Chapter 14 – Spectroscopy

There are four major analytical techniques used for identifying the structure of organic molecules

1. Nuclear Magnetic Resonance or NMR is the single most important technique for elucidating the structure of organic molecules. It allows us to determine the exact structure of an organic compound. We can identify all of the protons and also all of the carbon atoms. It is the technique which we will spend the most time studying since it is the most useful.

2. Infrared Spectroscopy or IR is useful for identifying certain functional groups. It is based on the vibrations between atoms.

3. Ultraviolet-Visible or UV-Vis Spectroscopy. This shows the electron distribution in molecules and is especially useful in showing the π-electrons such as those found in conjugated systems.

4. Mass Spectroscopy or MS gives the molecular weight of a compound and is very useful when trying to identify an unknown.

Review of Electromagnetic (or EM) Radiation

Electromagnetic radiation has the properties of both particles and waves. The particles are called photons and each has a certain amount of energy called a quantum.

The energy of a photon and the frequency – which is a wave property – are related by Planck's constant:

$E = h\nu$ h = Planck's constant = 6.63×10^{-34} J.s
ν = frequency in Hertz (Hz) or cycles per second.

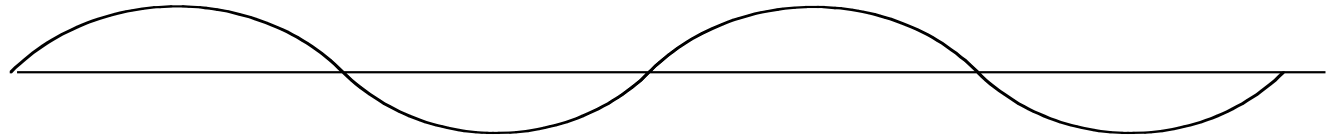
Since EM radiation travels at c, the speed of light ($c = 3.0 \times 10^{8}$ m/s):

$c = \nu\lambda$ where λ is the wavelength.

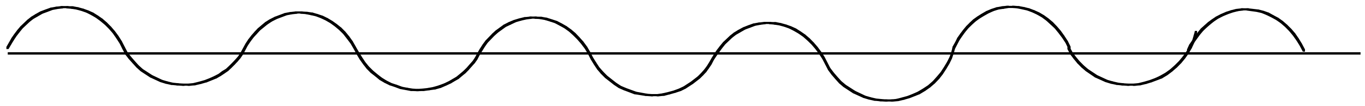
Therefore, $E = hc/\lambda$

All we need in this course is a qualitative understanding of the above relationships. We see that:

The energy of a photon is directly proportional to its frequency and indirectly proportional to its wavelength and wavelength and frequency are inversely proportional. To remember this, think of a wave: a long slow wave has low frequency and low energy while a high-energy wave is the opposite:

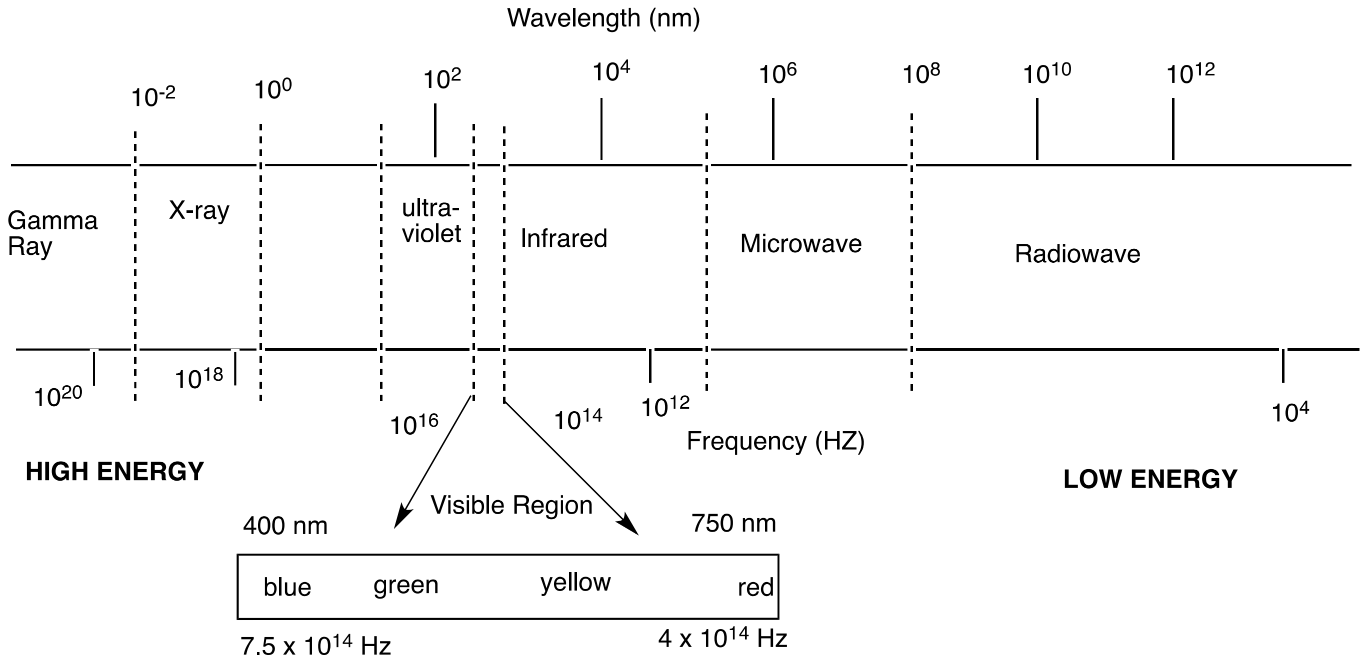


low frequency, low energy wave



high frequency, high energy wave

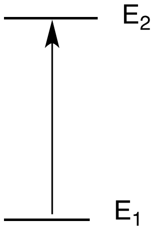
The following table gives a sense of the range of energies of photons in the EM spectrum that are used in the 4 analytical techniques discussed above:



13.2 Quantized Energy States

In order to be absorbed by a molecule, the energy of the photon must equal the energy difference between the two states. In other words, the transfer of energy between two objects occurs when their frequencies are matched. We call this resonance (as in Nuclear Magnetic Resonance)

Only certain energies are possible for electronic, vibrational and nuclear spin states.
The energy states are said to be quantized.



$$\Delta E = E_2 - E_1 = hv$$

More of the molecules exist in the lower energy state E_1 than in the higher energy state E_2. Excitation of a molecule from E1 to E2 requires input of just the correct amount of energy, Δ□E.

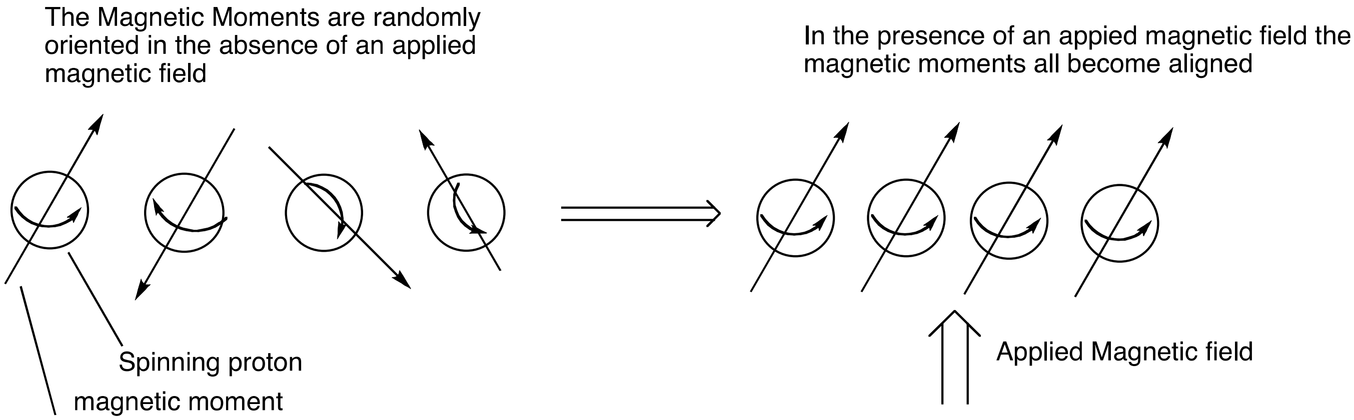
This amount is different for each type of spectroscopy.

13.3 Proton (^{1}H) NMR

Nuclear magnetic resonance spectroscopy depends on absorption of energy when the nucleus is excited from one spin state to another.

Not all atoms can be studied by NMR because not all atoms have the property of spin. Fortunately both carbon and the proton have spin.

