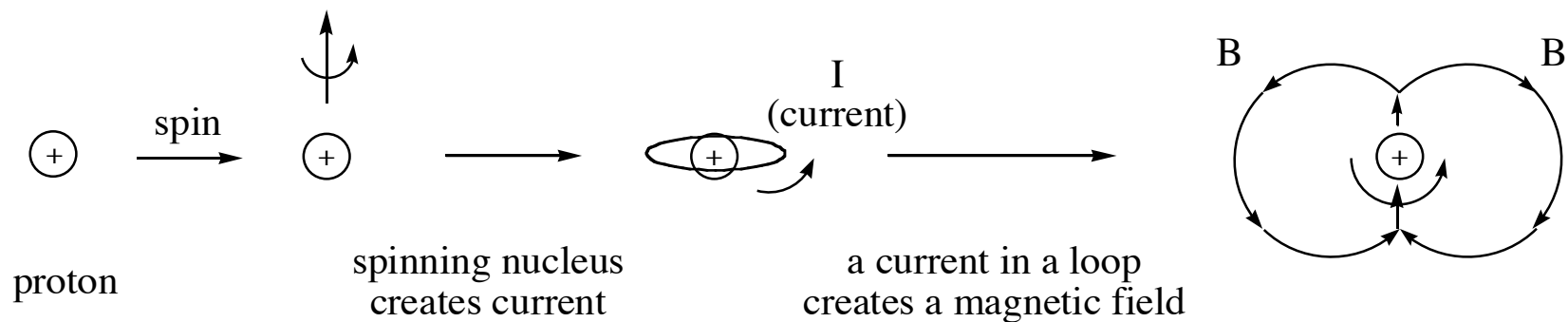


Nuclear Magnetic Resonance (NMR)

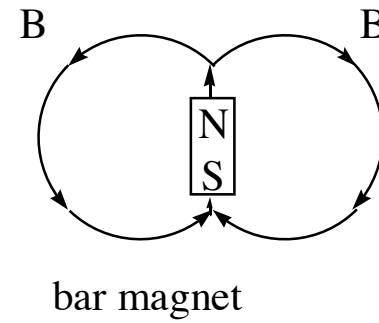
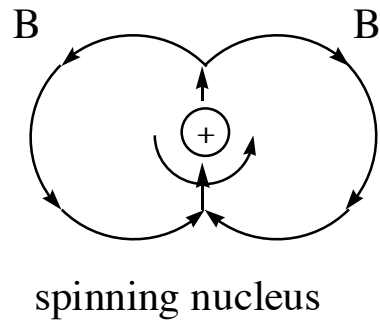
The most common tool for an organic chemist to determine structure

Any nucleus with an odd atomic number or odd mass has a 'nuclear spin'

This spin creates a magnetic moment for the nucleus



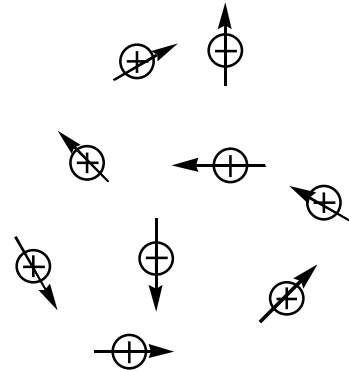
This Magnetic Field is Analogous to a Bar Magnet



the nuclear spins behave similar to tiny bar magnets

In Solution There Are Many Nuclear Spins Occurring

Hence many tiny bar magnets are present



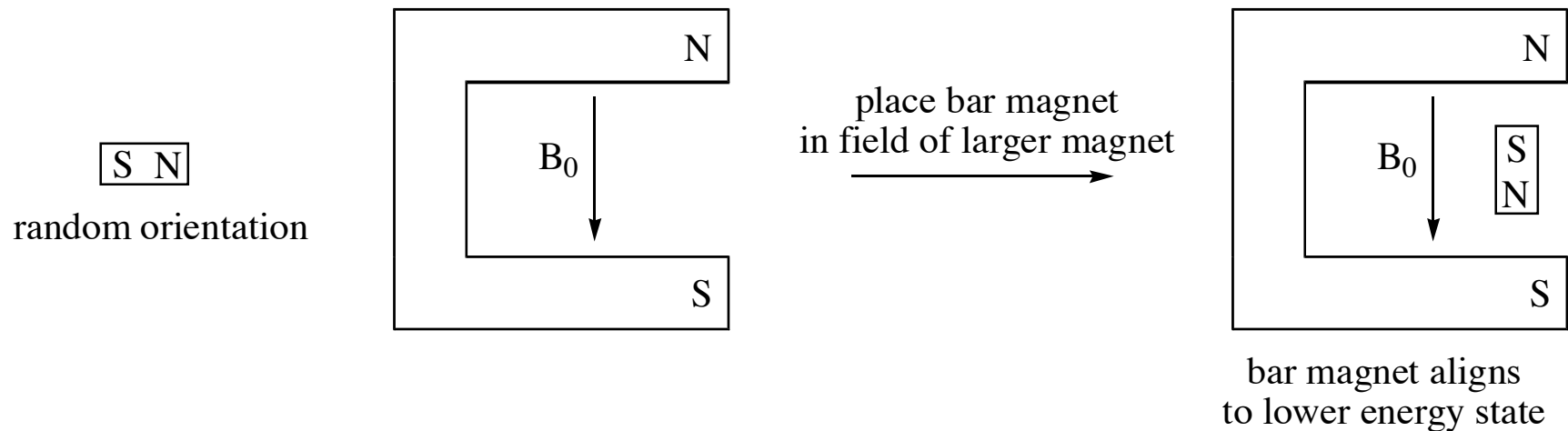
each spinning direction is random

(there is no energy difference between spinning in any direction)

