Organic Chemistry
Mechanistic Patterns
(Ogilvie)
Chapter 13

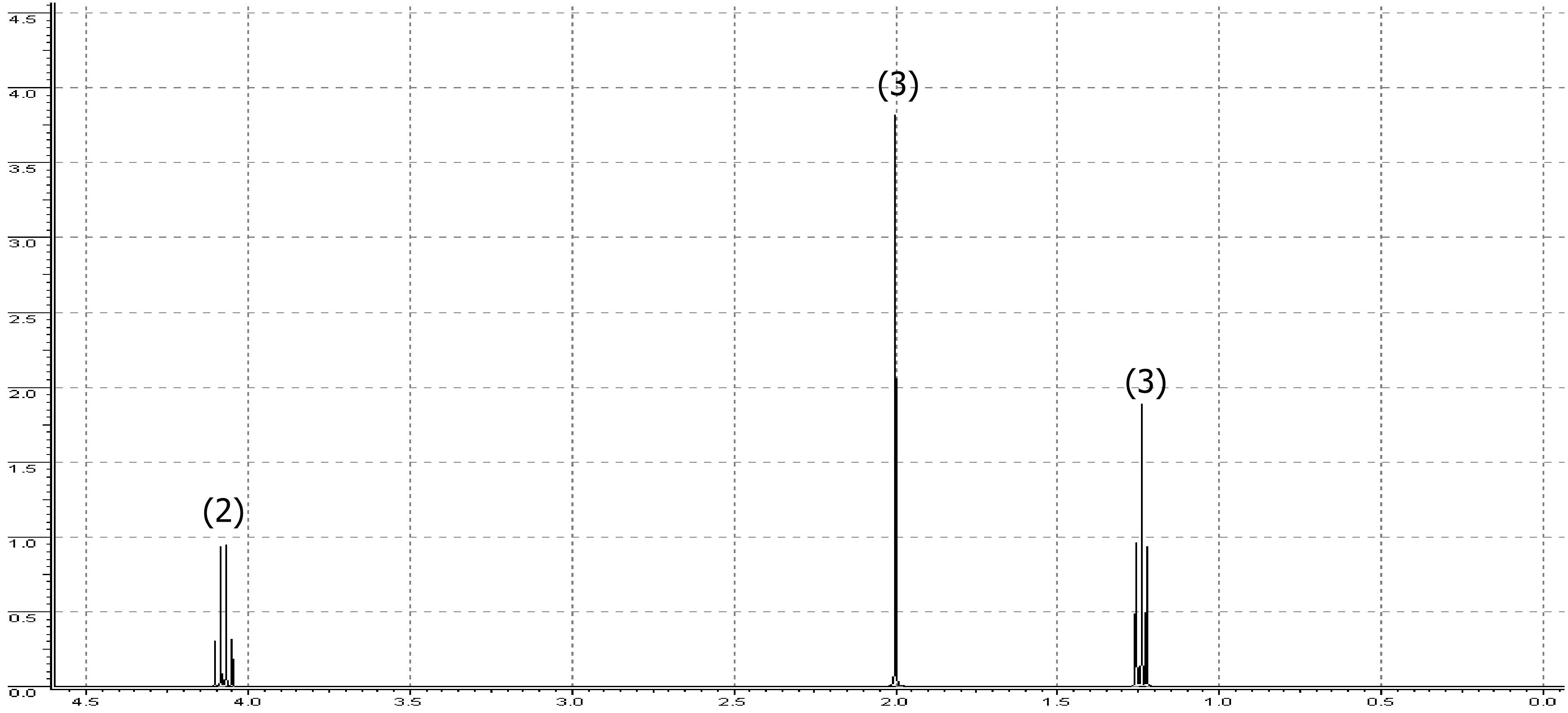
CHEMISTRY 2600

Topic #2: Using Spectroscopy to Identify Molecules:
Nuclear Magnetic Resonance (NMR)
Spring 2021
Dr. Susan Findlay

Thanks to Prof. Peter Dibble for many of the diagrams and spectra.

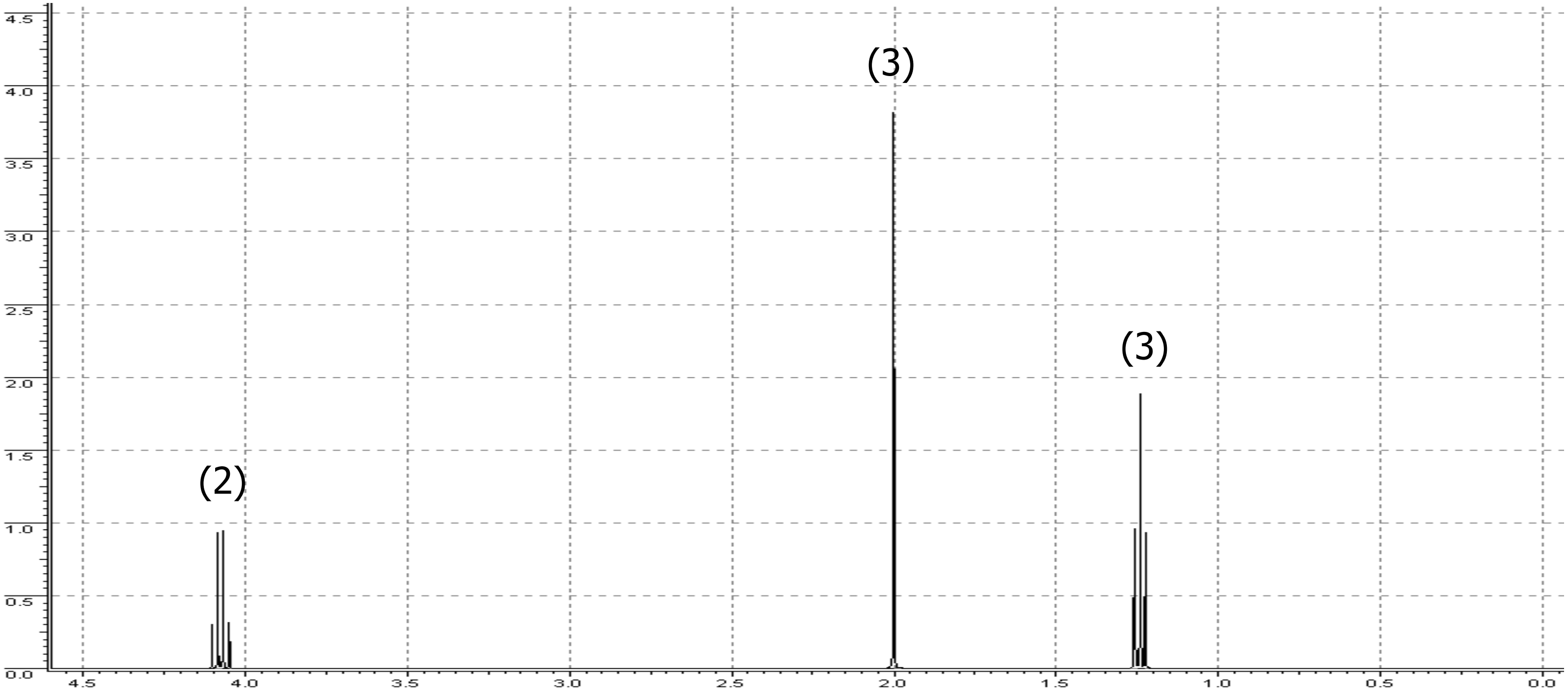
NMR is REALLY Useful!