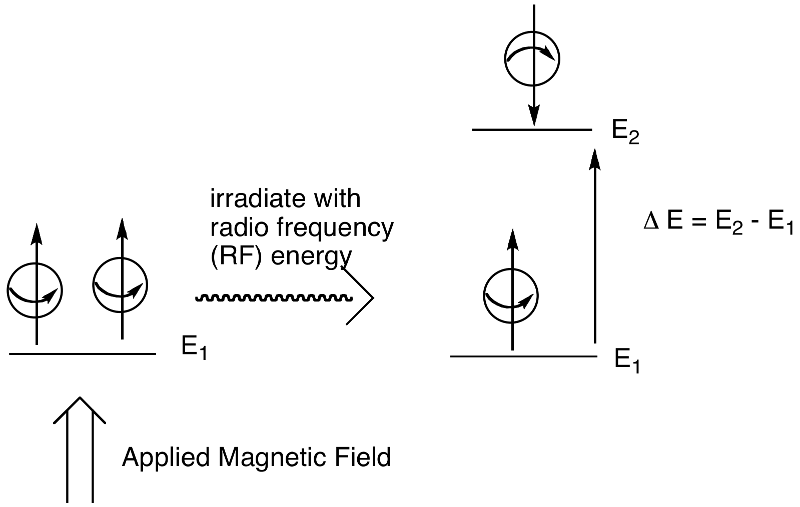
For the proton, there are two spin states, +1/2 and -1/2. The proton, of course, has a + charge and since it is spinning it will create a magnetic field. So the proton (and the carbon) atom is a tiny magnet.



In the absence of an externally applied magnetic field all the protons with spin +1/2 and -1/2 are randomly oriented and have the same energy.

In the presence of an applied field, however, the protons all become aligned with the applied magnetic field and now there is the possibility of two different energy states:

(1) The low energy state is the state where the magnetic moment is aligned with the magnetic field (as shown above) and (2) a higher energy state in which the magnetic moment is opposed to the external magnetic field as show below:



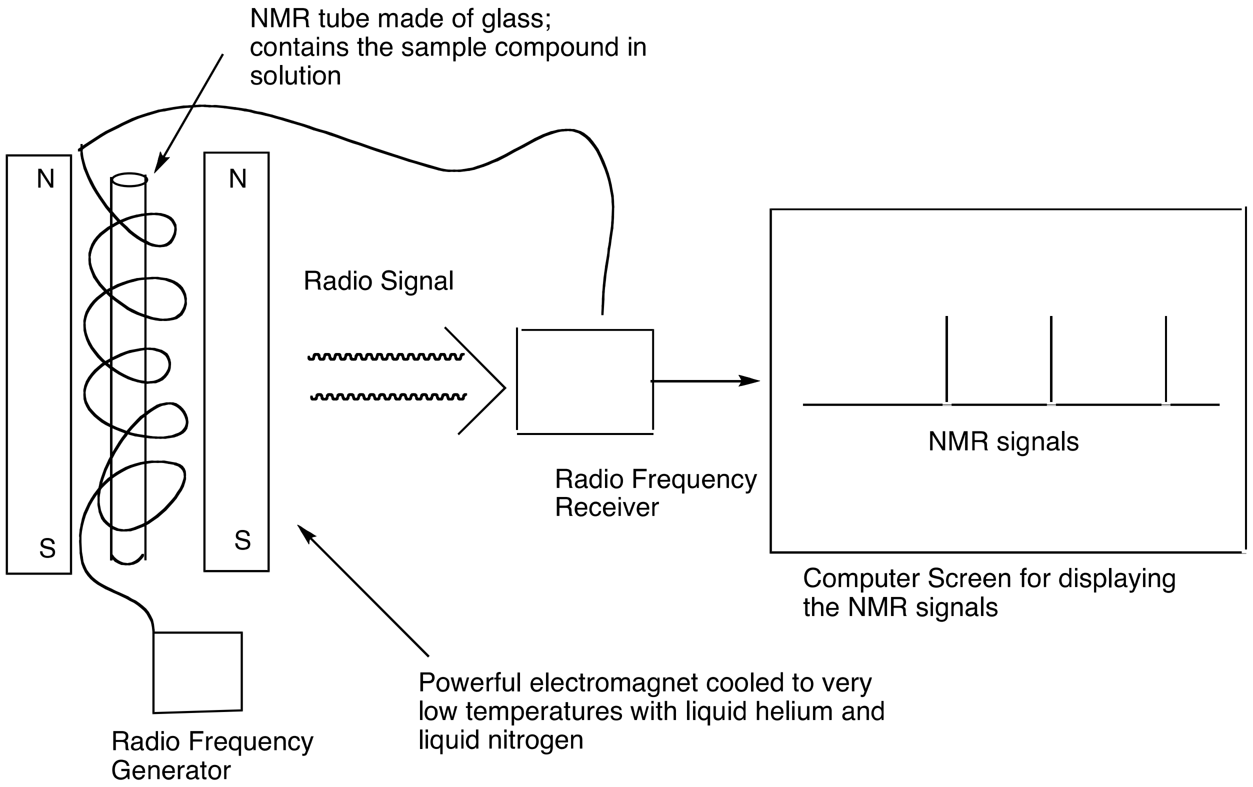
In the presence of a magnetic field, the two protons on the left have the same energy and their magnetic moments are aligned with the applied field.

But when the protons are irradiated with a pulse of energy that has just the right frequency (the correct quantum of energy) the proton can absorb this energy and be raised to a higher energy level in which the magnetic moment is now opposed to the applied field as shown on the left of the diagram.

The energy required to do this is in the Radio Frequency (RF) range. This is a very small amount of energy. When this energy is absorbed we see a signal or peak in the NMR instrument. In modern instruments this is displayed on a computer screen.

The energy difference between the two states depends on the strength of the applied magnetic field. The applied magnetic field must be very powerful in order to produce a measurable difference. It has often been described as taking the weight of a ship with a paper clip on it and then taking the weight of the ship without the paper clip in order to measure the weight of the paper clip. The differences in energy, ΔE are tiny and very difficult to measure accurately. The applied magnetic field is typically a very powerful electromagnet and the detectors for measuring the signals must be very sensitive – and therefore very expensive!! Research grade NMR instruments can cost more than one million dollars and even smaller instruments cost $500,000.

A schematic drawing of one is shown below:



13.4 Nuclear Shielding and Proton (^{1}H) Chemical Shifts

Each proton gives a signal in the NMR and each proton is affected by its environment so that protons in different environments will give different signals.
The electron density around each type of proton and in the bonds to that proton will affect the magnetic environment of that proton.

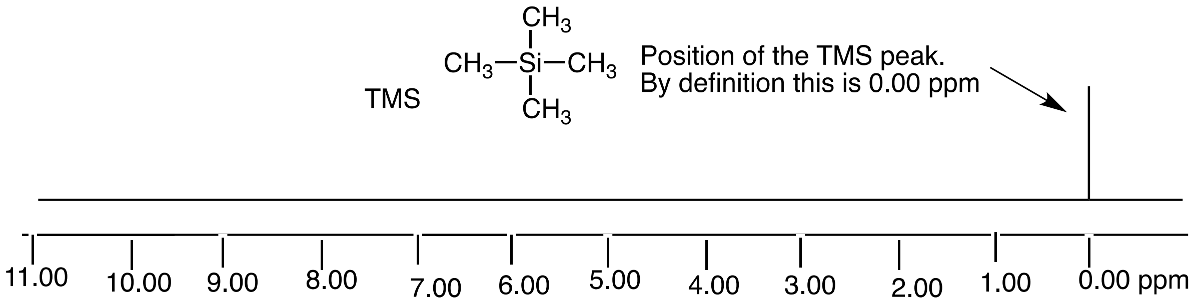
Electrons are also spinning charges and they create a small magnetic field that affects the magnetic field experienced by the proton.

We call this shielding and we say that the proton is shielded by the electrons around it from experiencing the full effect of the applied magnetic field.

So each type of proton will absorb at a different position (or different frequency of energy) depending on its environment.

The position of the absorption peak is called the chemical shift. We use the symbol δ□- a small Greek delta- for the chemical shift.

All chemical shifts are measured relative to a reference standard. This is the position of the peak given by tetramethylsilane or TMS.



Each time an NMR spectrum is taken, a small amount of TMS is included in the NMR tube along with the compound of interest so as to define the 0.00 position. All chemical shifts are then reported as “shifts” away from this zero position.

TMS was chosen as the standard because it is very electron rich. Silicon is more electropositive than carbon and so donates electrons to the methyl protons, “shielding” them from the applied field. Most other compounds will have protons that are less shielded than TMS. For historical reasons, the NMR scale is written from right to left.