and hence the magnetic moments will cancel

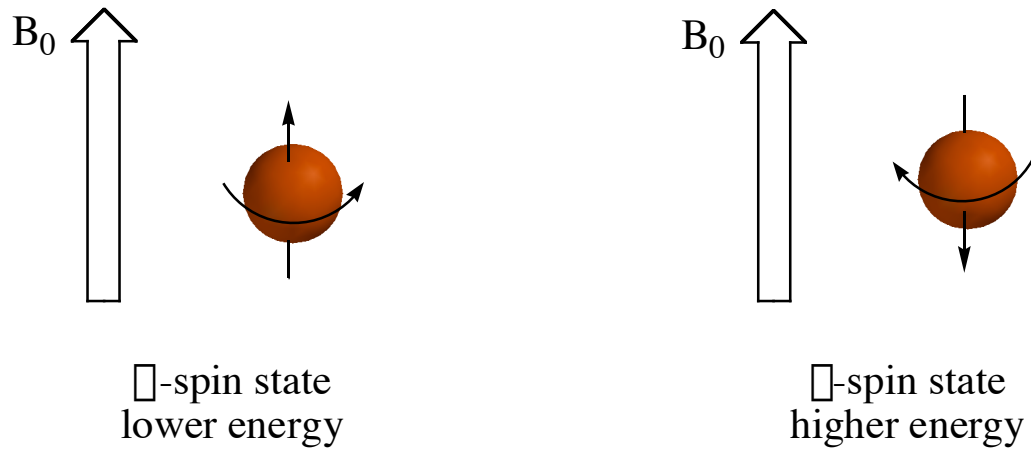
Consider the Bar Magnet Analogy

In the presence of a larger magnetic field the bar magnet will align itself



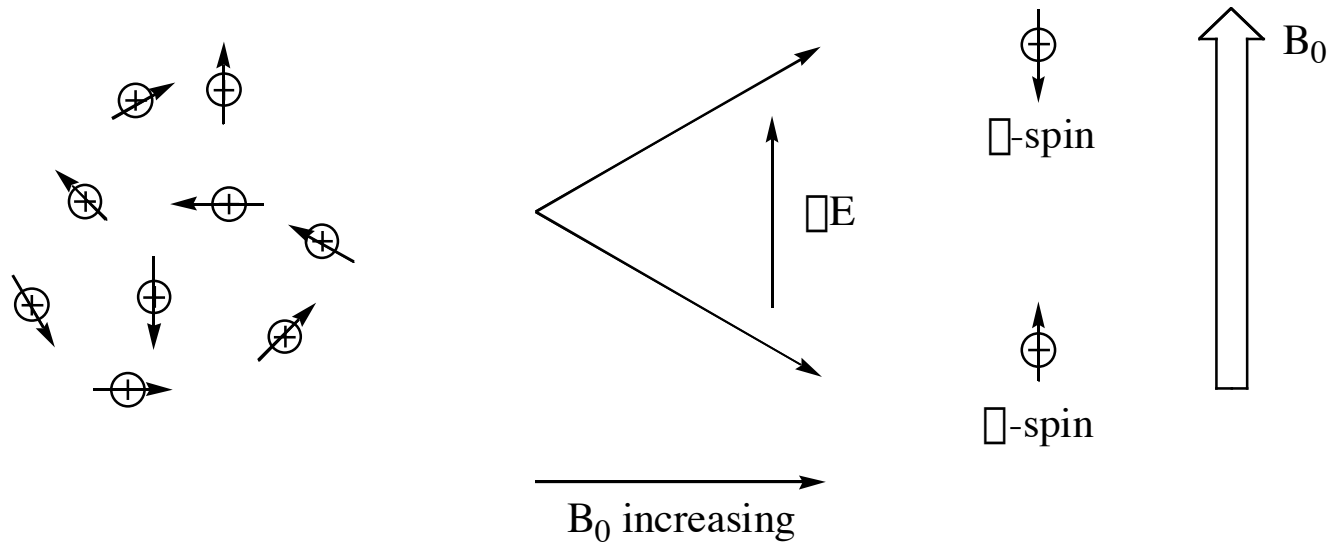
the same result will occur if we place a spinning nucleus
in the field of a large magnetic field

In the presence of an external magnetic field the spinning nucleus can align in one of two ways (with or against the field)



in the presence of the large external magnetic field (B_0)
the spins must be in one of these two directions

The nuclear spins are therefore no longer random



there will be more spins in the α -state than β -state

the difference in energy is dependent upon the external magnet strength

The difference in energy is dependent upon two terms

-external magnetic field and gyromagnetic ratio

energy difference between α - and β -state spins = $\Delta E = \Delta(h/2\pi) B_0$

Δ = gyromagnetic ratio

this term is dependent upon which nucleus is spinning

it is constant for a given nucleus

H for example has $\Delta = 26,753 \text{ sec}^{-1} \text{ gauss}^{-1}$

At this point in the discussion we know the following items:

- 1) a nucleus with an odd atomic number or odd mass will have a nuclear spin
- 2) this spinning of a charged nucleus will cause a current
- 3) this current will create a magnetic field similar to a bar magnet
- 4) in solution the spinning direction of the nucleus is random
- 5) in the presence of a large external magnetic field, however, the nuclear spin must be either in the α -state (lower energy) or β -state
- 6) the energy difference between the α - and β -states is dependent on the strength of the external magnetic field (B_0) and the nucleus that is spinning (which has a unique gyromagnetic ratio, γ)

Resonance

A key remaining point is the nucleus in the α -state can be changed to the β -state

-need the exact amount of energy that separates the two states

we know this energy difference (ΔE)

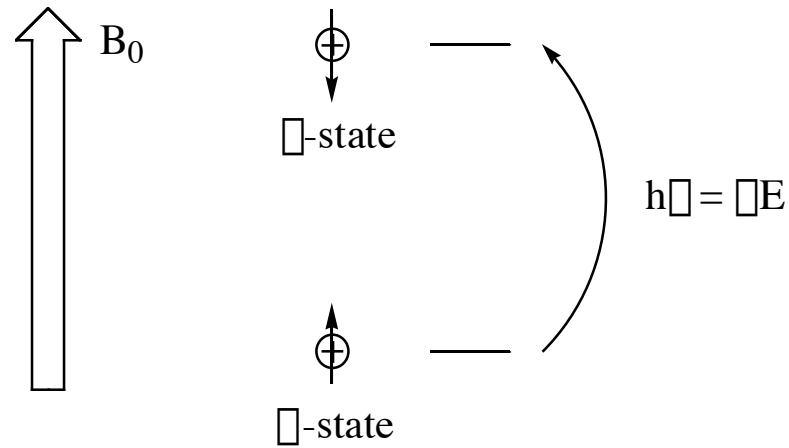
we can supply this energy by absorption of the appropriate wavelength of light

$$\Delta E = h\nu$$

With infrared spectroscopy we supplied light in the infrared region
to cause a bond vibration

In NMR we supply energy in the radio frequency region to cause the transition of nucleus
from the α -state to the β -state

This absorption of energy will cause the spin state to change



with exact combination of external magnetic field (B_0) and energy of photons (which happens to be in the radio frequency region for NMR) the nuclear spins are in resonance

called nuclear magnetic resonance (NMR)

The NMR machine can detect this absorption of energy for a sample

In practice either the radiofrequency is kept constant and the magnetic field strength is adjusted until resonance occurs or the magnetic field is kept constant and the radiofrequency is adjusted until resonance is obtained

Once the field strength and the radiofrequency are in 'resonance' the nucleus will absorb the energy of the radio waves

If this was all a NMR machine did it would be practically useless

-we could detect whether a compound had hydrogens

but that would be the only piece of information

almost all organic compounds have hydrogens so how does an NMR machine distinguish between the different compounds?