- Most organic chemists would agree that Nuclear Magnetic Resonance, or NMR, is the tool they find most useful for identifying unknown compounds (or confirming that they made what they intended to make) – so much so that most organic chemists can identify common solvents just by glancing at a ^{1}H NMR spectrum such as the one below:



NMR is REALLY Useful!

- What are we looking for? Each signal on a ^{1}H NMR spectrum contains information about a distinct type of ^{1}H atom in the molecule. Look at:
  - **Integration** (peak size) tells us the relative number of ^{1}H for each signal
  - **Chemical Shift** (peak location) tells us the chemical environment for each type of ^{1}H (proximity to electronegative atoms, pi systems, etc.)
  - **Multiplicity** (peak shape) tells us how many ^{1}H of other types are on neighboring C* *(a slight oversimplification that will be expanded upon later)*



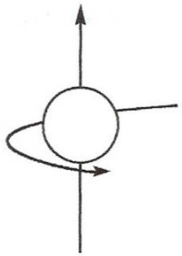
NMR is REALLY Useful!

- What can we conclude about this particular common solvent?

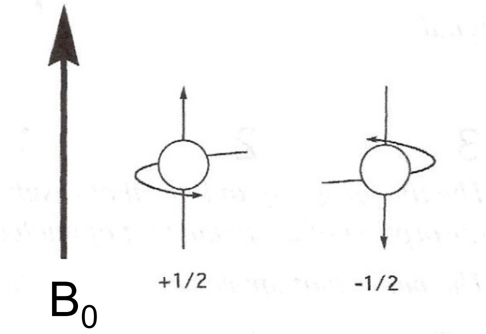
- What does ^{1}H NMR *not* tell us directly?

Even so, by the end of CHEM 2600, you'll easily be able to identify this and many other organic molecules from their ^{1}H NMR spectra alone!

How does ^{1}H NMR Work?



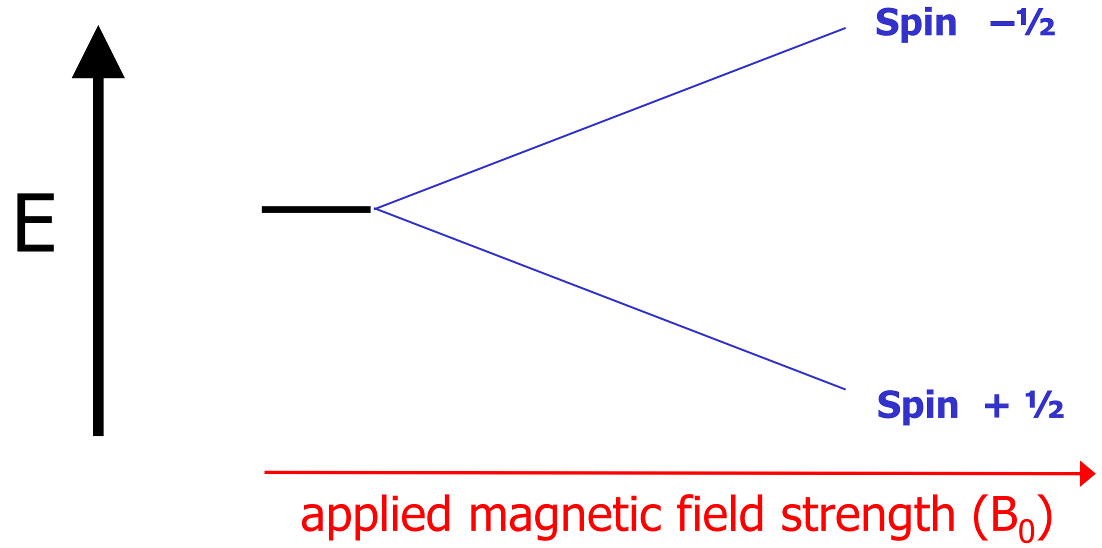
- Just as electrons have spin *(remember CHEM 1000…),* so do protons and neutrons. Thus, most nuclei have a net spin described by the quantum number I where $I = 0, \frac{1}{2}, 1, \frac{3}{2}, 2, \frac{5}{2}$, etc.
    - Nuclei with I = ½ include ^{1}H, ^{13}C, ^{19}F, ^{31}P *(easiest to analyze by NMR)*
    - Nuclei with I = 0 include ^{12}C, ^{16}O, ^{20}Ne *(cannot analyze by NMR)*
    - Nuclei with I = 1 include ^{14}N, ^{2}H *(difficult to analyze by NMR)*
- In the absence of a magnetic field, the nuclei in a sample can tumble, leaving the sample with no net spin due to averaging.
- If a magnetic field is applied, each nucleus will adopt one of 2I + 1 possible **spin states**, each having a slightly different energy depending on its orientation relative to the magnetic field. *e.g. ^{1}H shown at right*



- NMR is based on the energy difference between the different spin states. Knowing this, why is it impossible to analyze atoms with I = 0 by NMR?

How does ^{1}H NMR Work?

- The energy difference between the two spin states in the presence of a magnetic field is an example of Zeeman splitting *(recall CHEM 1000)* and, as the strength of the magnetic field increases, the energy difference also increases:



- The energy gap is small enough that there will be some nuclei in each spin state. The ratio can be calculated using a form of the Boltzmann equation:

$$\frac{N_{upper}}{N_{lower}} = e^{\frac{-\Delta E}{kT}}$$

- ΔE depends on the nucleus being studied and the strength of the magnetic field; k is the Boltzmann constant and T is temperature (in K)

How does ^{1}H NMR Work?

- In a 300 MHz ^{1}H NMR spectrometer, the ratio is 1,000,048 : 1,000,000. What does this tell us about the size of the energy gap (ΔE)?

- When a sample in a magnetic field is irradiated with radio waves of the appropriate frequency, nuclei in the lower energy spin state can absorb a photon, exciting them into the higher energy spin state. This is the "resonance" of NMR – not to be mixed up with drawing resonance structures!

- The first "continuous wave" NMR spectrometers worked as you might expect. The sample was irradiated with different frequencies of radio waves one at a time and a detector noted which frequencies were absorbed (the signals). These instruments were slower and less sensitive than modern NMRs, but they were revolutionary for their time!