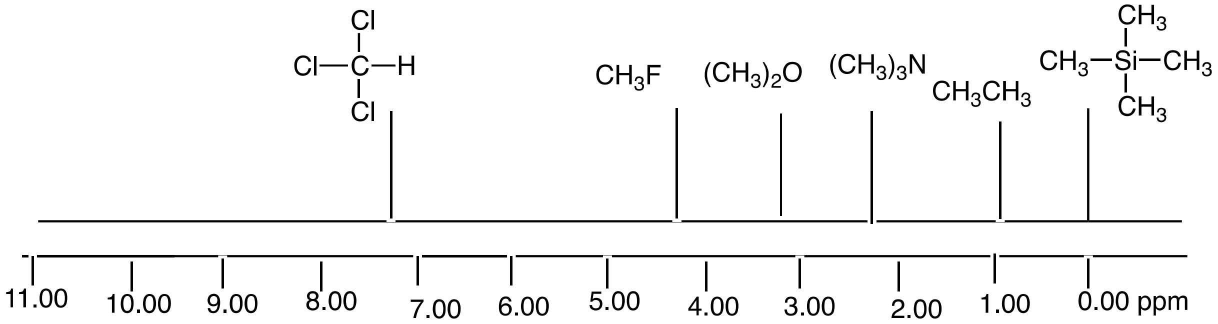
The units for the chemical shift are in parts-per-million or ppm. It is defined as:

$$\text{Chemical Shift } (\delta) = \frac{\text{Position of Signal - position of TMS peak}}{\text{spectrometer frequency}} \text{ X } 10^6$$

13.5 Protons in different environments experience different degrees of shielding and have different chemical shifts.

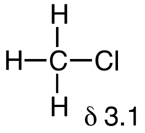
In general, the greater the electron density around a proton, the greater the shielding and the smaller the chemical shift.

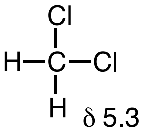
And conversely, the less the electron density around a proton, the greater the chemical shift. So, electron-withdrawing groups (EWG’s) on a carbon will INCREASE the chemical shift. Some examples are given below and more examples are given in chemical shift tables.

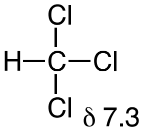


The decreased shielding is due mainly to an inductive effect – i.e. a pulling away of electron density through the bond – and so it decreases very rapidly with distance.

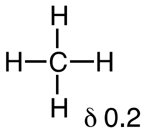
The deshielding effects of electronegative substituents are cumulative:

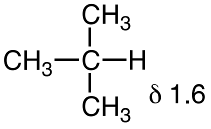

$H-\overset{H}{\underset{H}{C}}-Cl$

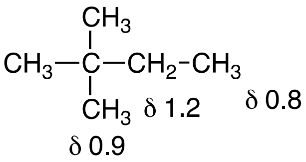

$H-\overset{Cl}{\underset{H}{C}}-Cl$


$H-\overset{Cl}{\underset{Cl}{C}}-Cl$

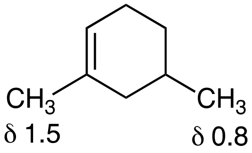
Carbon is slightly more electronegative than hydrogen, so replacing H's with carbons decreases the shielding and increases the chemical shift:

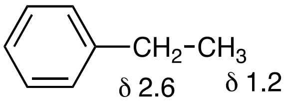

$H-\overset{H}{\underset{H}{C}}-H$


$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-H$

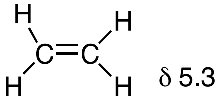

$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH_2-CH_3$

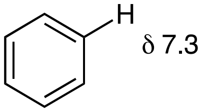
Sp^2 carbons are more electronegative than sp^3 carbons and will decrease shielding, increasing the chemical shift of nearby or attached protons:





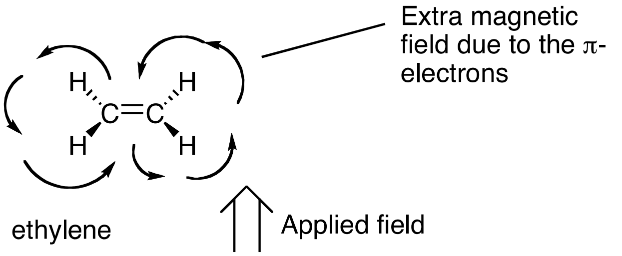
Hydrogens that are attached directly to double bonds (vinylic protons) or to aromatic rings (aryl protons) are especially deshielded.

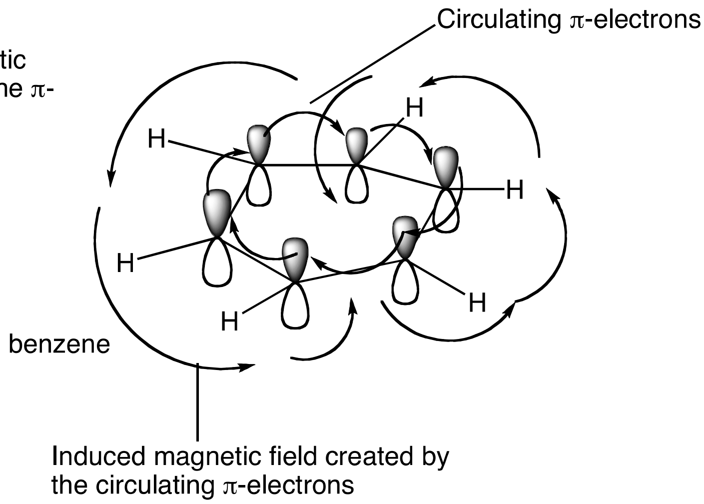




This extra deshielding is partly due to the increased electronegativity of the sp^2 carbon but it is also due to an extra induced magnetic field arising from the motion of the π-electrons. The H's of ethylene and benzene lie in a region of the molecule where in the induced magnetic field of the p-electrons reinforces the applied field and so it acts to deshield the H's.

In benzene the π-electrons are actually traveling in a circle and form a ring current, generating a significant magnetic field, which reinforces the applied field. In fact, since the development of the NMR instrument, the presence of an increased chemical shift for relevant protons is taken as proof of aromaticity.

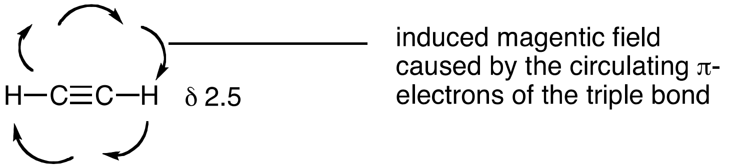




In acetylene (HCCH) we see a very different effect of the circulating p-electrons. The terminal H's of acetylene are MUCH more shielded than we would expect from the electronegativity of the sp carbon

(Recall electronegativity of carbon increases with increased s character in the order:
$sp > sp^2 > sp^3$)

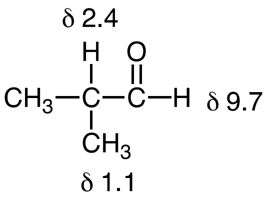
This is because the p-electrons circulating around the triple bond crate an induced magnetic field along the long axis of the triple bond, increasing the shielding and decreasing the chemical shift.



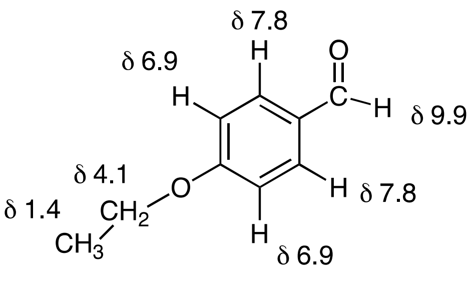
$H-C\equiv C-CH_2-O-CH_3$

δ 2.4 δ 4.0 δ 3.3

Carbonyls also deshield protons in a manner similar to the c=c bond and the oxygen makes the carbonyl carbon even more electron withdrawing.



$CH_3-\underset{CH_3}{\overset{H}{C}}-\overset{O}{\overset{\|}{C}}-H$



Protons next to carbonyls are also deshielded.

Exchangeable Protons: Protons attached to an oxygen –O-H or nitrogen –N-H are engaged in hydrogen bonding and exchange readily with each other and therefore have variable chemical shifts that depends on the temperature and on the concentration.

In general, an increase in H-bonding causes a decrease in shielding and an increase in chemical shift. A carboxylic acid has a chemical shift of 10 – 12 ppm for the terminal –O-H.

Since the range for most chemical shifts is only from 0.00 to 12.0 ppm, it is often the case that protons will have similar chemical shifts and that the signal cans overlap. Many times it can be difficult to distinguish the signals for individual protons.

The more powerful (and more expensive!) the applied magnetic field of the NMR instrument the better able it is to separate or resolve the different signals.

13.6 Interpreting ^{1}H NMR Signals

In the real world of chemistry, the chemist has an unknown compound and with the aid of the NMR he or she tries to figure out the structure of the compound based in part on its NMR spectrum. This is all interpreting the NMR spectrum.

There are four critical pieces of information contained in an NMR spectrum:

(1) The chemical shift, which as we have already seen, gives us information about the chemical environment of the proton and often we can determine what kind of proton it is simply from the chemical shift. The chemist has access to Chemical Shift tables which aid in this determination.