Shielding

Need to remember the structure of a compound

To reach the nucleus the radiowaves must pass through
the electron cloud surrounding the nucleus

The electrons are charged species that can rotate in the presence
of the external magnetic field

What this means is that the external magnetic field (B_0) is effectively reduced by the time
it reaches the nucleus (B_0 minus the field of the electron cloud)

This process is called shielding

The electrons are shielding the nucleus from the full external magnetic field

-the field at the nucleus is thus always less than the actual B_0

the critical point for a NMR experiment is that each hydrogen nucleus

will be shielded by different amounts

the degree of shielding is a direct result of the electron density around the nucleus

the greater the electron density the more shielded the hydrogen

therefore a NMR experiment tells you the electron density

around each hydrogen in the compound!!

For example, UTD has 270 MHz NMR's that students can use

With no shielding what is the magnetic field strength required to cause a proton to be in resonance at this radiofrequency?

$$\Delta E = h\nu = \gamma(h/2\pi) B_0$$

$$B_0 = 2\pi\nu / \gamma$$

$$270 \text{ MHz} = 270 \times 10^6 \text{ sec}^{-1}$$

$$B_0 = 2(2.7 \times 10^8 \text{ sec}^{-1})(3.14) / 26,753 \text{ sec}^{-1}\text{gauss}^{-1}$$

$$B_0 = 63,380 \text{ gauss for 270 MHz NMR}$$

But this is for an unshielded proton

The actual proton MUST experience a lower effective magnetic field

If the machine is set at 63,380 gauss the proton will not be in resonance and therefore it will not absorb the energy to change spin states

must supply a greater external magnetic field to cause resonance for a shielded proton

the amount of EXTRA magnetic field is dependent upon the degree of shielding

MORE electron density around a proton REQUIRES a larger external magnetic field

How can we predict how much the magnetic field must be increased?

By knowing the amount of electron density around a proton

Therefore **WHERE ARE THE ELECTRONS**

If we know where the electrons are located we can begin to predict how much the external magnetic field needs to be increased to cause resonance

Chemical Shifts

To record the position of an absorption scientists use a chemical shift

A standard is chosen, for NMR the standard chosen was tetramethylsilane (TMS)

Since silane is less electronegative than carbon, the methyl groups
(and hence the hydrogens on the methyl groups)
will have more electron density than a typical carbon compound

the chemical shift of TMS is defined as 0.00

the chemical shift for a different hydrogen is defined as follows:

chemical shift (ppm or δ) = (shift downfield from TMS, Hz)/(total frequency, MHz)

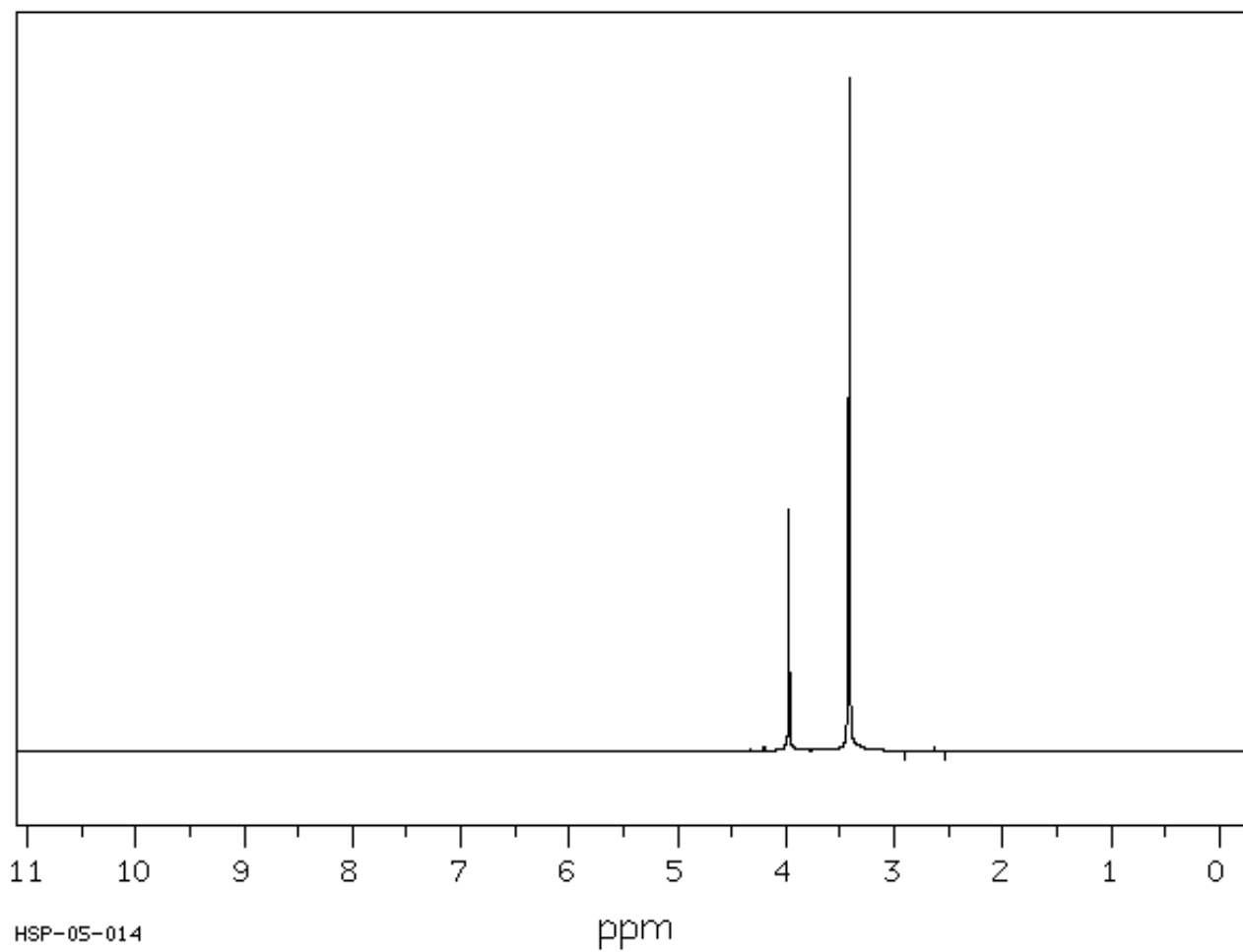
A NMR spectrum is recorded with increasing magnetic field towards the right