How does ^{1}H NMR Work?

- Modern “Fourier transform” NMR spectrometers work by hitting the sample with a “pulse” of radio waves of all frequencies and detecting which frequencies are given off as the sample relaxes to its original spin state distribution. Once it has relaxed, another pulse can be applied. In the same time as it would take to acquire data for one spectrum using a CW-NMR, data for many spectra can be acquired using a FT-NMR. They can be combined to give a better signal-to-noise ratio than possible using a CW-NMR for the same duration. As you can imagine, the output of a FT-NMR is complex, and the data must be processed by a computer to generate the type of spectrum shown on the first pages of these notes.

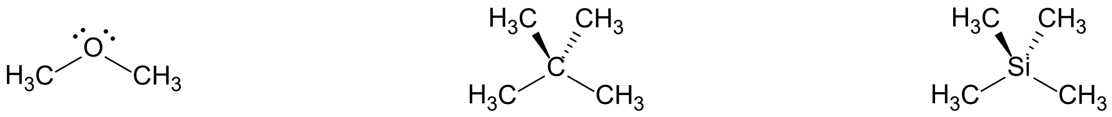
- It’s also worth noting that magnet technology has improved dramatically over the last several decades. While I used a 60 MHz NMR when I was an undergrad, you’ll be using a 300 MHz FT-NMR, and some biochemists and biologists use instruments with 1000+ MHz magnets. These larger magnets offer two significant advantages: greater sensitivity and better resolution between signals.

So, Why Isn't the Spectrum Just One Signal?

- While all ^1H in a given magnetic field will absorb radio waves of approximately the same frequency, the electrons in a molecule also have spin and generate their own magnetic fields, **shielding** ^1H nuclei from some of the external magnetic field.

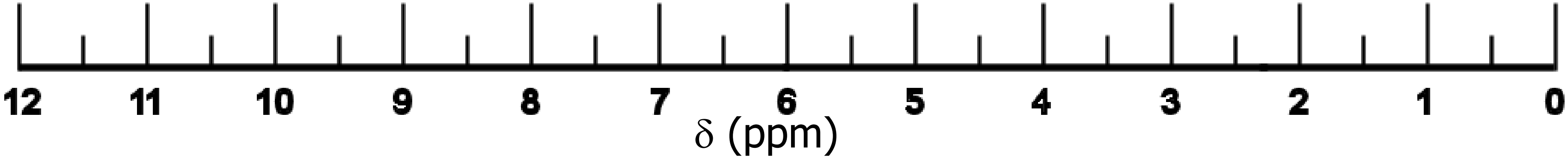
- Thus, ^1H with more electron density around them generally absorb lower energy (and therefore lower frequency) radio waves than ^1H surrounded by less electron density.

  e.g. dimethyl ether vs. 2,2-dimethylpropane vs. tetramethylsilane



So, Why Isn’t the Spectrum Just One Signal?

- **Shielding** of a nucleus moves the signal further right **(upfield)** on an NMR spectrum while **deshielding** moves the signal further left **(downfield).**



So, Why Isn't the Spectrum Just One Signal?

- The amount of shielding of a nucleus is relative, and most ^{1}H NMR signals are downfield of that for tetramethylsilane (TMS). As such, TMS is often used as a standard with its **chemical shift** set to zero.

- Since the frequency of the radio waves absorbed is proportional to the external magnetic field, the same molecule will absorb different frequencies in different instruments. To circumvent this problem, we define chemical shift (δ) as being in units of parts per million (ppm):

$$\delta = \frac{\upsilon_{\text{signal downfield of TMS}}\,(in\ Hz)}{\text{spectrometer frequency}\ (in\ MHz)}\ ppm$$

So, Why Isn’t the Spectrum Just One Signal?

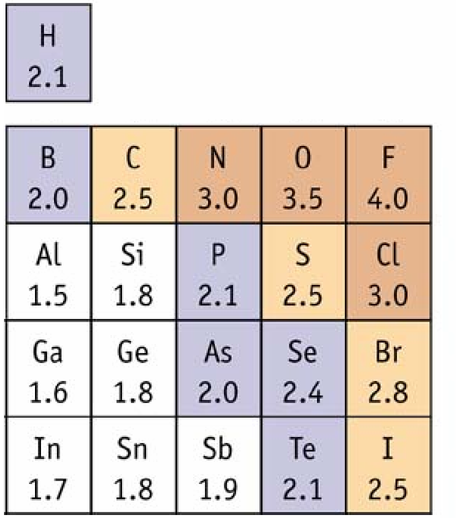
- Most ^1H nuclei have chemical shifts between 0 and 13 ppm in $CDCl_3$ (one of the most commonly used solvents for ^1H NMR).
- Be aware that chemical shifts are solvent-dependent – especially for OH groups!
- Why couldn’t you use $CHCl_3$ as a solvent for ^1H NMR instead of $CDCl_3$? It would be much cheaper…

Chemical Shifts (σ Bonds & Inductive Effects)

- Chemical shift of a ^1H correlates well with the electronegativity of the surrounding atoms as long as:
  - the ^1H is bonded to C
  - there are no π bonds nearby

- In an alkane, chemical shifts depend on whether the ^1H is attached to a primary, secondary or tertiary carbon:

methane	0.23 ppm
ethane	0.86 ppm
propane	0.91 ppm and 1.37 ppm
2-methylpropane	0.96 ppm and 2.01 ppm



H 2.1				
B 2.0	C 2.5	N 3.0	O 3.5	F 4.0
Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0
Ga 1.6	Ge 1.8	As 2.0	Se 2.4	Br 2.8
In 1.7	Sn 1.8	Sb 1.9	Te 2.1	I 2.5

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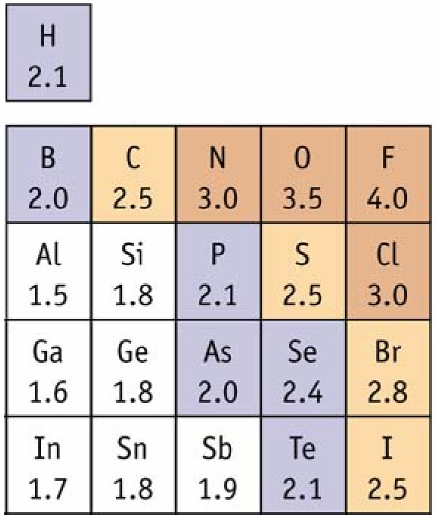
(Image modified)

Chemical Shifts (σ Bonds & Inductive Effects)

- More dramatic changes in chemical shift are seen when atoms with greater electronegativity are attached to the C bearing the ^1H:

H_3C-H	0.23 ppm
H_3C-I	2.16 ppm
H_3C-Br	2.68 ppm
H_3C-Cl	3.05 ppm
H_3C-OH	3.40 ppm *(for the CH_3 group)*
H_3C-F	4.26 ppm



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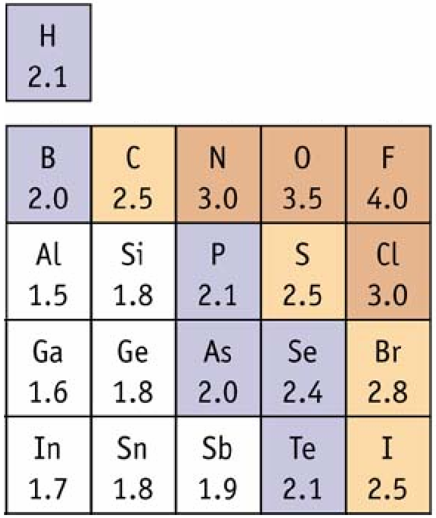
(Image modified)

Chemical Shifts (σ Bonds & Inductive Effects)

- Increasing the number of electronegative atoms moves the signal farther downfield:
  - CH_3Cl 3.05 ppm
  - CH_2Cl_2 5.30 ppm
  - $CHCl_3$ 7.27 ppm
- The effect decays as the distance to the electronegative atom increases:
  - -**CH_2**Br 3.30 ppm
  - -**CH_2**CH_2Br 1.69 ppm
  - -**CH_2**CH_2CH_2Br 1.25 ppm



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In 1.7	Sn 1.8	Sb 1.9	Te 2.1	I 2.5

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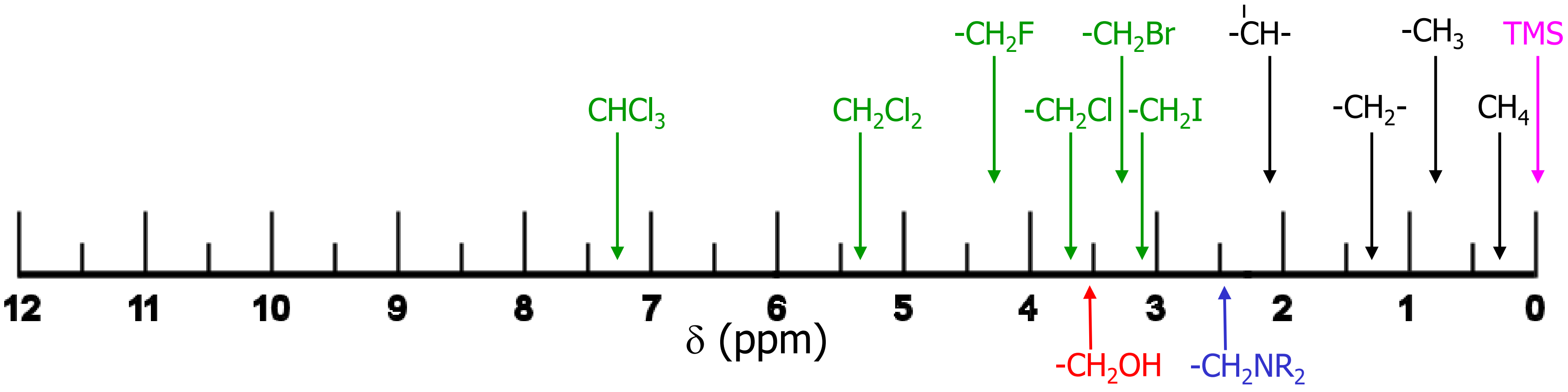
Chemical Shifts (σ Bonds & Inductive Effects)

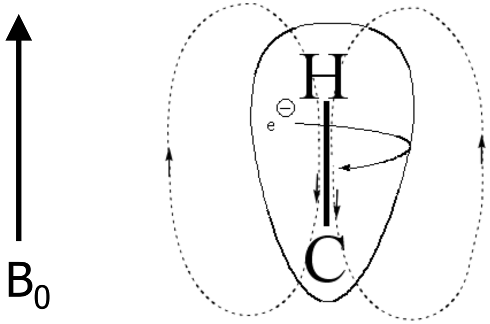
- When electronegative atoms pull electron density toward themselves through sigma bonds in this way, we call that an **inductive effect.**

- Inductive effects contribute significantly to the chemical shifts we observe on ^{1}H NMR spectra:

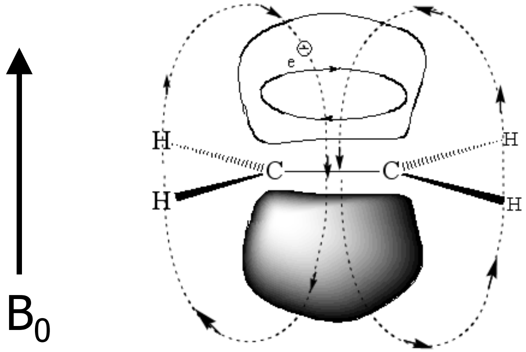


Chemical Shifts (π Bonds & Anisotropic Effects)

- **Electrons in σ bonds shield** ^{1}H by generating magnetic fields that oppose the external magnetic field felt by the ^{1}H:

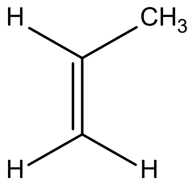


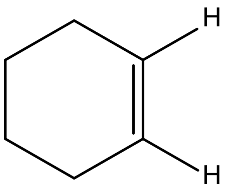
- The magnetic fields generated by π **bonds** tend to be larger than those generated by σ bonds. Also, at a vinyl ^{1}H, the magnetic field generated by the π electrons aligns with the external magnetic field, **deshielding the vinyl ^{1}H**:



Chemical Shifts (π Bonds & Anisotropic Effects)

- A typical vinyl ^{1}H has a chemical shift between 4.5 and 6 ppm.
  e.g. propene cyclohexene





- Allylic ^{1}H are also slightly deshielded relative to a ^{1}H in a saturated compound.

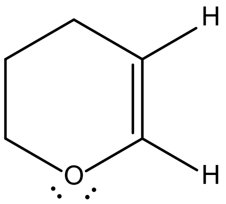
"vinyl ^{1}H" means "^{1}H attached to C of an alkene"

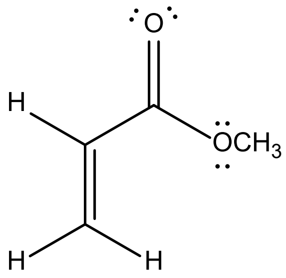
"allylic ^{1}H" means "^{1}H attached to tetrahedral C next to an alkene"

Chemical Shifts (π Bonds & Anisotropic Effects)

- Resonance may give a vinyl ^{1}H a chemical shift higher or lower than would otherwise be expected.

  e.g. dihydropyran methyl propenoate

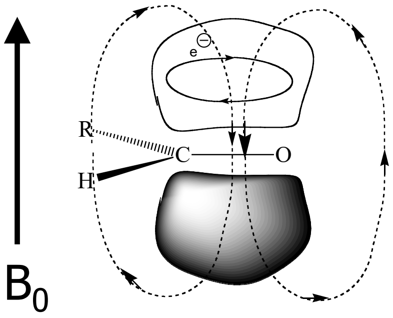




While the oxygen atoms are inductively electron-withdrawing *(via σ bonds)*, the resonance effects are stronger.