For example, if a NMR signal appears between 4 – 6 ppm there is a good chance that it may be due to a proton attached directly to a double bond (i.e. it could be part of an alkene).

Or, if there is a chemical shift in the 7 – 8ppm range, there is strong possibility that the proton is attached to an aromatic ring.

(2) The number of signals in the NMR spectrum. This tells us how many kinds of protons there are in the molecule.

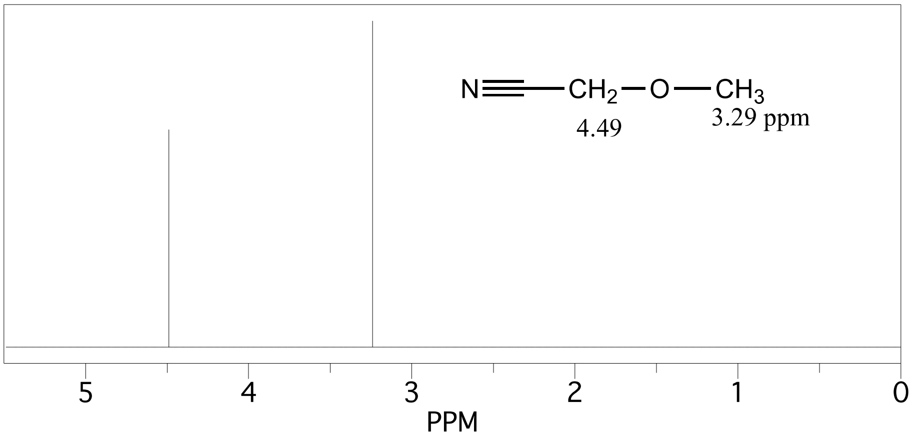
(3) The intensity of the signals as measured by the area under each peak, which gives the relative ratios of the different kinds of protons. We call this the **integral**.

(4) The multiplicity or splitting of each signal, which tells us how many protons are next to the one giving the signal.

Chemical Shift equivalence: if two protons are in the same chemical environment, they will have the same chemical shift. Even though each proton will give a signal, the two signals fall in exactly the same place and appear as one signal.

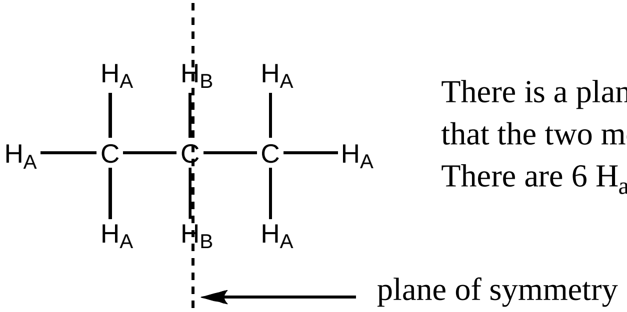
But note: the fact that there are two protons giving rise to this signal, means that the signal will be twice as intense; i.e. the signal will integrate for two protons.

For the following molecule, there will be two signals in the NMR and they will have integral ratios of 2:3.



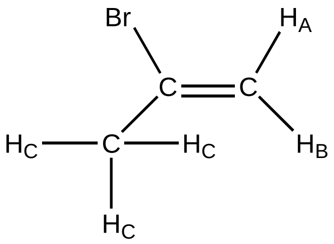
Propane will have two signals in the proton NMR in the ratio of 6:2. There is a plane of symmetry in the molecule (dotted line passing though the H_B protons).

Note the labeling convention: We label protons that have the same signal with the same letter, starting with A, B, etc.



There is a plane of symmetry cuttting the molecule in half so that the two methyl groups are identical.
There are 6 H_a protns and 2 H_B protons

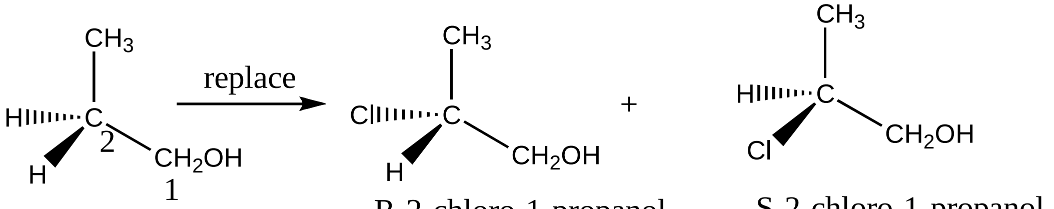
With alkenes, when there is restricted rotation around the C=C bond we often see different signals:



The H's are NOT the same; H_A is *cis* to the Br while H_B is *trans* and so they are in different environments.
The protons on the methyl group are of course in a different environment as well.

H_A and H_B are said to be diastereotopic hydrogens. Replacement of H_A or H_B with a Cl would give different molecules.

Enantiotopic H's are hydrogens that would give different enantiomers if replaced with a Cl atom. For example:



R-2-chloro-1-propanol S-2-chloro-1-propanol

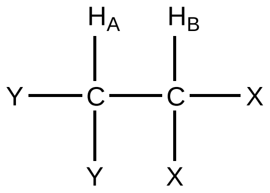
The two protons on C2 are enantiotopic in so far as they would give enantiomeric molecules if they were each replaced by a Cl.

Enantiotopic protons give the SAME signal in the NMR.

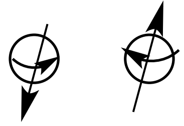
13.7 Spin-Spin splitting

Protons are affected by neighboring protons on adjacent carbons. The signal at H_A is affected by the signal at H_B. H_B is a tiny magnet and its magnetic field affects the magnetic field of the proton on the next carbon.

There are two possible spin states for H_B and therefore two different magnetic fields generated by H_B. The proton at H_A will therefore be split into 2 possible peaks.

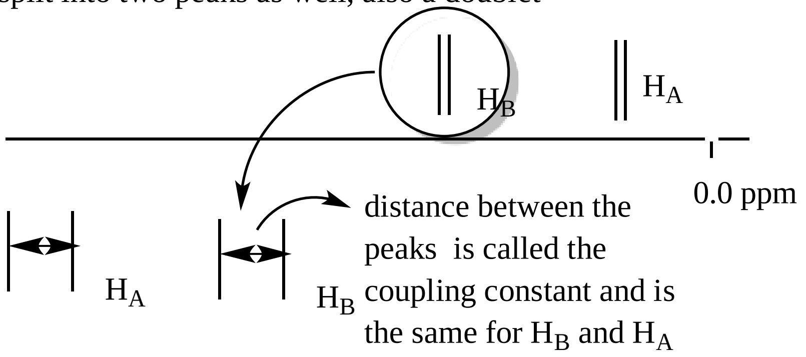


H_B can exist as either



The magnetic moment of H_B will affect the magnetic moment of H_A

Therefore, H_A will be split into 2 peaks, called a doublet and H_B will be split into two peaks as well, also a doublet

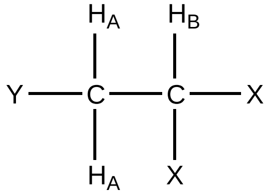


distance between the peaks is called the coupling constant and is the same for H_B and H_A

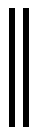
Therefore we have the **n + 1** rule: if a proton has **n** neighboring proton on adjacent carbons and the protons are all in the same environment, then the proton will be split into **n + 1** peaks. Note that all the neighboring protons **n** must be in the same chemical and magnetic environment and on adjacent carbons for the **n+1** rule to be in effect.

And also note that for splitting to occur H_A must be in a different chemical and magnetic environment from H_B. If two protons are the same (i.e. both H_A) then no splitting occurs because the magnetic fields they generate are the same.

For:



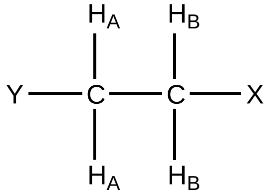
H_A has n=1, therefore it is a doublet



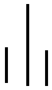
H_B has n=2, therefore it is a triplet

Note that there is a distinctive pattern to the peaks. The middle peak is about 2x larger than the two outside peaks which are usually about the same height

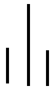
For:



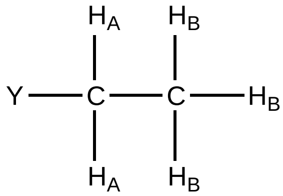
Now H_A has n=2, therefore it is a triplet



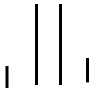
H_B has n=2, therefore it is a triplet



For:



Now H_A has n=3, therefore it is a quartet



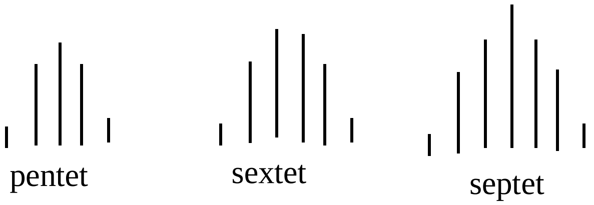
H_B has n=2, therefore it is a triplet

Note again the distinctive pattern for the quartet, the two outside lines are the same height and about 1/4 the height of the inside two lines.

