambda\nu$$

…where $c = 3.0 \times 10^{8}$ meter/second and λ = wavelength for the light. These two equations can be used to identify a common spectroscopic unit called *wavenumber, v* , which is equal to $1/\lambda$…

$$E = h\nu = hc/\lambda = hcv$$

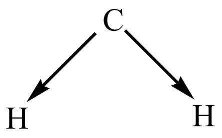
$$v = \text{wavenumber} = \text{has units of } (\text{cm}^{-1}) = 1/\lambda$$

Since molecules are flexible, moving collections of atoms constantly oscillating around average positions, bond lengths and bond angles are continuously changing due to this vibration. A molecule absorbs infrared radiation when the vibration of the atoms in the molecule produces an oscillating electric field with the same frequency as the frequency of incident IR "light".

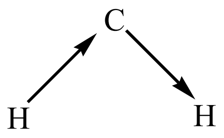
All of the motions can be described in terms of two types of molecular vibrations; stretching and bending. Stretches change the lengths of bonds while bends changes the bond angles. Bends and stretches can have variations. For example, a stretch can be symmetric or asymmetric. Bending can occur in the plane of the molecule or out of plane; it can be scissoring, like blades of a pair of scissors, or rocking, where two atoms move in the same direction.

Different stretching and bending vibrations can be visualized by considering the CH_2 group in hydrocarbons. The arrows indicate the direction of motion. The stretching motions require more energy than the bending ones.