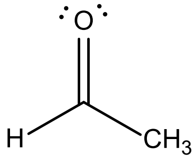
Chemical Shifts (π Bonds & Anisotropic Effects)

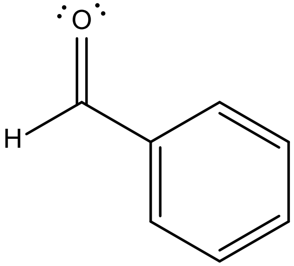
- A similar effect is observed for aldehydes:



- The **aldehyde ^{1}H is deshielded** by both the double bond and the oxygen atom, giving it a chemical shift between 9.5 and 10.5 ppm.

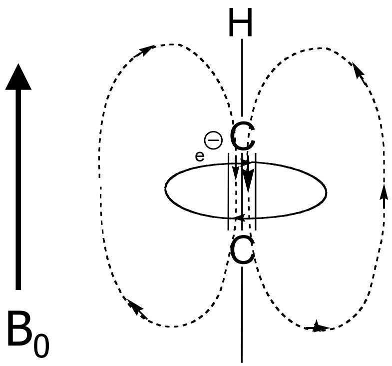
  e.g. ethanal *(acetaldehyde)* benzaldehyde





Chemical Shifts (π Bonds & Anisotropic Effects)

- An **alkynyl ^{1}H is shielded** by the magnetic field from the π electrons, giving it a chemical shift between 1.5 and 3 ppm. Compare the geometry of an alkyne to that of an alkene or aldehyde…

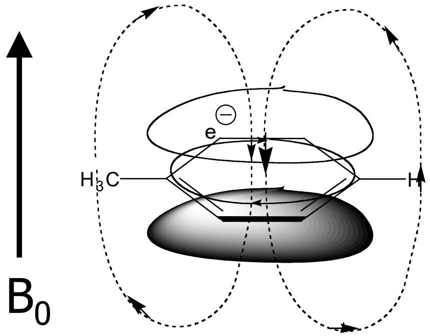


e.g. propyne

$H_3C—C≡C—H$

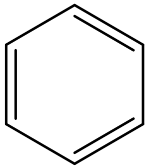
Chemical Shifts (π Bonds & Anisotropic Effects)

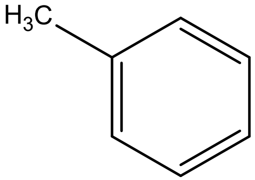
- If a ^{1}H NMR contains peaks between 6.5 and 9 ppm, it most likely corresponds to an aromatic compound.

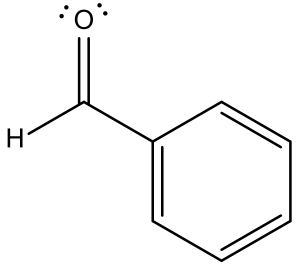


- Like vinyl ^{1}H, aryl ^{1}H are deshielded by the π electrons. *If an alkene is conjugated to a benzene ring or carbonyl group, those vinyl ^{1}H will often appear in or near the aromatic region too.*

e.g. benzene toluene benzaldehyde





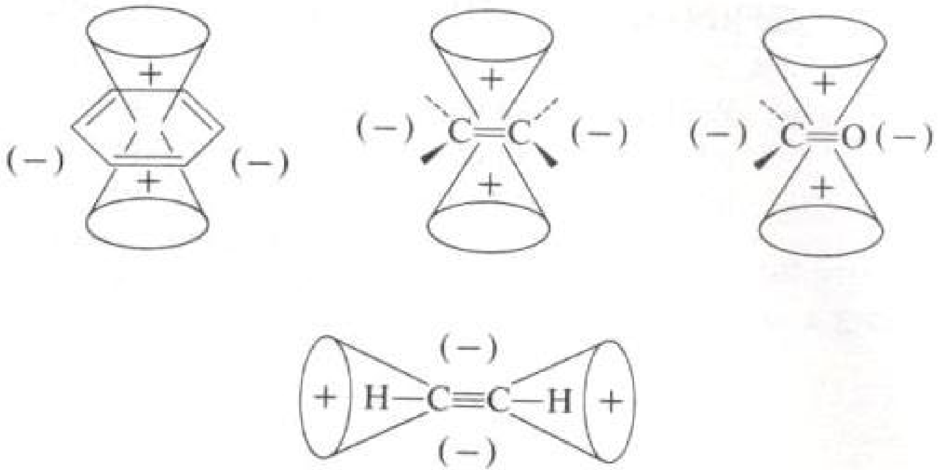


Chemical Shifts (π Bonds & Anisotropic Effects)

- Geometry is key to the anisotropic effect! Just as the ^{1}H on the outside of a benzene ring are strongly deshielded, a ^{1}H ***inside*** an aromatic system would be strongly shielded.