The reason for the distinctive patterns of the peaks is simple and is given in your text. It is based on probablity on Pascal's Triangle: there are more ways to make the signals that form the two inner peaks, therefore they are more intense.

This is a very characteristic pattern. It is an ethyl group isolated from other protons. So whenever you see a quartet and a triplet, you will know that you have an ethyl group in your molecule.

So For: n=1 we have a doublet
n=2 triplet
n=3 quartet
n=4 pentet
n=5 sextet
n=6 septet

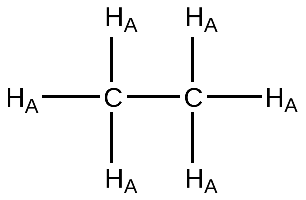


For n > 6 we generally just call it ia multiplet, since it can be very difficult to distinguish all of the individual peaks.

When we begin to look at real molecules and apply the **n + 1** rule in practice it is very important to remember that protons that are in the same chemical and magnetic environment do NOT split each other. They will each give a signal but the signals all have the same chemical shift and so appear as one signal (but of course will have an intensity corresponding to the number of protons that give rise to that signal).

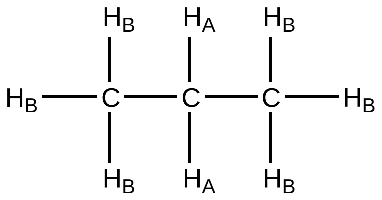
Real Examples:

CH_3CH_3



Here all of the protons are in the same environment and therefore all have the same chemical shift. The signal will integrate for six protons - i.e. it will be six times as intense as a signal that has only one proton.

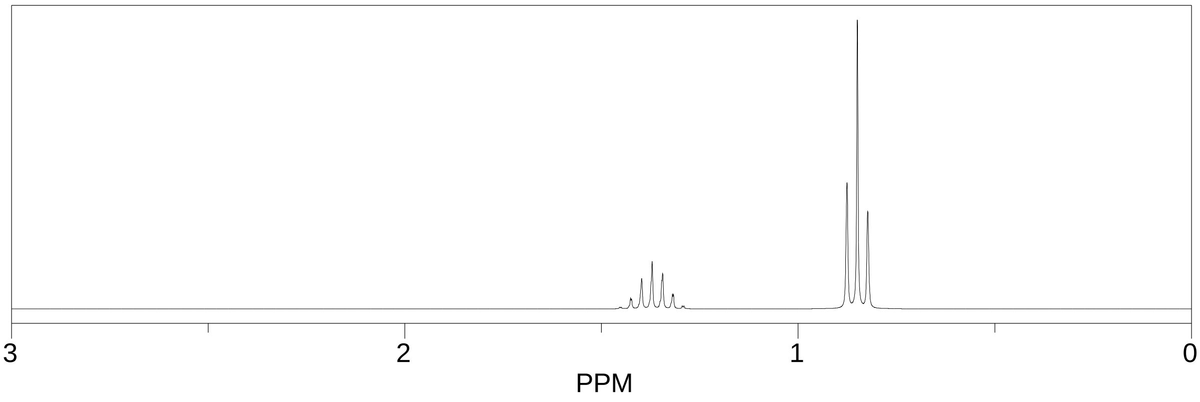
$CH_3CH_2CH_3$



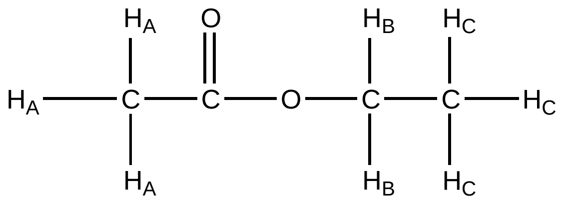
Now there are two kinds of protons, H_A and H_B in the ration of 2:6 or 1:3.

H_A: n=6, therefore it is a septet
H_B: n=2, therefore it is a triplet

The NMR is given below:

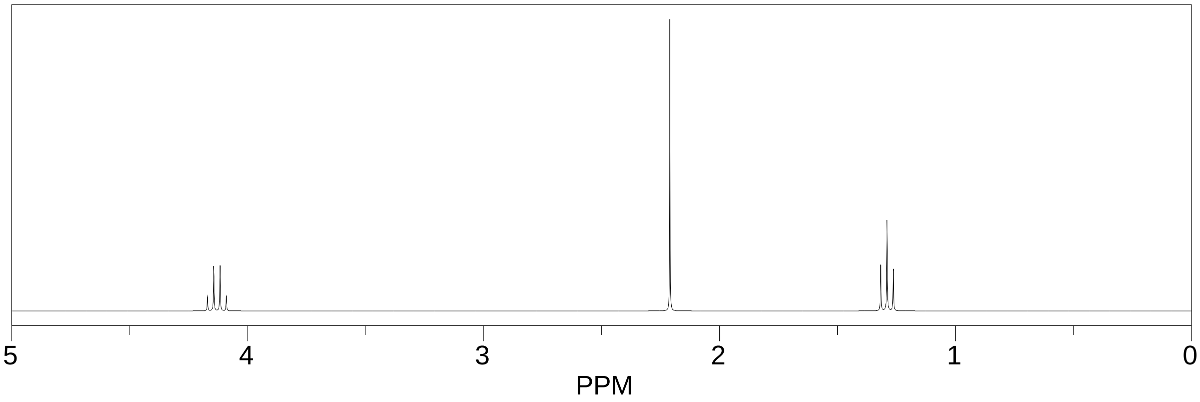


For: ethyl acetate

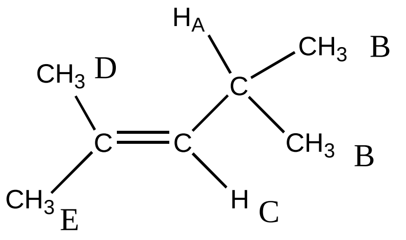


H_A: n = 0, therefore it is a singlet integrating for 1H
H_B: n= 3, therefore it is a quartet, integrating for 2H
H_C: n = 2, it is a triplet for 3H

The NMR is given below:

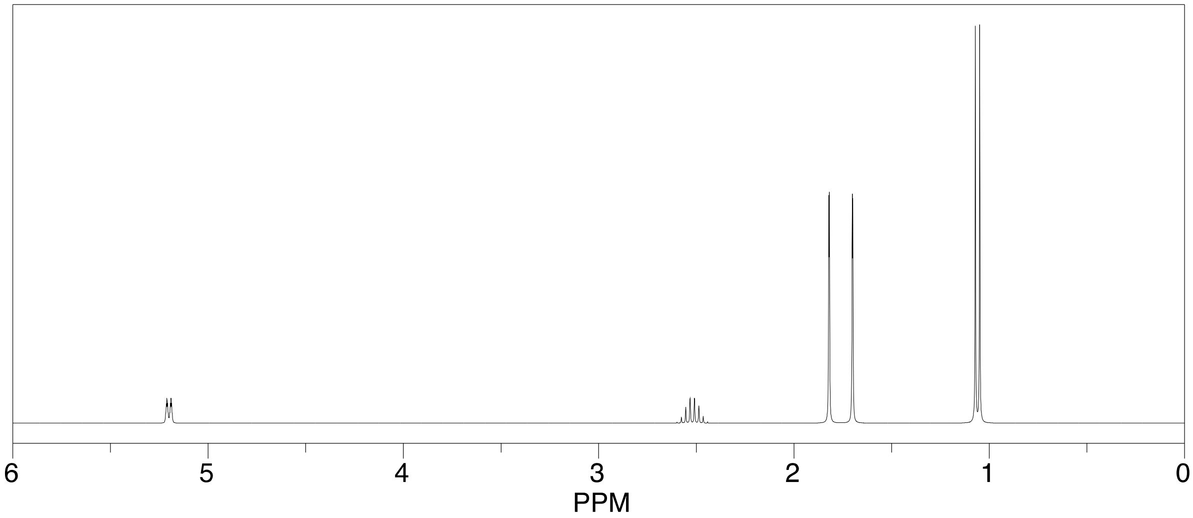


For:

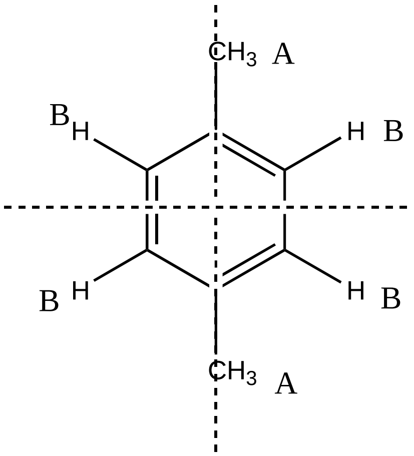


H_A n = 7, multiplet, 1H
H_B n = 1, doublet, 6H
H_C n = 1, doublet, 1H
H_D n = 0, singlet
H_E n = 0, singlet

Note that we do not see free rotation around the C=C bond, so the 2 methyl groups are NOT in the same environment and will give different signals. The environments are very similar and so the chemical shifts will be similar.