A more shielded proton (more electron density around the proton) would therefore be further to the right (called upfield)

A less shielded proton (less electron density around the proton) would therefore be further to the left (called downfield)

Since the δ is measured by shift downfield a positive δ number means the proton has less electron density (or less shielding) than TMS

An advantage of δ is the number is the same regardless of which instrument is used

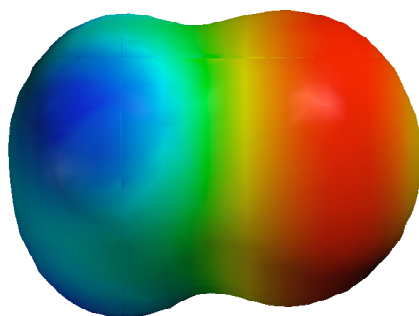


← downfield
upfield →

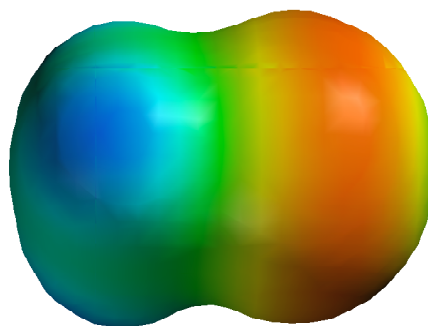
Predicting Chemical Shifts is Therefore the Same as
Predicting Electron Density Around Nucleus

Consider Methyl Halides

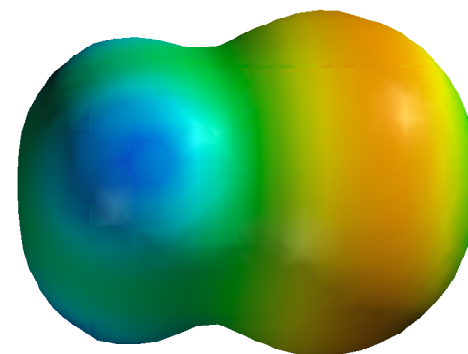
CH₃Cl



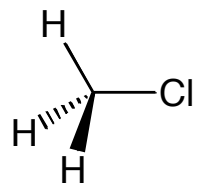
CH₃Br



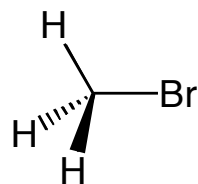
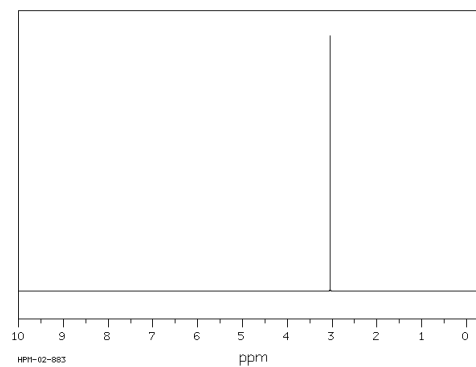
CH₃I



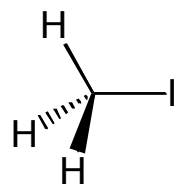
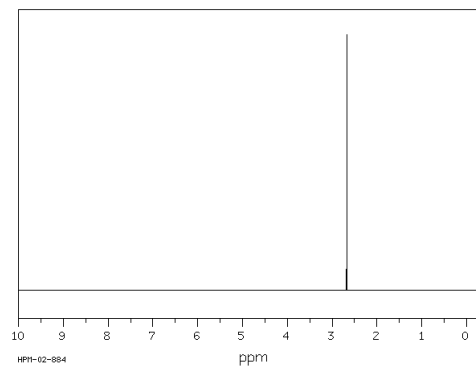
as the electronegativity of the Halide increases
there is less electron density around the hydrogens