inplane stretches

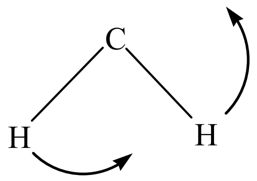


symetrical

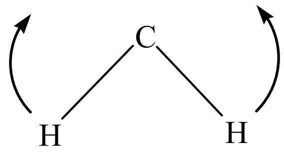


asymetrical

inplane bends



rocking



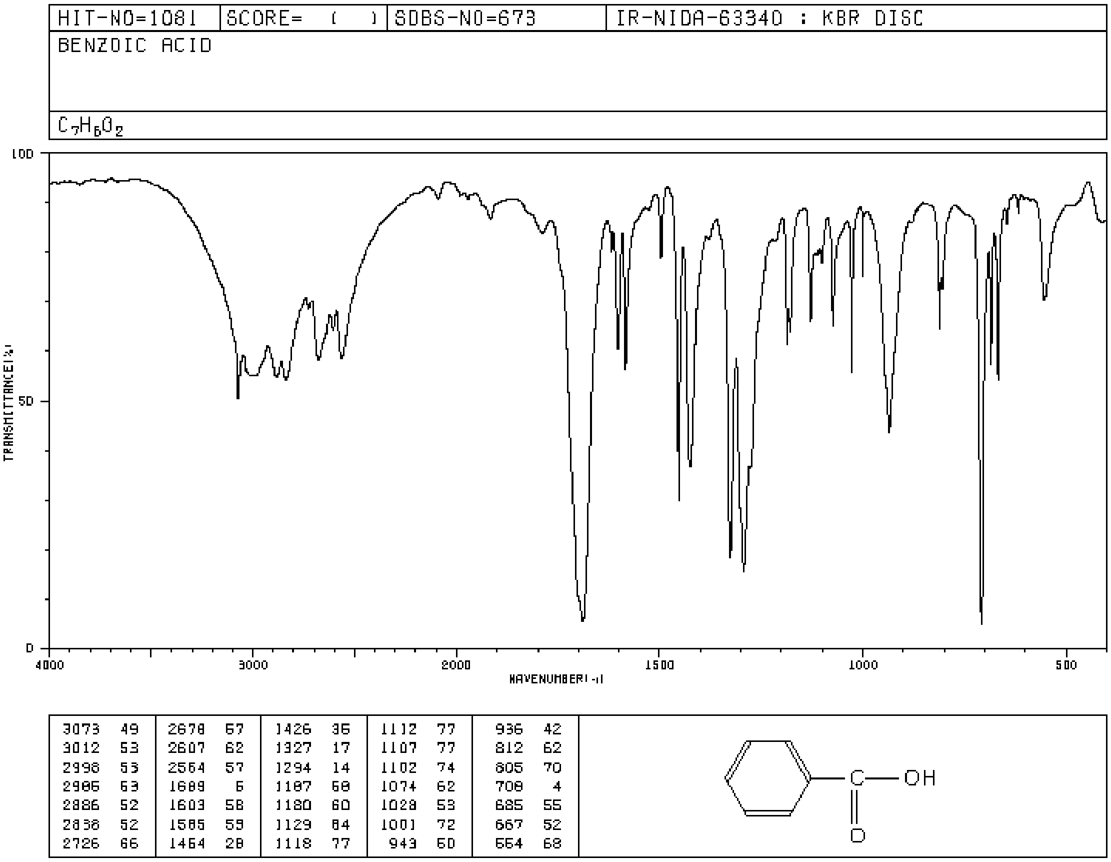
scissoring

Again, molecules absorbs a unique set of IR light frequencies which match the natural vibrational modes of the molecule. The resulting IR spectrum is often likened to a person's fingerprints. Even though an IR spectrum is characteristic for an entire molecule, there are certain groups of atoms in a molecule that give rise to absorption bands at or near the same wavenumber, regardless of the rest of the structure of the molecule. These persistent characteristic bands enable you to identify major structural features of the molecule after a quick inspection of the spectrum and the use of a correlation table. The correlation table is a listing of functional groups and their characteristic absorption frequencies.

Table of IR Absorptions *Functional Group*	*Characteristic Absorption(s)* (cm^{-1})	*Notes*
Alkyl C-H Stretch	2950 - 2850 (m or s)	Alkane C-H bonds are fairly ubiquitous and therefore usually less useful in determining structure.
Alkenyl C-H Stretch Alkenyl C=C Stretch	3100 - 3010 (m) 1680 - 1620 (v)	Absorption peaks above 3000 cm^{-1} are frequently diagnostic of unsaturation
Alkynyl C-H Stretch Alkynyl C≡C Stretch	~3300 (s) 2260 - 2100 (v)	
Aromatic C-H Stretch Aromatic C-H Bending Aromatic C=C Bending	~3030 (v) 860 - 680 (s) 1700 - 1500 (m,m)	
Alcohol/Phenol O-H Stretch	3550 - 3200 (broad, s)	See "Free vs. Hyrdogen-Bonded Hydroxyl Groups" in the Introduction to IR Spectra for more information
Carboxylic Acid O-H Stretch	3000 - 2500 (broad, v)	
Amine N-H Stretch	3500 - 3300 (m)	Primary amines produce two N-H stretch absorptions, secondary amides only one, and tetriary none.
Nitrile C≡N Stretch	2260 - 2220 (m)	
Aldehyde C=O Stretch Ketone C=O Stretch Ester C=O Stretch Carboxylic Acid C=O Stretch Amide C=O Stretch	1740 - 1690 (s) 1750 - 1680 (s) 1750 - 1735 (s) 1780 - 1710 (s) 1690 - 1630 (s)	The carbonyl stretching absorption is one of the strongest IR absorptions, and is very useful in structure determination as one can determine both the number of carbonyl groups (assuming peaks do not overlap) but also an estimation of which types.
Amide N-H Stretch	3700 - 3500 (m)	As with amines, an amide produces zero to two N-H absorptions depending on its type.

All figures are for the typical case only -- signal positions and intensities may vary depending on the particular bond environment.

The infrared spectrum for a molecule is a graphical display that shows the frequencies of IR radiation absorbed on the x axis and the % of the incident light that passes through the molecule without being absorbed (i.e., transmission) on the y axis. The spectrum has two regions. The *fingerprint* region (1250 cm^{-1} to 400 cm^{-1}) is unique for a molecule and the *functional group* region (4000 cm^{-1} to 1250 cm^{-1}) is similar for molecules with the same functional groups.