For:

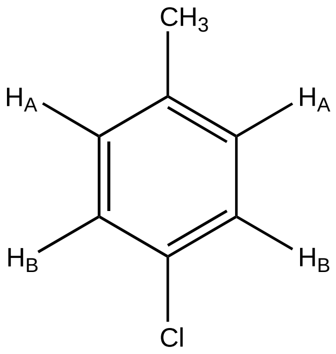


In 1,4-dimethylbenzene (*para*-xylene) we see only two peaks due to the two planes of symmetry in the molecule.

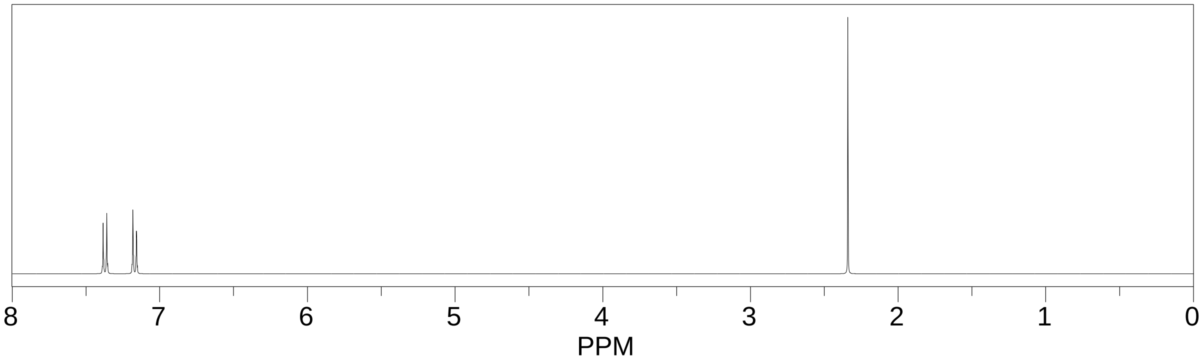
H_B is a singlet integrating for 4 H's because its neighbor is another H_B and neighbors that are the same - i.e. that have the same chemical environment - do NOT split each other becuase literaly their magnetic fields are the same.
H_C is also a singlet, integrating for 6 H's.

To repeat: a proton is not split by a neighbor if that neighbor is in the same chemical environment. For spitting to occur, the proton must be on an adjacent carbon and must be in a different chemical environment. Remember, the proton is a little magnet that generates a magnetic field. This field will be perturbed (i.e. split) only if the neighboring magnetic field is different.

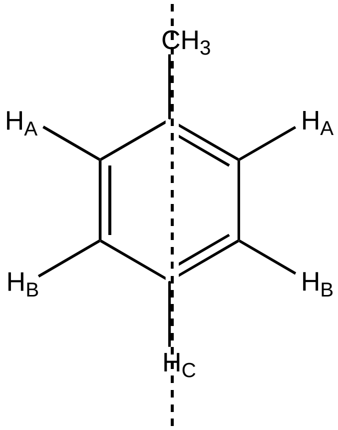
For:



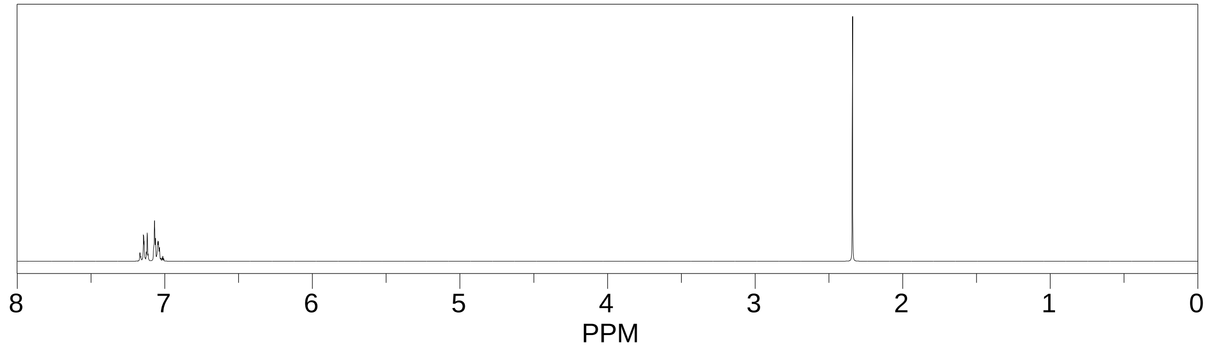
Now there is only one plane of symmetry in the molecule (see dotted line) and therefore two sets of peaks, H_A and H_B. They are both doublets, integrating for two H's.



For:



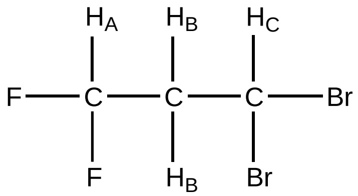
Here we have a plane of symmetry and so we have three types of protons and in theory we should see three separate sets of signals. H_A should be a doublet for 2H's, H_B should be split by H_A into a doublet and then each of these lines spit again by H_C into what is called a doublet of doublets (see below) for 2H's and H_C should be a trtiplet for 1H. In reality, however, we often see the peaks overlapping since they have very similar chemical shifts and therefore we just see a jumble of peaks which we call a broad singlet or sometimes we call it a multiplet if the peaks are partially resolved.



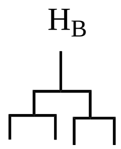
Complex Spectra

We have said that the **n + 1** rule applies only when all of the neighboring protons are in the same environment and so exert the same magnetic field on the proton in question. If the neighboring protons are themselves in different environments, they will exert different magnet fields and the splitting patterns become more complex.

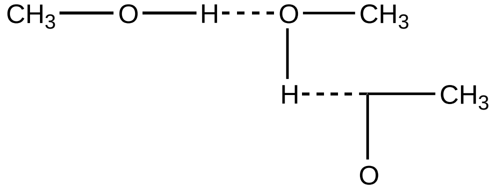
For:

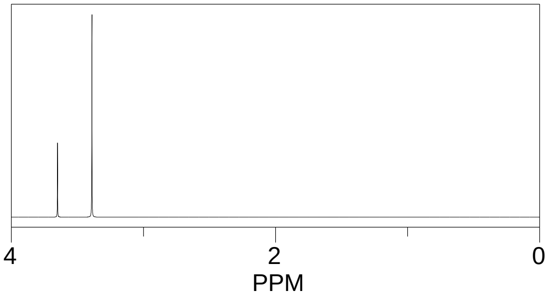


So H_B has two neighbors, H_A and H_C but they are not in the same environment. Therefore H_B will be split by H_A into a doublet and then each of these lines will be split by H_C into a doublet. So the result is that we see 4 lines of H_B. H_A and H_C are both normal triplets. This is pictured schematically below.



Exchangeable Protons: These are protons attached to oxygen and nitrogen and so they are capable of hydrogen bonding. The chemical shifts of these protons are variable, depending on the concentration and the solvent, and they are often broadened. Also, we usually do not see spin-spin coupling with neighboring protons.





Carbon13 NMR

Carbon 12, the most abundant isotope of carbon does not give an NMR signal but carbon 13 (^{13}C) does and we can take NMR's of the carbon nuclei. The principles behind ^{13}C NMR are similar to those behind ^{1}H NMR. Each type of carbon gives a signal and the chemical shift depends on the specific environment of that carbon.

Carbons that are surrounded by electron withdrawing groups have a **large** chemical shift, just like protons and carbons that in electron rich environments have a **small** chemical shift. We still use TMS as the reference standard.

There are some differences, however. One important difference is that ^{13}C NMR is much less sensitive than ^{1}H NMR. ^{13}C has a low natural abundance: only 1.1% of carbons are ^{13}C isotopes and also the intensity of the signal produced by the carbon nucleus is much lower than that for proton. This means that the acquisition of a ^{13}C spectrum takes much longer than that for a ^{1}H spectrum.

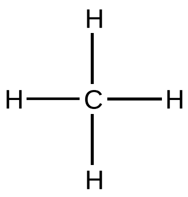
Another difference is that the chemical shift range for carbon NMR is much larger than for protons. It typically ranges from 0.00 ppm to about 220 ppm. This is actually very helpful; since the signals are spread out over a broader range, they are less likely to overlap.

Another major difference is that we generally run the carbon spectra so that we see **only one peak** for each carbon with no spin-spin coupling. Carbon 13 atoms are tiny magnets, like the proton atoms, and their magnetic field does interact with the adjacent protons but we can turn this coupling off when we run the experiment. This greatly simplifies the appearance of the spectra and makes identification of each peak much easier.