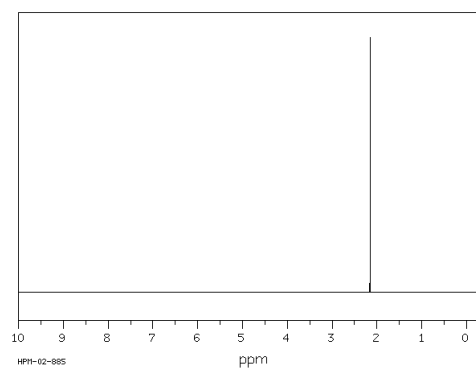
□ of H's 3.0



□ of H's 2.7

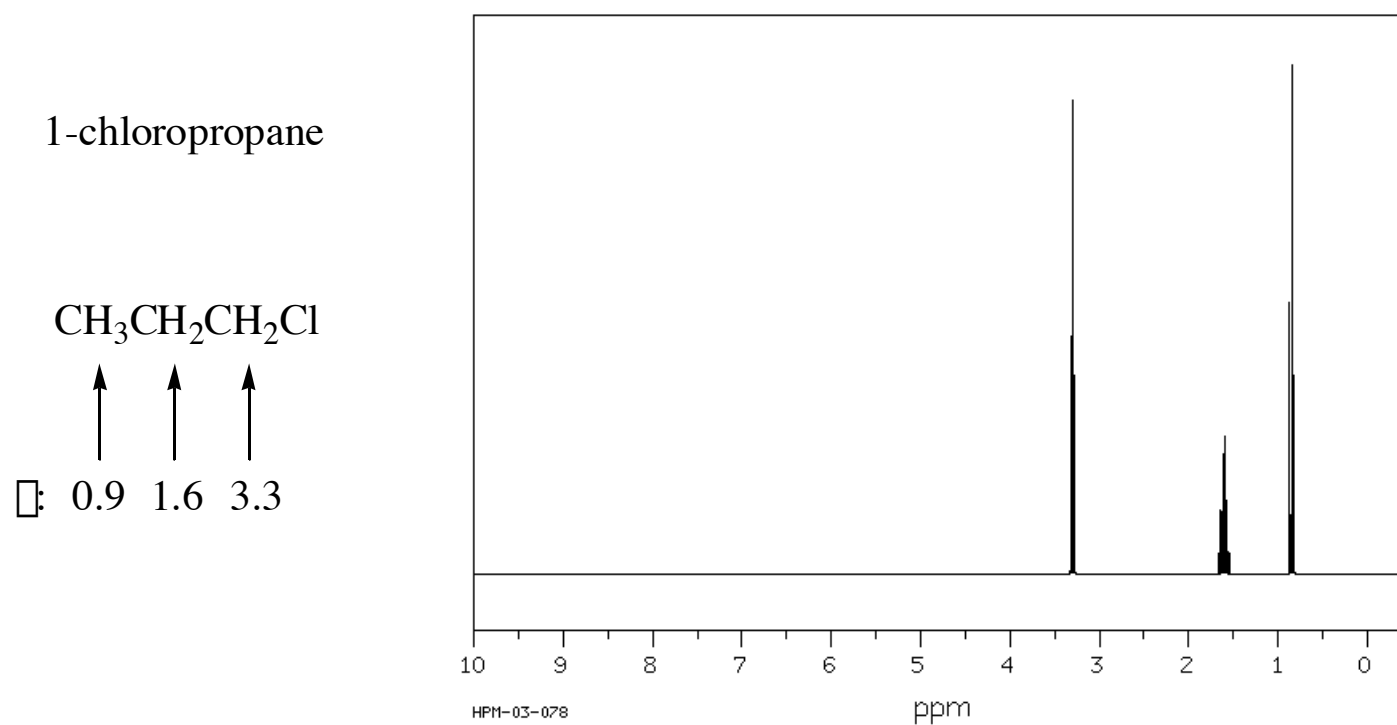


□ of H's 2.2



The chemical shift is lowered the further removed from electronegative atom

- saw same trend for pKa effect in acidity



also notice that we see more than one peak for each type of Hydrogen

Number of Signals

A NMR gives much more information than only the electron density around the nucleus of interest (although that alone is a tremendous amount of information)

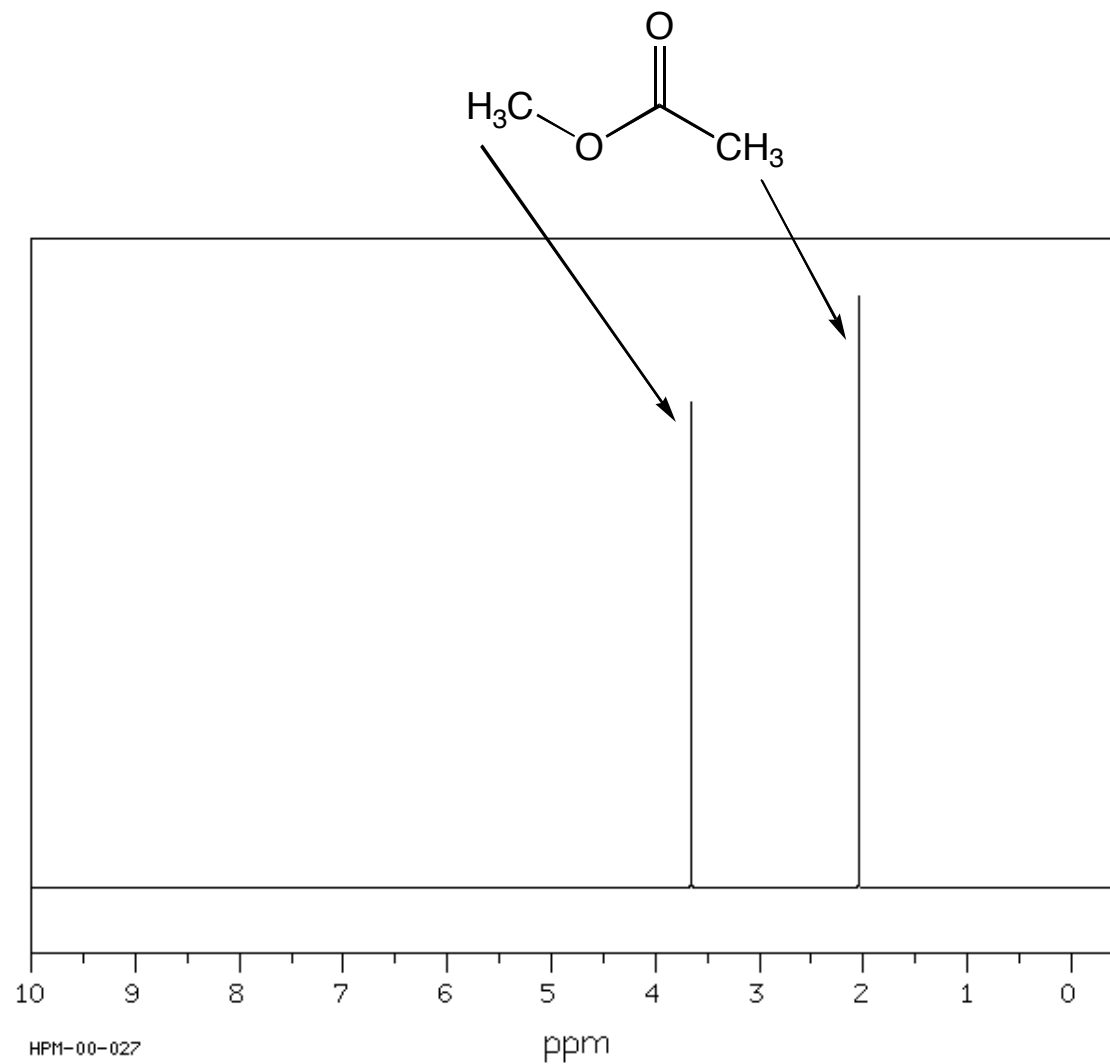
Each different type of nucleus will have its own unique chemical shift

In the example above with 1-chloropropane there are three different types of hydrogens (one α to chlorine, one β to chlorine and one γ to chlorine)