HIT-NO=1081	SCORE= ( )	SDBS-NO=673	IR-NIDA-63340 : KBR DISC

BENZOIC ACID

$C_7H_6O_2$

3073	49	2678	67	1426	36	1112	77	936	42
3012	53	2607	62	1327	17	1107	77	812	62
2998	53	2564	57	1294	14	1102	74	805	70
2986	63	1689	6	1187	68	1074	62	708	4
2886	52	1603	58	1180	60	1028	53	685	55
2838	52	1585	59	1129	84	1001	72	667	52
2726	66	1464	28	1118	77	943	60	664	68

Every molecule will have its own characteristic spectrum. The bands (peaks) that appear depend on the types of bonds and the structure of the molecule. Study the sample spectra in your books, noting similarities and differences, and relate these to structure and bonding within the molecules.

When you analyze the spectra, it is easier if you follow simple series of steps.

1. Look first for the carbonyl C=O band. Look for a strong band at 1820-1660 cm-1. This band is usually the most intense absorption band in a spectrum. It will have a medium width. If you see the carbonyl band, look for other bands associated with functional groups that contain the carbonyl by going to step 2. If no C=O band is present, check for alcohols and go to step 3.
2. If a C=O is present you want to determine if it is part of an acid, an ester, or an aldehyde or ketone. At this time you may not be able to distinguish aldehyde from ketone and you will not be asked to do so.

ACID	Look for indications that an O-H is also present. It has a broad absorption near 3300-2500 cm^{-1}. This actually will overlap the C-H stretch. There will also be a C-O single bond band near 1100-1300 cm^{-1}. Look for the carbonyl band near 1725-1700 cm^{-1}.

ESTER	Look for C-O absorption of medium intensity near 1300-1000 cm^{-1}. There will be no O-H band.
ALDEHYDE	Look for aldehyde type C-H absorption bands. These are two weak absorptions to the right of the C-H stretch near 2850 cm^{-1} and 2750 cm^{-1} and are caused by the C-H bond that is part of the CHO aldehyde functional group. Look for the carbonyl band around 1740-1720 cm^{-1}.
KETONE	The weak aldehyde CH absorption bands will be absent. Look for the carbonyl C=O band around 1725-1705 cm^{-1}.

3. If no carbonyl band appears in the spectrum, look for an alcohol O-H band.

ALCOHOL	Look for the broad OH band near 3600-3300 cm^{-1} and a C-O absorption band near 1300-1000 cm^{-1}.

4. If no carbonyl bands and no O-H bands are in the spectrum, check for double bonds, C=C, from an aromatic or an alkene.

ALKENE	Look for weak absorption near 1650 cm^{-1} for a double bond. There will be a CH stretch band near 3000 cm^{-1}.
AROMATIC	Look for the benzene, C=C, double bonds which appear as medium to strong absorptions in the region 1650-1450 cm^{-1}. The CH stretch band is much weaker than in alkenes.

5. If none of the previous groups can be identified, you may have an alkane.

ALKANE	The main absorption will be the C-H stretch near 3000 cm^{-1}. The spectrum will be simple with another band near 1450 cm^{-1}.

6. If the spectrum still cannot be assigned you may have an alkyl bromide.

ALKYL BROMIDE	Look for the C-H stretch and a relatively simple spectrum with an absorption to the right of 667 cm^{-1}.

6.2 Nuclear Magnetic Resonance: Good bonds make meddling neighbors

Like electrons, nuclei have spin. All nuclei have a charge. In some nuclei, this charge "spins" on the nuclear axis, thus generating a magnetic dipole along the axis. The angular momentum of this spinning charge is described in terms of I (spin numbers) which have values of 0, ½, 1, $^3/_2$, 2, $^5/_2$, etc. (0 denotes "no spin"). The magnitude of this spin-induced dipole has is called the nuclear magnetic moment (μ).

Each proton and neutron has its own spin, and I is a result of these two spins. If…

n + p = even, then I = 0, 1, 2, 3…
n + p = odd, then I = ½, $^3/_2$, $^5/_2$…

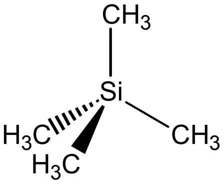
I	isotope	p	n	p+n
0	^{12}C, ^{16}O	6, 8	6, 8	12, 16
½	***^1H, ^{13}C, ^{15}N, ^{19}F,***	***1, 6, 7, 9***	***0, 7, 8, 10***	***1, 13, 15,19***
1	^2H, ^{14}N	1, 7	1, 7	2, 14
$^3/_2$	^{11}B, ^{35}Cl	5, 17	6, 18	11, 35
2				
$^5/_2$	^{17}O	8	9	