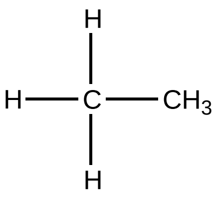
Another difference is that the integrals for the carbon signals are generally unreliable. The intensity of the carbon signals is influenced by several factors.

Chemical shift tables are given in the text.

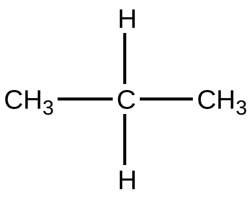
Here are some examples: (the numbers are in ppm)



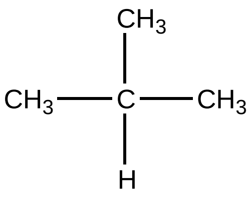
CH_4



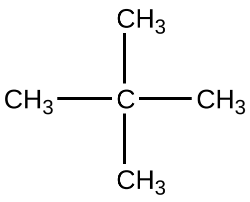
CH_3CH_3



$CH_3CH_2CH_3$



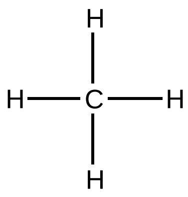
$(CH_3)_3CH$



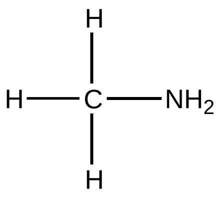
$(CH_3)_4C$

^{13}C	-2	8	16	25	28
^{1}H	2	0.9	1.3	1.7	

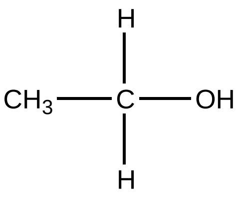
Carbon is more electronegative than hydrogen, so increasing the number of carbons attached, deshields the carbon (and the proton) and increases the chemical shift.



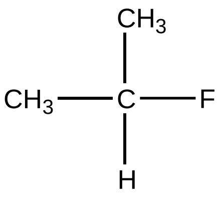
CH_4



CH_3NH_2



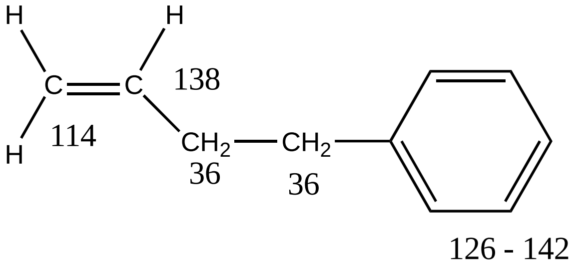
CH_3CH_2OH



$(CH_3)_2CHF$

^{13}C	-2	27	50	75
^{1}H	2	2.5	3.4	4.3

Hybridization effects are similar to those in ^{1}H NMR:

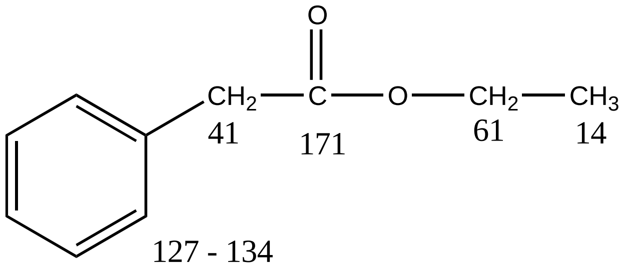


As in proton NMR, acetylenes are much farther up-field (i.e. have a smaller chemical shift) than expected due to ring currents.

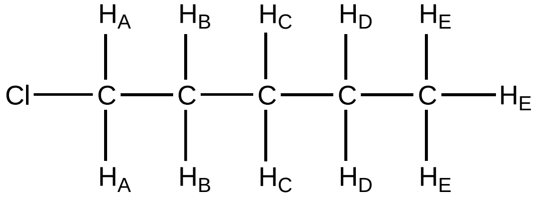
$H-C\equiv C-CH_2-CH_2-CH_3$

68 84 22 20 13

The carbonyl carbon is the least shielded in the spectrum. It is sp^2 hybridized and it is attached to an electron-withdrawing oxygen.

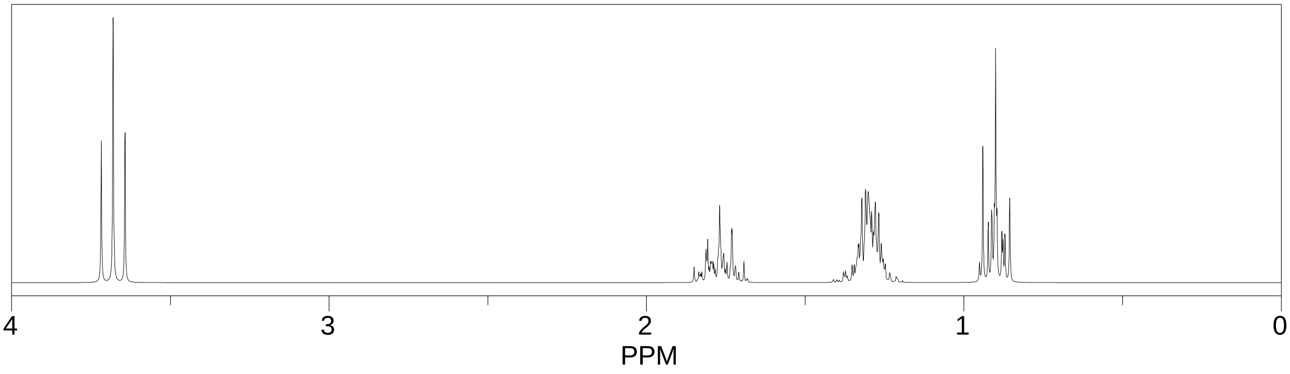


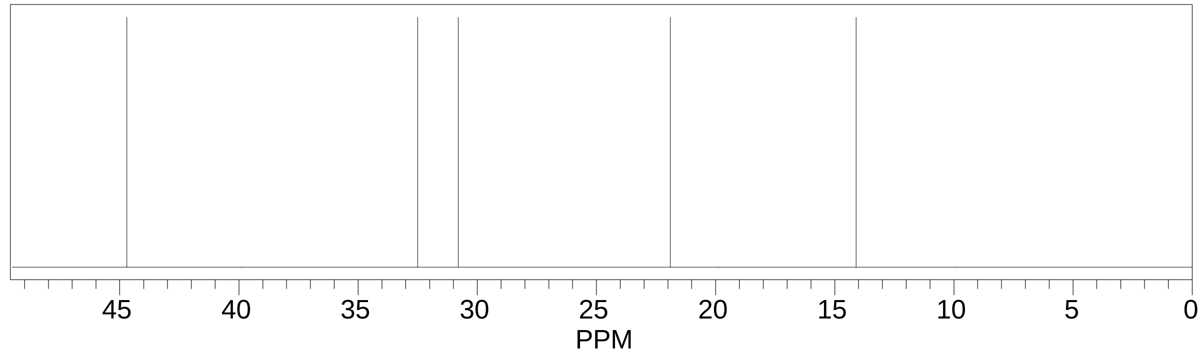
For: 1-chloropentane



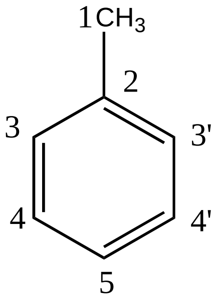
There are five different types of protons and expect five signals. The patterns will be complex for H_B, H_C, and H_D. H_A will give a clean triplet for 2H and H will give a triplet for 3H.

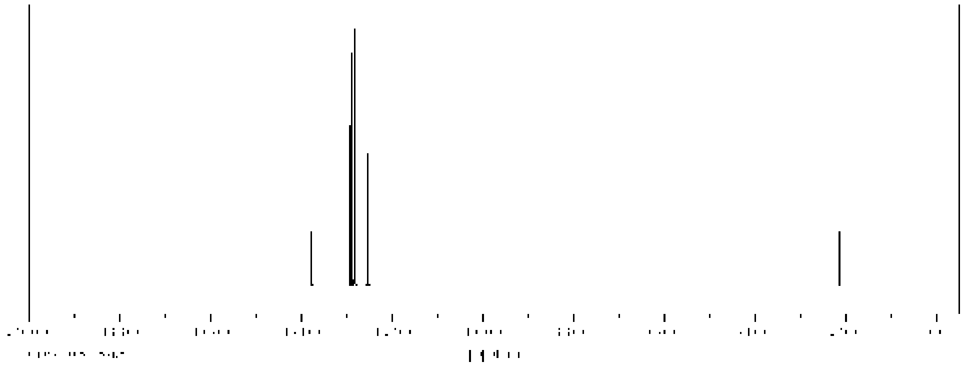
We should see five peaks in the carbon NMR.





For: Toluene we expect five carbon peaks since we have a plane of symmetry running through the benzene ring.