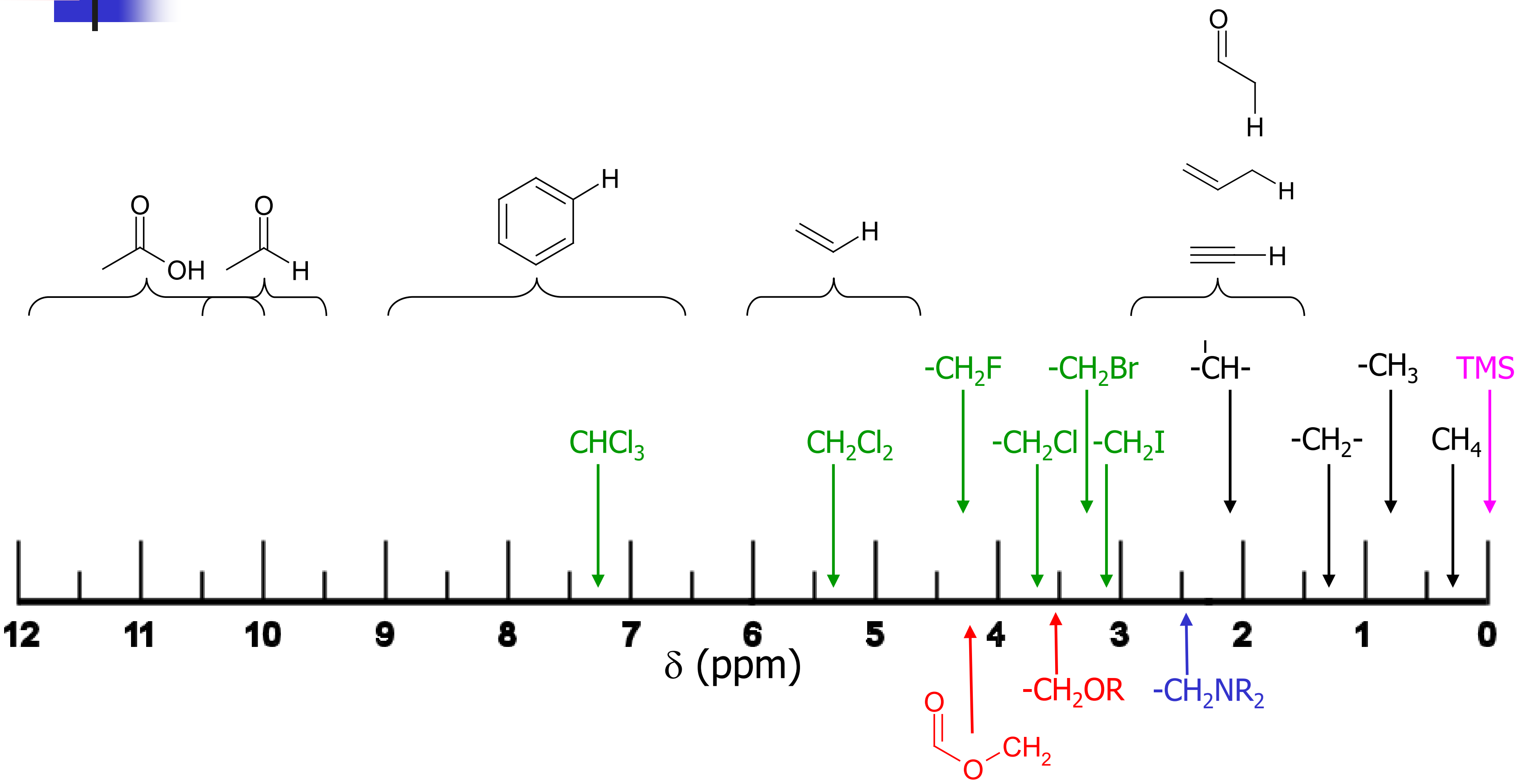
- Any thoughts on how to get a ^{1}H <u>inside</u> an aromatic system?

Chemical Shifts (π Bonds & Anisotropic Effects)



► **FIGURE 3.23** Anisotropy caused by the presence of π electrons in some common multiple-bond systems.

Chemical Shifts Summary



The absence of NH and OH shifts is intentional. They can appear anywhere between 0 and 14 ppm! Only carboxylic acids are somewhat consistent in their chemical shift. NH and OH peaks are often much broader in shape than CH peaks.

Symmetry and Chemical Shift Equivalence

- Whether two ^{1}H will give different peaks on a ^{1}H NMR spectrum or whether they'll be represented by the same peak depends on their relationship.
  - Homotopic ^{1}H are **chemically equivalent** and **shift equivalent**. They will always be represented by the same peak.
  - Enantiotopic ^{1}H are shift equivalent in achiral environments. They only give different peaks in chiral environments.
  - Diastereotopic ^{1}H are <u>not</u> shift equivalent. They may coincidentally give overlapping peaks (that may even merge together to look like one peak), but they give different peaks.
  - Constitutionally different ^{1}H are <u>not</u> shift equivalent. They may coincidentally give overlapping peaks (that may even merge together to look like one peak), but they give different peaks.

Symmetry and Chemical Shift Equivalence

- Atoms/groups that can be exchanged by bond rotation *without breaking any bonds* are **homotopic** (“the same”).

  e.g.

- Atoms/groups are also **homotopic** if they can be exchanged by rotating the whole molecule *without breaking any bonds.*

  e.g.

Symmetry and Chemical Shift Equivalence

- Atoms/groups that are **constitutionally different** are <u>not</u> shift equivalent *(though it is possible for them to have very similar – even overlapping – chemical shifts).*

  e.g.

Symmetry and Chemical Shift Equivalence

- Atoms/groups that can be exchanged by reflection in an internal mirror plane of symmetry (but cannot be exchanged by rotation) are **enantiotopic**.

  e.g.

- As long as the molecule is not placed in a chiral environment, enantiotopic atoms/groups are shift equivalent.

Symmetry and Chemical Shift Equivalence

- If two atoms/groups are not constitutionally different, not homotopic and not enantiotopic, they are **diastereotopic**.

  e.g.

- Diastereotopic atoms/groups are <u>not</u> shift equivalent *(though it is possible for them to have very similar – even overlapping – chemical shifts)*.

Symmetry and Chemical Shift Equivalence

- Generally, the easiest way to determine the topicity of a pair of atoms is to perform a substitution test. Essentially, pretend each of the H is a D instead and compare the resulting molecules. You are allowed to rotate/spin/flip the molecules as much as you like as long as you do not break any bonds.
  - If you get the same molecule, the atoms are homotopic.
  - If you get a pair of <u>enantio</u>mers, the atoms are <u>enantio</u>topic.
  - If you get a pair of <u>diastereo</u>mers, the atoms are <u>diastereo</u>topic.
  - If none of the above, the atoms are constitutionally different.

Symmetry and Chemical Shift Equivalence

e.g. Determine the topicity of the red hydrogen atoms in each chlorocyclopropane molecule below.