To be a useful analyte for NMR, the nucleus must have a nonzero spin, and more specifically, we tend to deal mostly with nuclei that have I = ½. So, how does NMR work? Well…

-spinning charged particle generates a magnetic field.
(think of spinning nuclei as bar magnets)
-w/o magnetic field, random orientations
-apply magnetic field orientation <u>with</u> and <u>against</u> field.
-apply radiowave (1-100m) to induce "flip" between <u>with</u> to <u>against</u> (higher energy)
-flipping @ specific energy = Peak

As for the analysis, we typically dissolve a few mg's of sample (pure) in a *deuterated* solvent. Like D_2O, $DCCl_3$

Standard =



TMS (tetramethylsilane)

Now, consider the equation that governs NMR…

$\nu = \gamma B_0/2\pi$ (γ = gyromagnetic ratio specific to nucleus, B_0 field strength)

As B increases, so does the frequency needed to induce "flip" (ν). Small magnetic fields mean that the frequency range required to "flip" is small, therefor the resolution of the instrument is low. Strong magnetic fields, mean that the available frequency range is large, therefore the resolution of the instrument is high. So how does someone relate a measurement on one instrument using one magnet to another using a different magnet? We have to normalize the scale.

Scale = ppm - relative scale

-on a 60 MHz instrument
30 Hz / 60 MHz = 0.5 ppm
150 Hz / 300 MHz = 0.5 ppm

At ODU- 400MHz instrument. 0.5 ppm = 200Hz
Higher energy – better resolution, better structural detail.

The Chemical Shift

Principle: The nucleus (proton) will resonate at a particular frequency depending on the magnetic field strength that the nucleus experiences. The effective magnet field that the nucleus experiences is equal to the applied magnetic field, minus the shielding effect of the electron.

$$H\text{ (effective)} = H_0\text{ (applied)} - H\text{ (shielding)}$$

Shielding is due to the movement of electrons, which create their own small magnetic field, which acts in the opposite direction to the applied field, resulting in shielding of the nucleus. In general, protons bonded to electro-negative groups, e.g. oxygen or nitrogen, will be less shielded than protons bonded to groups that are electropositive or neutral e.g. carbon. The phenomena of shielding means that the resonant frequency of the proton (or other NMR active nuclei) will give us direct information on the chemical environment of the proton.

How does this translate into interpretation of spectra? The effective B that a proton on a methyl group sees is smaller that the effective B that a proton on an O sees. Therefore the frequency needed to "flip" the spin and give us a peak is less (when the standard is TMS)

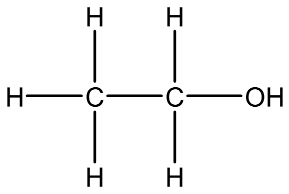
CHARACTERISTIC PROTON CHEMICAL SHIFTS

Type of Proton	Structure	Chemical Shift, ppm
Cyclopropane	C_3H_6	0.2
Primary	R-C**H**$_3$	0.9
Secondary	R$_2$-C**H**$_2$	1.3
Tertiary	R$_3$-C-**H**	1.5
Vinylic	C=C-**H**	4.6-5.9
Acetylenic	triple bond,CC-**H**	2-3
Aromatic	Ar-**H**	6-8.5
Benzylic	Ar-C-**H**	2.2-3
Allylic	C=C-C**H**$_3$	1.7
Fluorides	**H**-C-F	4-4.5
Chlorides	**H**-C-Cl	3-4
Bromides	**H**-C-Br	2.5-4
Iodides	**H**-C-I	2-4
Alcohols	**H**-C-OH	3.4-4
Ethers	**H**-C-OR	3.3-4
Esters	RCOO-C-**H**	3.7-4.1
Esters	**H**-C-COOR	2-2.2
Acids	**H**-C-COOH	2-2.6
Carbonyl Compounds	**H**-C-C=O	2-2.7
Aldehydic	R-(**H**-)C=O	9-10
Hydroxylic	R-C-O**H**	1-5.5
Phenolic	Ar-O**H**	4-12
Enolic	C=C-O**H**	15-17
Carboxylic	RCOO**H**	10.5-12