Infrared Spectroscopy
This is very useful in identifying certain functional groups. As we mentioned before it is based on the vibrations between atoms. These vibrations are of just the correct energy to absorb infrared radiation. This is the portion of the spectrum between microwaves and the visible region (2.5 x 10^{-6} m and 16 x 10^{-6} m. We use units of micrometer (μm which equal 10^{-6}m) and we use wavenumbers, which are reciprocal centimeters (cm^{-1}).

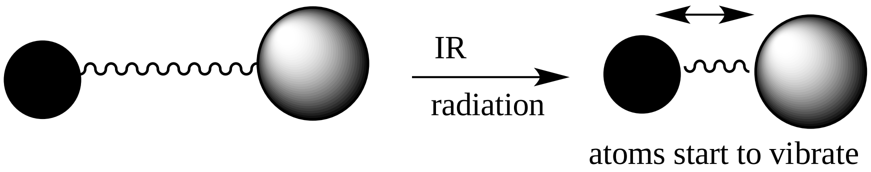
The region 2.5 – 16 μm corresponds to 4000 – 625 cm^{-1}

A reason for using wavenumbers is that they are directly proportional to energy and inversely proportional to wavelength.

Therefore, 4000 cm^{-1} is the high energy region
625 cm^{-1} is the low energy region

EM radiation in the 4000 – 650 cm^{-1} region corresponds to the separation between adjacent vibrational states in organic compounds. Absorption of a photon of IR radiation excites a molecule from its lowest or ground vibrational state to a higher one.

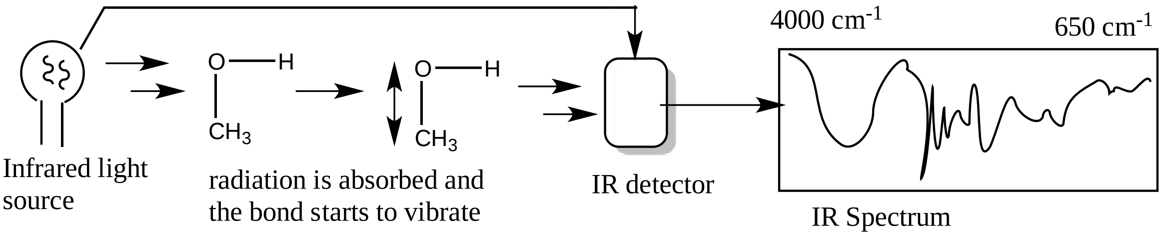
Think of atoms as being connected by tiny springs. These springs – or covalent bonds – can vibrate at certain frequencies depending on the masses of the atoms and the strengths of the bonds involved.



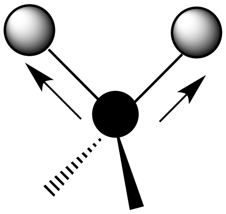
The frequency of a given stretching vibration is determined by two factors: (1) the mass of the bonded atoms and (2) the strength of the bond.

Triple bonds are stronger (stiffer) than double bonds and double bonds are stronger than single bonds. Therefore, triple bonds will vibrate at higher frequency than double bonds and double bonds will vibrate at higher frequency than single bonds.

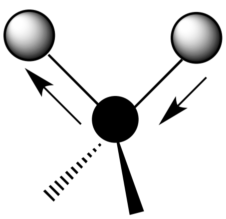
Below is pictured a schematic view of an Infrared Spectrometer. Unlike a NMR instrument, the IR spectrometer is relatively simple. It consists of a light source that emits infrared light. Lasers are typically used in modern instruments. The light is absorbed by the molecule, which starts to vibrate. The difference in energy leaving the light source and the light that passed through the molecule is measured. This difference is called the **absorbance** and it is what results in a peak in the infrared spectrum. In modern instruments these are displayed on a computer screen.



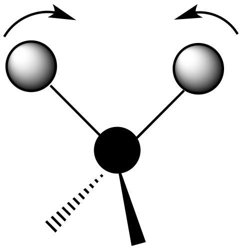
There are many peaks in an infrared spectrum because there are many types of vibrations. These include stretching and bending modes, with symmetric stretches, anti-symmetric stretches, in-plane bending, out-of-plane bending, etc.



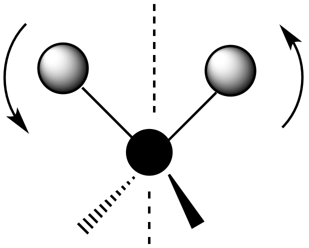
Symmetric stretching



Asymmetric stretching



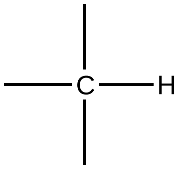
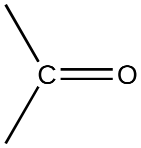
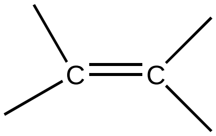
In-plane bending vibration



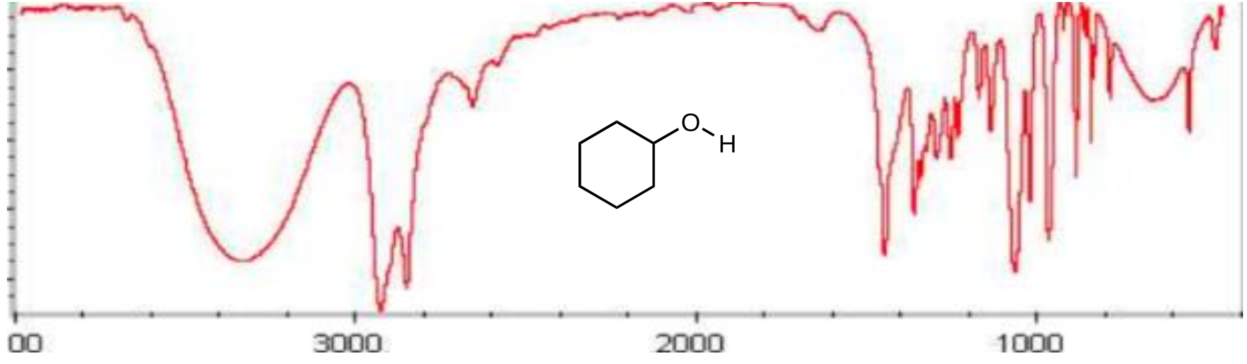
out-of-plane bending vibration

For this reason IR spectra can be very difficult to interpret. It is impossible to assign all of the peaks in an IR spectrum. There are literally hundreds of overlapping vibrations. But there are characteristic peaks that indicate that a certain functional group is present. Just as in NMR we have tables of chemical shifts, we have tables for the frequency of IR absorbances.

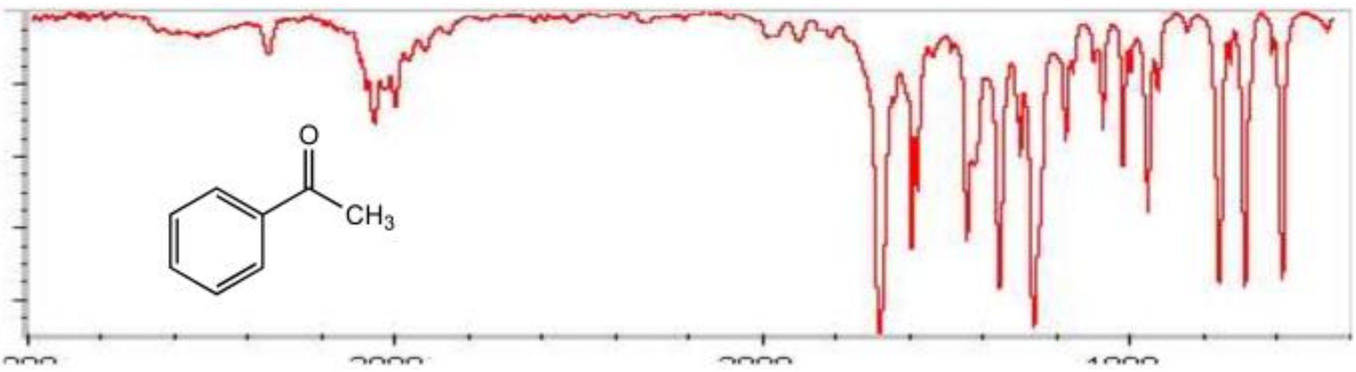
Important ones for us are:

Functional Group		Frequency of IR Absorption in cm^{-1}	
O—H	Alcohol	3200 - 3500	strong, broad
N—H	Amine	3300 - 3500	strong, broad
C=C—H	alkene aromatics C-H stretch	3010 - 3500	strong, sharp
	alkanes	2850 - 2960	strong, sharp
	Carbonyls ketones aldehydes esters	1680 - 1780	strong
	alkene C-C stretch	1620 - 1680	moderate to weak

Some actual IR spectra:
Cyclohexanol



Acetophenone


O
CH3