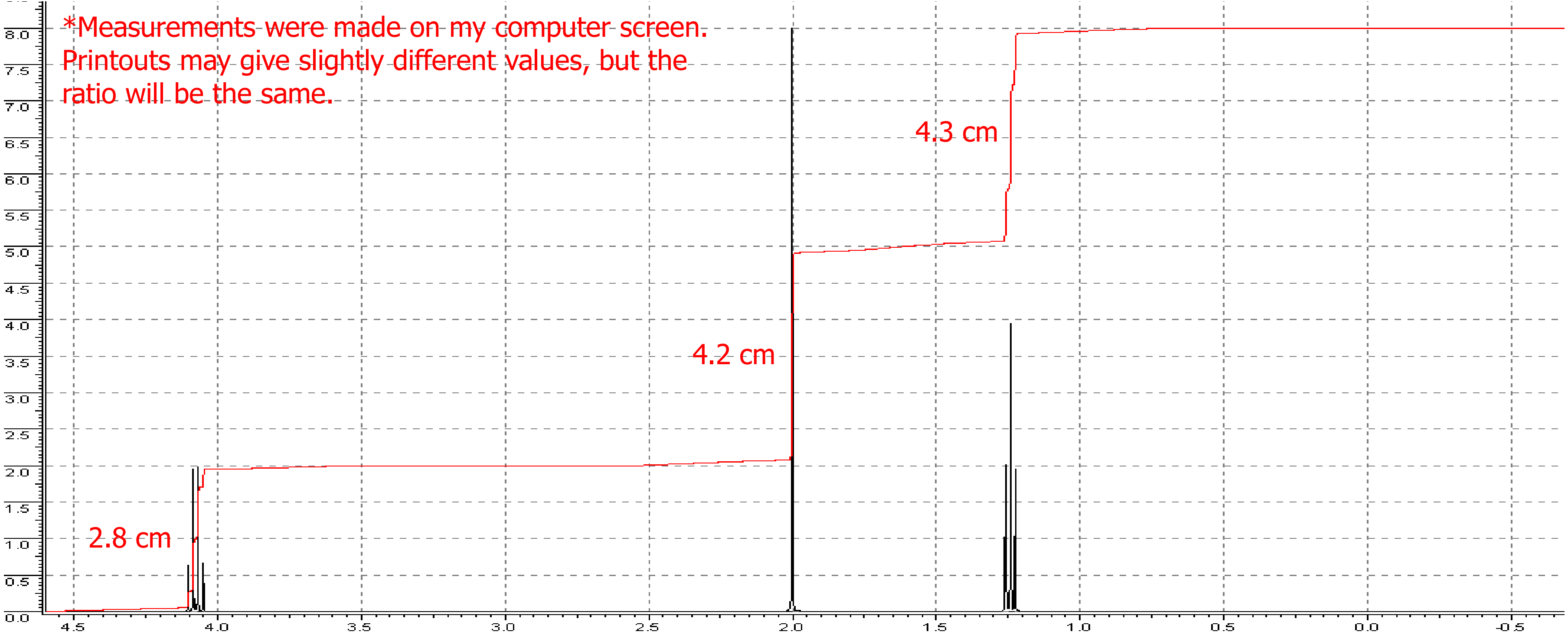
Symmetry and Chemical Shift Equivalence

e.g. Determine the topicity of the methylene (CH_2) protons in chloroethane.

Integration

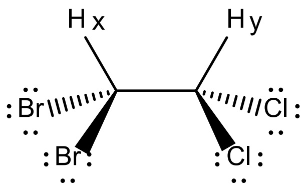
A “type” of ^1H in this context means a “set of shift equivalent ^1H”

- The number of signals on a ^1H NMR tells us how many different types of shift inequivalent ^1H there are in a molecule, and the chemical shift of each tells us about its chemical environment.
- The magnitude of each peak tells us how many ^1H of that type are present in the molecule **relative to the other types of ^1H**. This information is usually presented as integral traces:


*Measurements were made on my computer screen. Printouts may give slightly different values, but the ratio will be the same.

Multiplicity and Spin-Spin Coupling

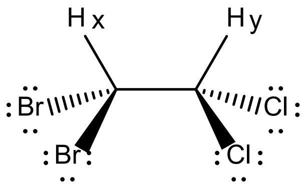
- Just as electrons can shield or deshield nearby nuclei, so can other nuclei. In the ^1H NMR spectrum for 1,1-dibromo-2,2-dichloroethane, we see two signals, each consisting of two lines. Why?



  - Each ^1H has a spin, so each ^1H is generating its own magnetic field. Recall that approximately half of the H_x are "spin up" and half are "spin down" *(random distribution)*. The same can be said for H_y.
  - Thus, half of the sample will have the magnetic field from H_y aligned with the external magnetic field, **deshielding H_x**. The other half of the sample will have the magnetic field from H_y opposing the external magnetic field, **shielding H_x**. As a result, half of the H_x will have a chemical shift slightly downfield of the signal center while half of the H_x will have a chemical shift slightly upfield of the signal center. The result is a signal consisting of two lines (a doublet).
  - This effect is known as spin-spin coupling – or **coupling** for short.
  - The distance between two lines in a signal is referred to as the **coupling constant (J)**. Coupling constants are reported in Hz as they do not depend on the instrument's magnetic field.

Multiplicity and Spin-Spin Coupling

- So, how does the ^{1}H NMR look?



δ (ppm)

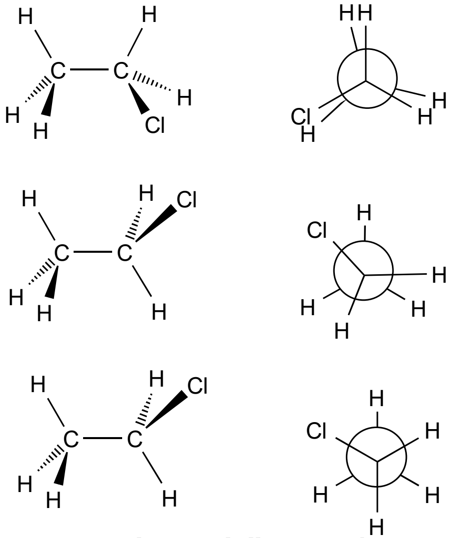
Multiplicity and Spin-Spin Coupling

- Important points about spin-spin coupling
  - Coupling is not visible for ^1H giving peaks with the same chemical shift *(even if this is coincidental and not due to topicity).*
  - Coupling must be mutual. If H_x couples to H_y then H_y must couple to H_x <u>with the same coupling constant</u>.
  - Coupling is a through-bond phenomenon – not a through-space phenomenon.
    - Most common is 3-bond coupling between vicinal ^1H (H-C-C-H)
    - 2-bond coupling can be observed between non-shift-equivalent geminal ^1H (H-C-H)
    - 4-bond coupling is relatively commonly observed if at least one π bond is present between the ^1H (H-C-C=C-H or similar). Long range coupling of this nature tends to give small coupling constants.

Multiplicity and Spin-Spin Coupling

- Important points about coupling constants
  - They are independent of the external magnetic field strength.
  - They depend on:
    - The number and type of bonds between the nuclei
    - The type of nuclei
    - The molecule’s conformation
- Vicinal coupling constants (^3J) depend on the overlap between the C-H bonds and can often be estimated using the Karplus curve:

e.g.