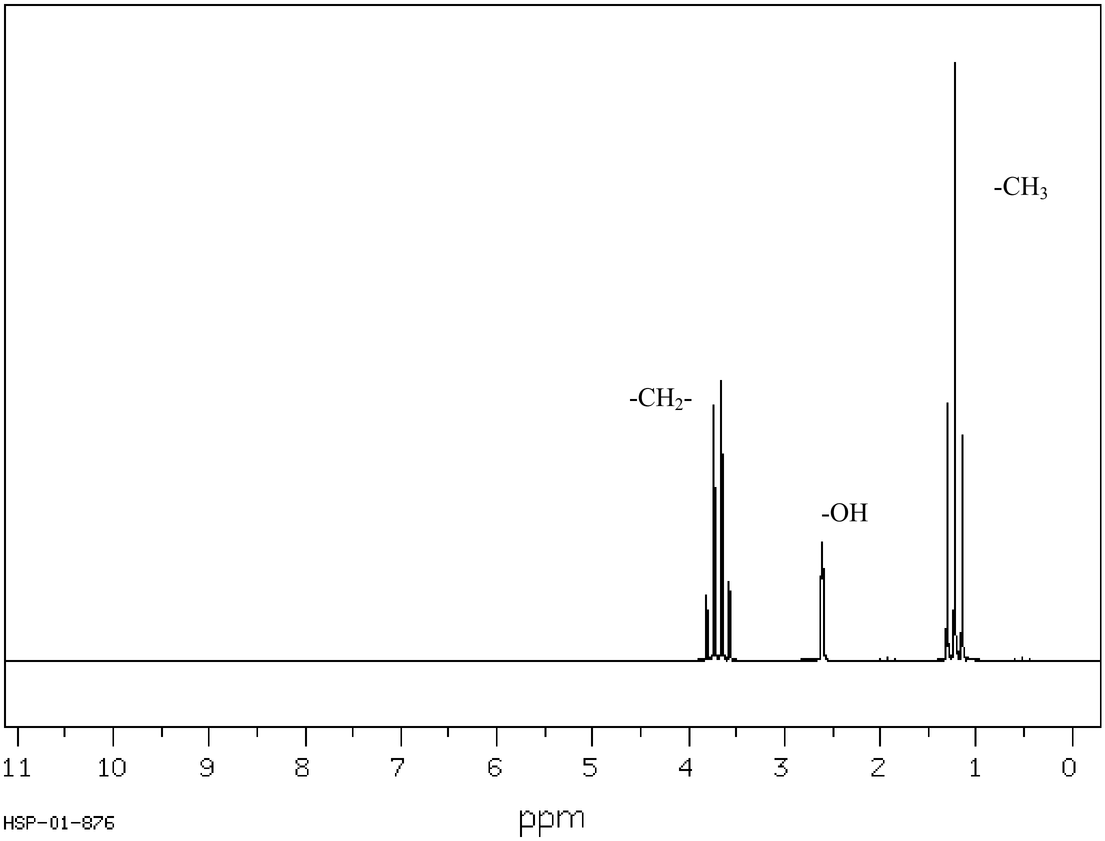
The Spectra.

So, What does a typical NMR spectrum look like? Consider ethanol.

ethanol



Ethanol has 3 different kinds of hydrogens…a $-CH_3$ group, a $-CH_2-$ group and an -OH group. The NMR spectrum (90 MHz) for ethanol looks like…

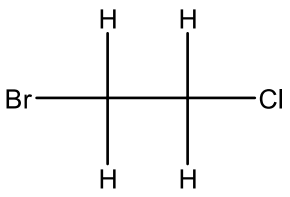


Why? For the interpretation you will either just need to read the book or come to class…

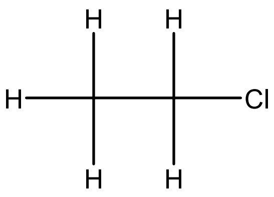
<u>Splitting</u> – peaks are dependent on magnetic environment – ***adjacent*** hydrogens can impact the signal (peak) in a dramatic way.