Each different hydrogen has a different chemical shift

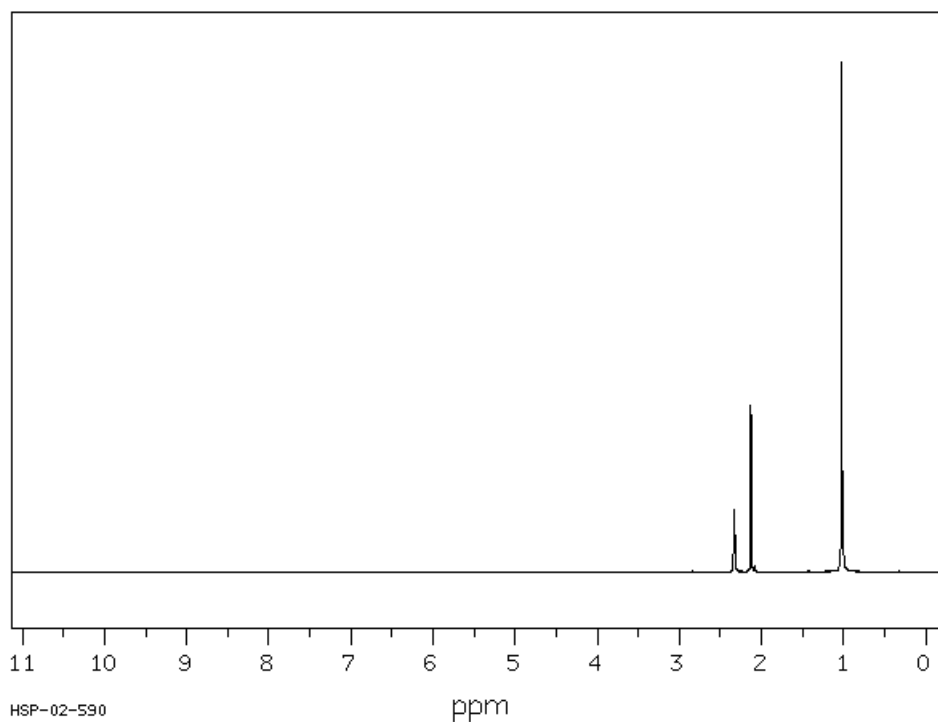
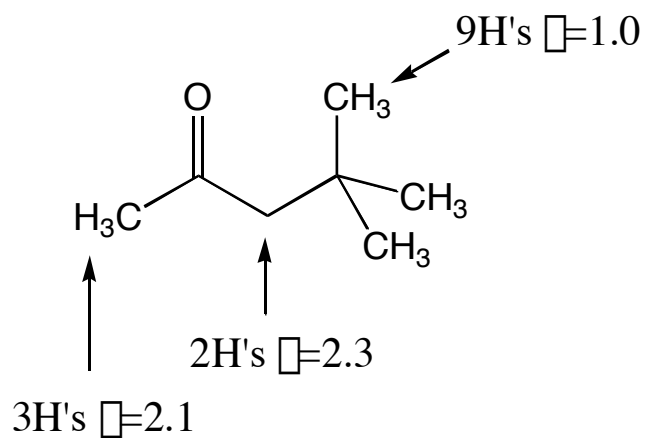
$$\delta = 3.3, \delta = 1.6, \delta = 0.9$$

By Counting Number of Different Peaks We Know Number of Different Hydrogens



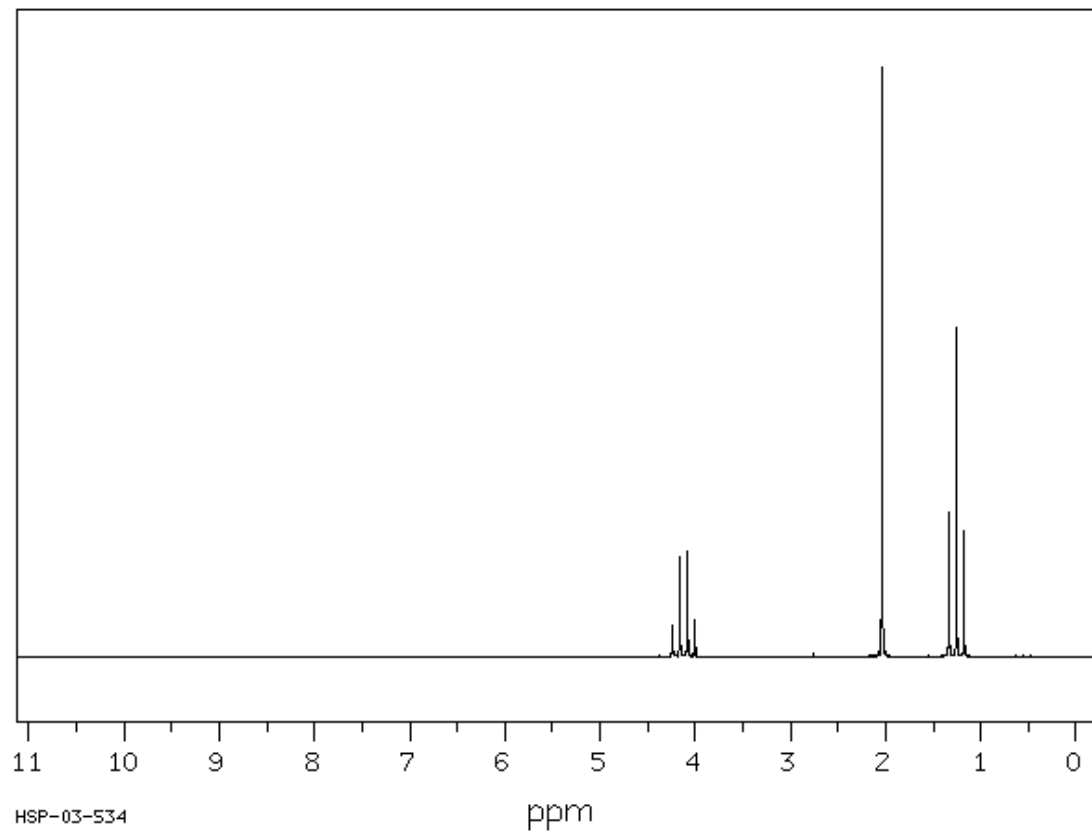
Area of Peaks

In a ^1H NMR spectrum the area of each peak indicates the relative number of hydrogens of that type



Spin-Spin Splitting

Remember we saw a NMR with additional signals



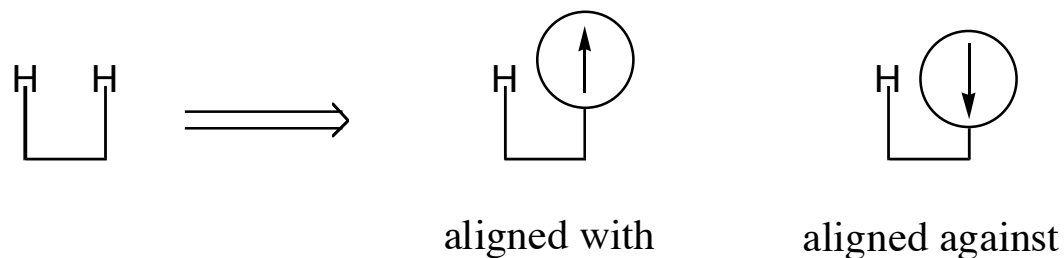
In addition to the electron density surrounding the proton allowing shielding,

Each proton acts like its own magnetic field

If one magnet is close to another it will feel its magnetic field

This is what occurs in a proton NMR

A proton will feel the effect of neighboring protons



in the field of one additional proton therefore we would observe two signals

As the number of neighboring protons increases the number of signals increase

Can predict the splitting by knowing the number of magnetically equivalent hydrogens causing the splitting

Pascal's triangle

# of protons causing splitting	peak area				
0	1				
1	1	1			
2	1	2	1		
3	1	3	3	1	
4	1	4	6	4	1

N+1 Rule

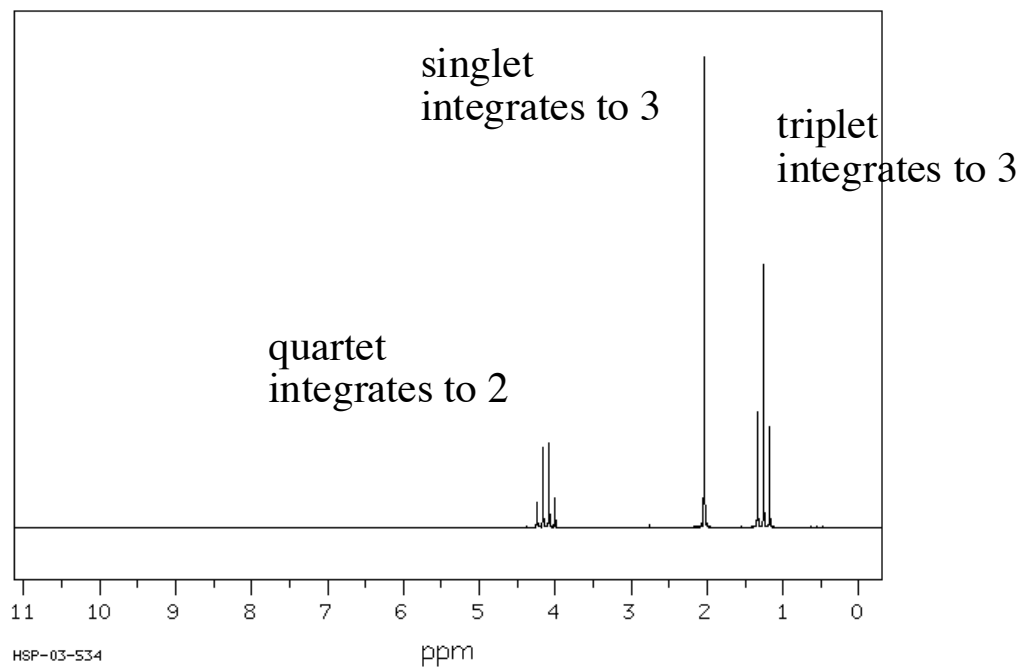
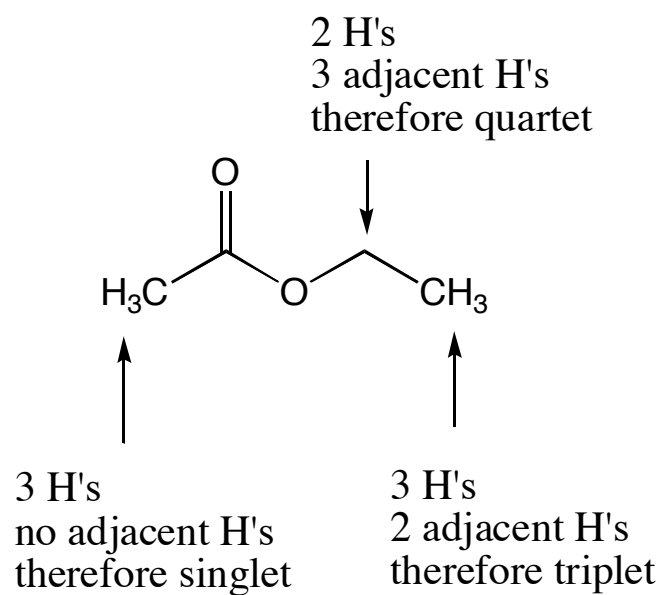
The number of observed splittings is also called the N+1 rule

If you have N number of magnetically equivalent hydrogens causing the splitting
you then have N+1 peaks in the spectrum

a proton does not cause splitting with itself but only with neighboring protons
must be within a short distance to observe the splitting

for alkanes normally observe the splitting only for hydrogens
attached to adjacent carbons

Knowing this we can interpret the spectrum



Coupling Constants

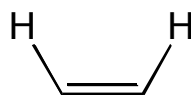
The splitting caused by adjacent hydrogens (or any magnetically active species) is called J coupling and it is a constant value

A proton, which splits a neighboring proton by a J value, will also be split itself by the same J value (reciprocal splitting)

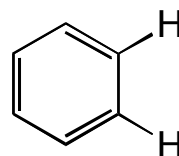
The magnitude of this J coupling can also be characteristic of the type of proton