Identical = same magnetic environment

1-bromo-2-chloroethane



chloroethane



	A	B	A	B
#peaks	3	3	3	4

for 1 equivalent H

↓ and ↑
1 1

for 2 equivalent H's

↑↑ ↑↓ ↓↑ ↓↓
1 2 1

for 3 equivalent H's

↑↑↑ ↑↑↓ ↑↓↑ ↓↑↑ ↑↓↓ ↓↑↓ ↓↓↑ ↓↓↓
1 3 3 1

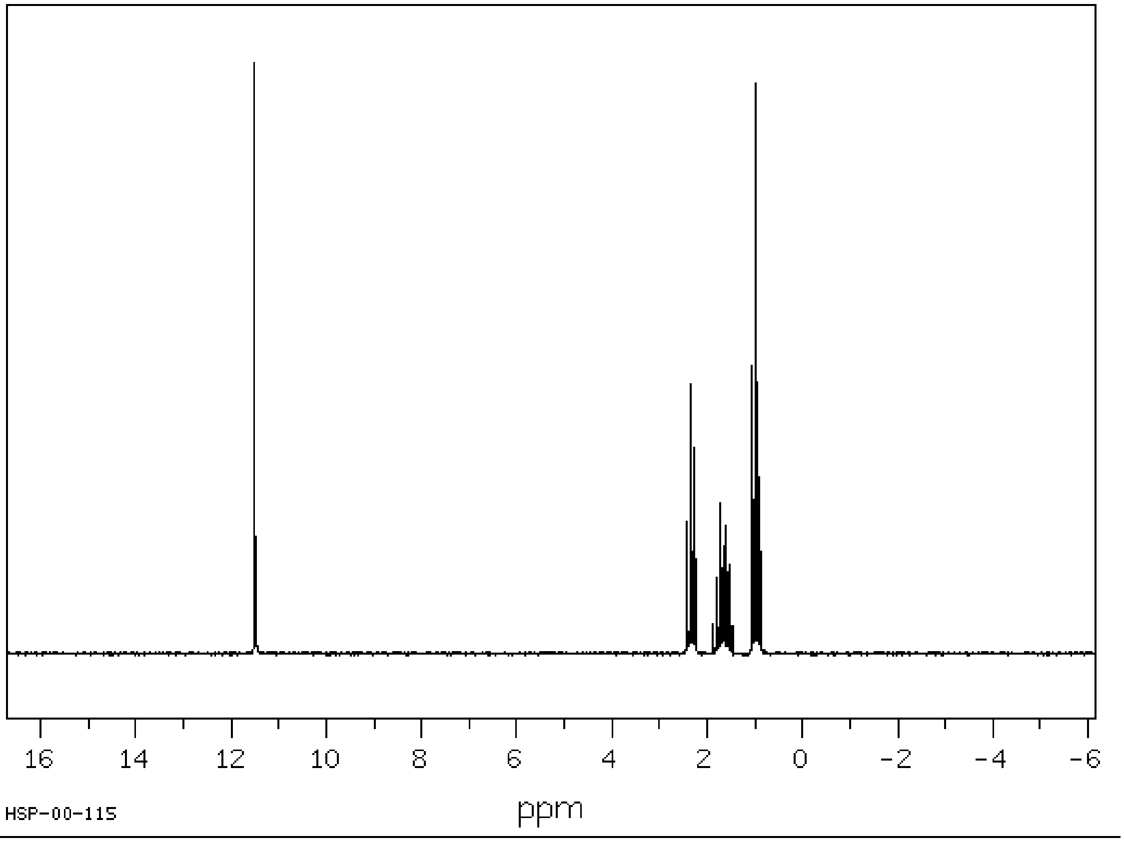
Peak Splitting follows Pascals triangle

1 1	2
1 2 1	3
1 3 3 1	4
1 4 6 4 1	5
1 5 10 10 5 1	6

Integration - # of peaks

So, here is an integrated problem for you…

One mole of an unknown organic acid produces 176 g of CO_2 and 72 g of H_2O upon combustion. The NMR of the unknown compound is shown below. Identify the compound and assign the NMR peaks to the specific groups of H's in your molecule.



More examples to follow in class as time permits…

^{13}C NMR…Same as proton NMR, but no splitting, bigger scale, and less sensitive.