Most alkane protons have a J constant of $\sim 7\text{Hz}$

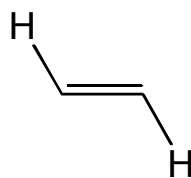
Other Characteristic J Couplings



10 Hz

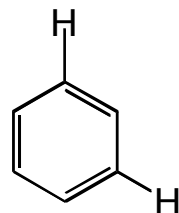


8 Hz

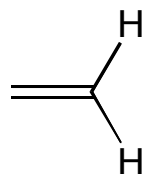


15 Hz

trans always larger
than cis



2 Hz

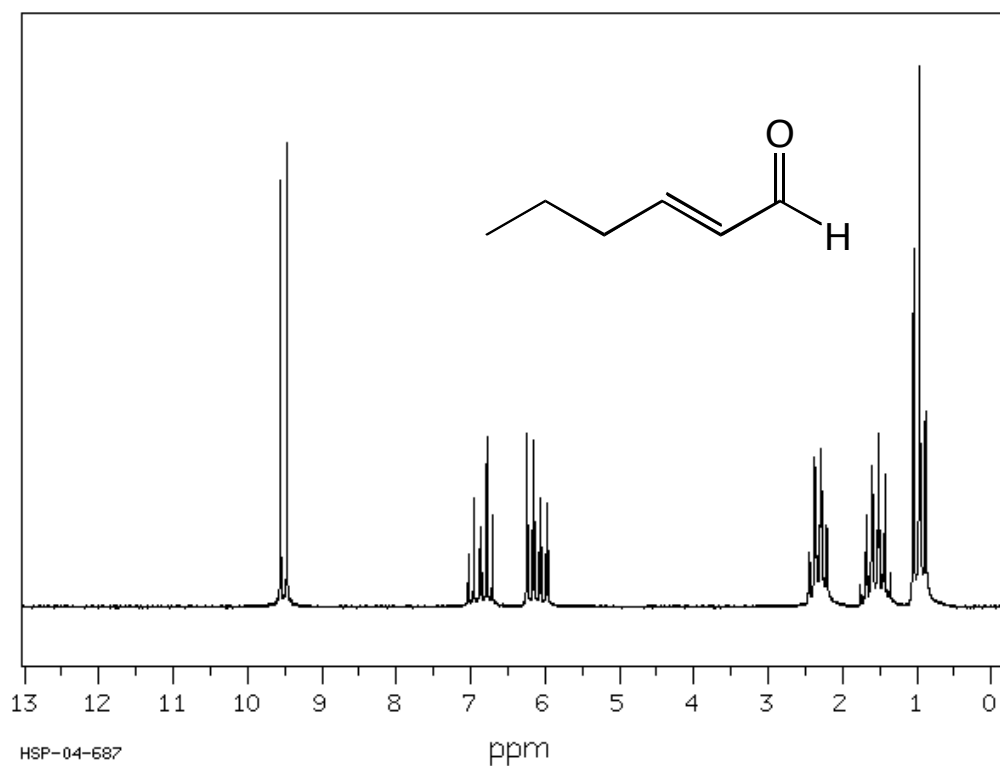


2 Hz

most convenient to distinguish cis from trans alkenes

Complex Splitting

Most of the cases we have observed so far are relatively quite simple
In many examples, though, the splitting is caused by more than one magnetically
equivalent adjacent proton



Stereochemical Nonequivalence

Remember that all magnetically equivalent protons will have the same chemical shift

If the protons have a stereochemical nonequivalence, however,
they will have different shifts

the magnitude of this difference is entirely dependent on the structure
(can be quite small and not observable)

If the protons are stereochemically nonequivalent they will in addition split each other

Time Dependence

NMR takes a certain amount of time to record

Therefore anything with a lifetime shorter than the recording length will not be observed,
in practice need a lifetime of ~ 1 sec to observe

This is true for any of the alkanes where bond rotation is much quicker than this time
scale and hence the observed spectrum is an average of all the bond rotations

If the process is slower than the NMR, however,
the NMR can distinguish the different conformers

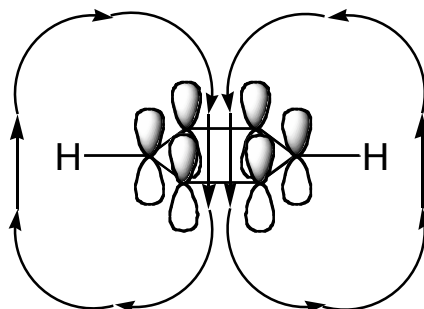
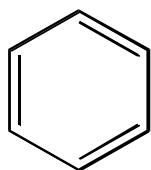
sometimes a NMR will be taken at different temperatures
to slow down the process to observe by NMR

Some Characteristic Functional Groups

We have observed many functional groups (and will see others to come)

The NMR can distinguish if these groups are present by the characteristic chemical shifts for these functional groups

Aromatic Groups (e.g. Benzene)



the electrons in the ring can circulate and cause a ring current
this current will generate an induced magnetic field which will cause deshielding of aromatic hydrogens

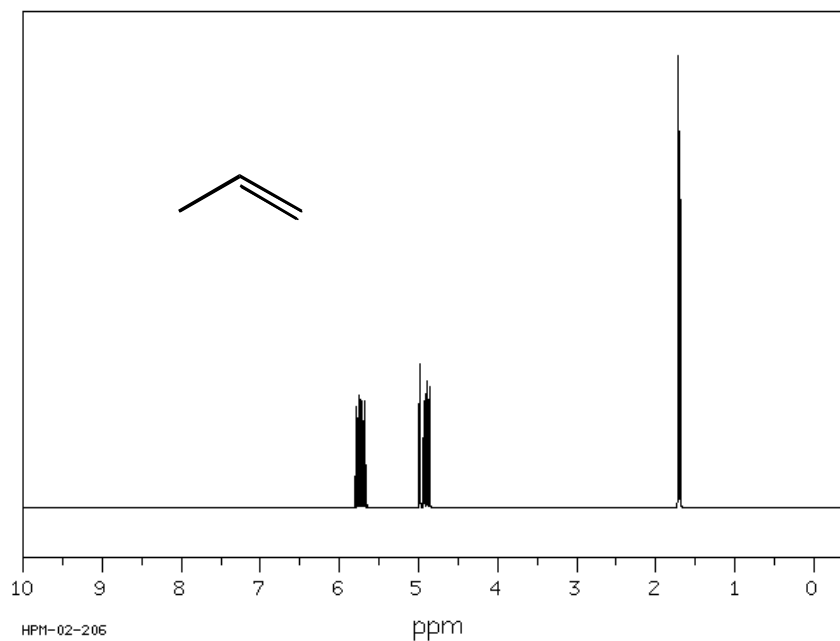
due to this effect aromatic hydrogens have chemical shifts in 7-8 ppm range

Alkenes

Alkenes are deshielding in the same way as aromatic hydrogens

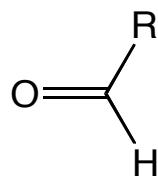
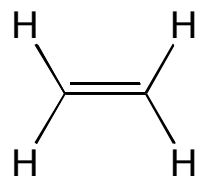
Since there are far less of an effect with only 2 electrons of an alkene relative to 6 electrons in benzene the deshielding is less

Alkenes have chemical shifts in the 5-6 ppm range



Aldehyde

An aldehyde is similar to an alkene



in addition to the induced magnetic field caused by the double bond, however, the aldehyde hydrogen is further deshielded by the electron withdrawing effect of the carbonyl group

due to this the aldehyde hydrogen has a chemical shift of 9-10 ppm

Hydrogen-Bonded Protons

Protons that can hydrogen bond, e.g. alcohols, amines and carboxylic acids,
can exist in many states on the NMR time scale

Each state can have a slightly different chemical shift

Therefore these groups can often appear broader than the
traditional sharp peaks for other functional groups

the exact position can also depend on the degree of hydrogen bonding

alcohols 4.5 ppm (varies widely)

amines 3.5 ppm (varies widely)

carboxylic acids >11 ppm

(approximate positions)

Position of Common Functional Groups in ^1H NMR