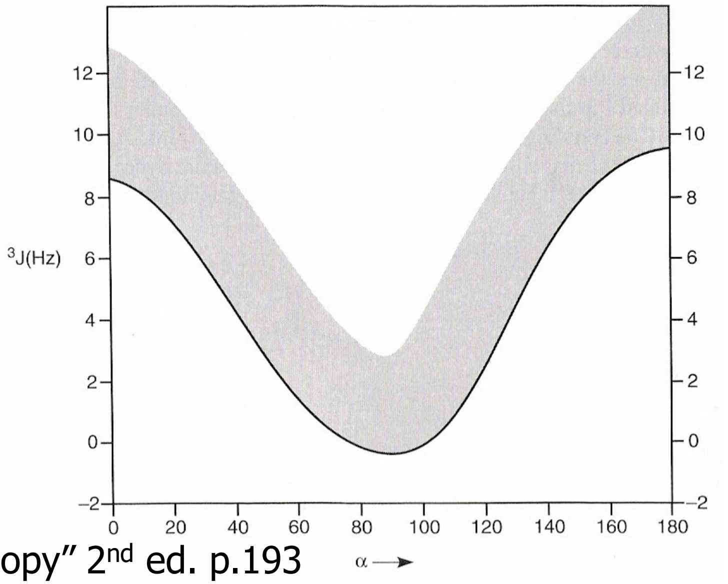
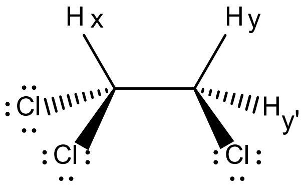


Figure from Pavia, Lampman & Kriz (1996) “Introduction to Spectroscopy” 2nd ed. p.193

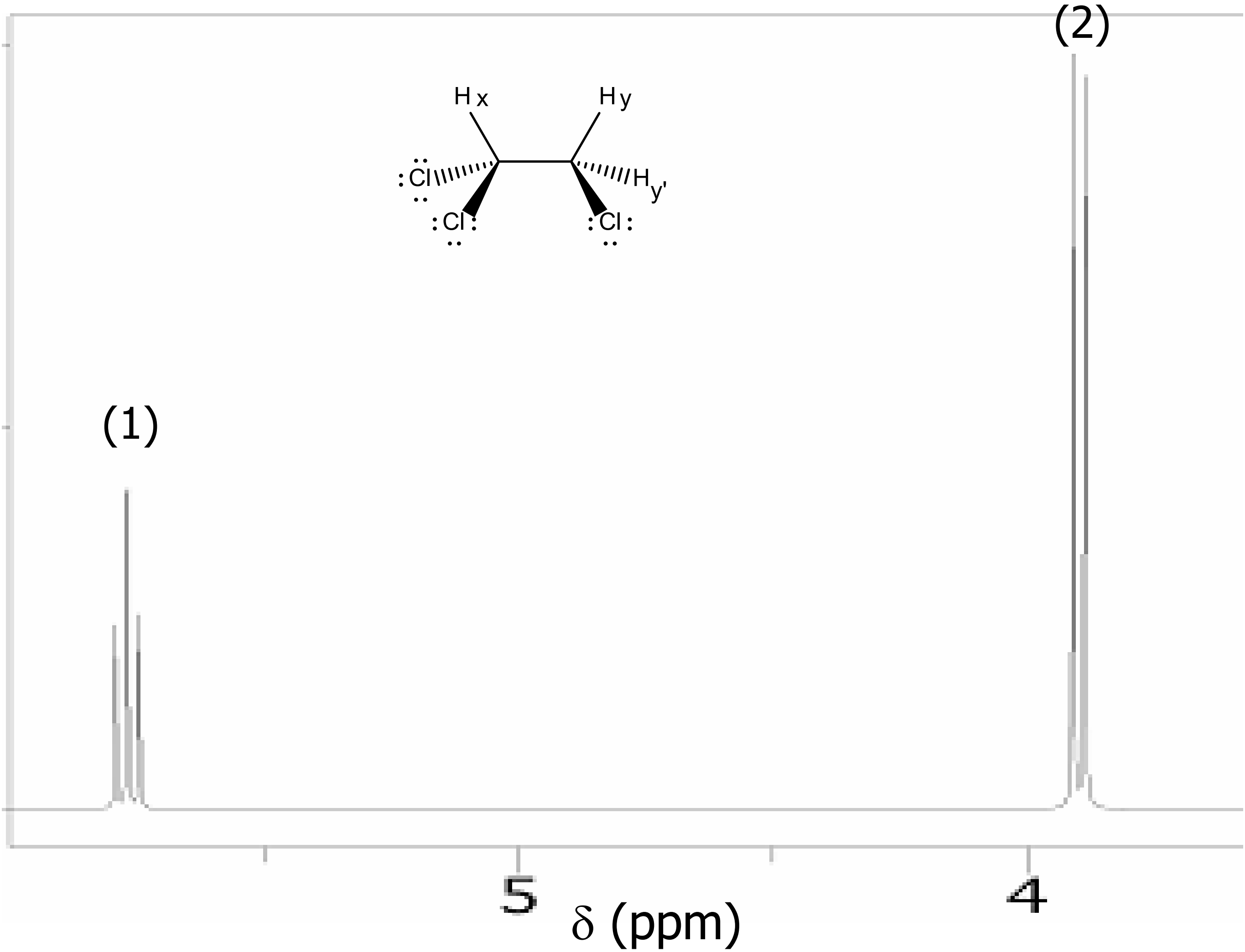
Multiplicity and Spin-Spin Coupling

- In the ^{1}H NMR spectrum of 1,1,2-trichloroethane, we see two signals. One consists of two lines (a doublet); the other of three lines in a 1 : 2 : 1 ratio (a triplet). Why?
  - H_y and $H_{y'}$ are shift equivalent because they are enantiotopic.
  - The signal for H_y & $H_{y'}$ is a doublet because both atoms couple to H_x. Since half the H_x are spin-up and half are spin-down, the $H_{y+y'}$ signal is split into two lines with coupling constant ^3J.
  - The signal for H_x is also split due to coupling with H_y and $H_{y'}$. There are four possible spin combinations for H_y and $H_{y'}$



Multiplicity and Spin-Spin Coupling

- …and here's what the ^{1}H NMR looks like:



Multiplicity and Spin-Spin Coupling

- Thus, assuming no 2- or 4-bond coupling,:
  - A ^{1}H with no vicinal ^{1}H gives a singlet
  - A ^{1}H with one vicinal ^{1}H gives a doublet
  - A ^{1}H with two vicinal ^{1}H gives a triplet
  - A ^{1}H with three vicinal ^{1}H gives a quartet *(as in example on pp. 2-3)*

- This can be extended to give the "n+1 rule":

For simple aliphatic systems, the number of lines in a given signal is n+1 where n is the number of vicinal protons.

- Be aware that the "n+1 rule" does not work for any system where there is more than one coupling constant. As such, it tends not to work for rigid systems such as rings, and it will not work if there is geminal coupling and/or long range coupling in addition to the vicinal coupling

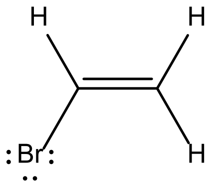
Multiplicity and Spin-Spin Coupling

- For it to be appropriate to use the “n+1 rule”, the peak **MUST** have the right shape – not just the right number of lines.
- For simple splitting patterns, Pascal’s triangle gives us the right peak ratio:

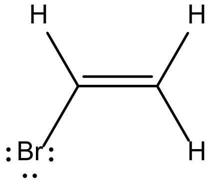
Multiplicity and Spin-Spin Coupling

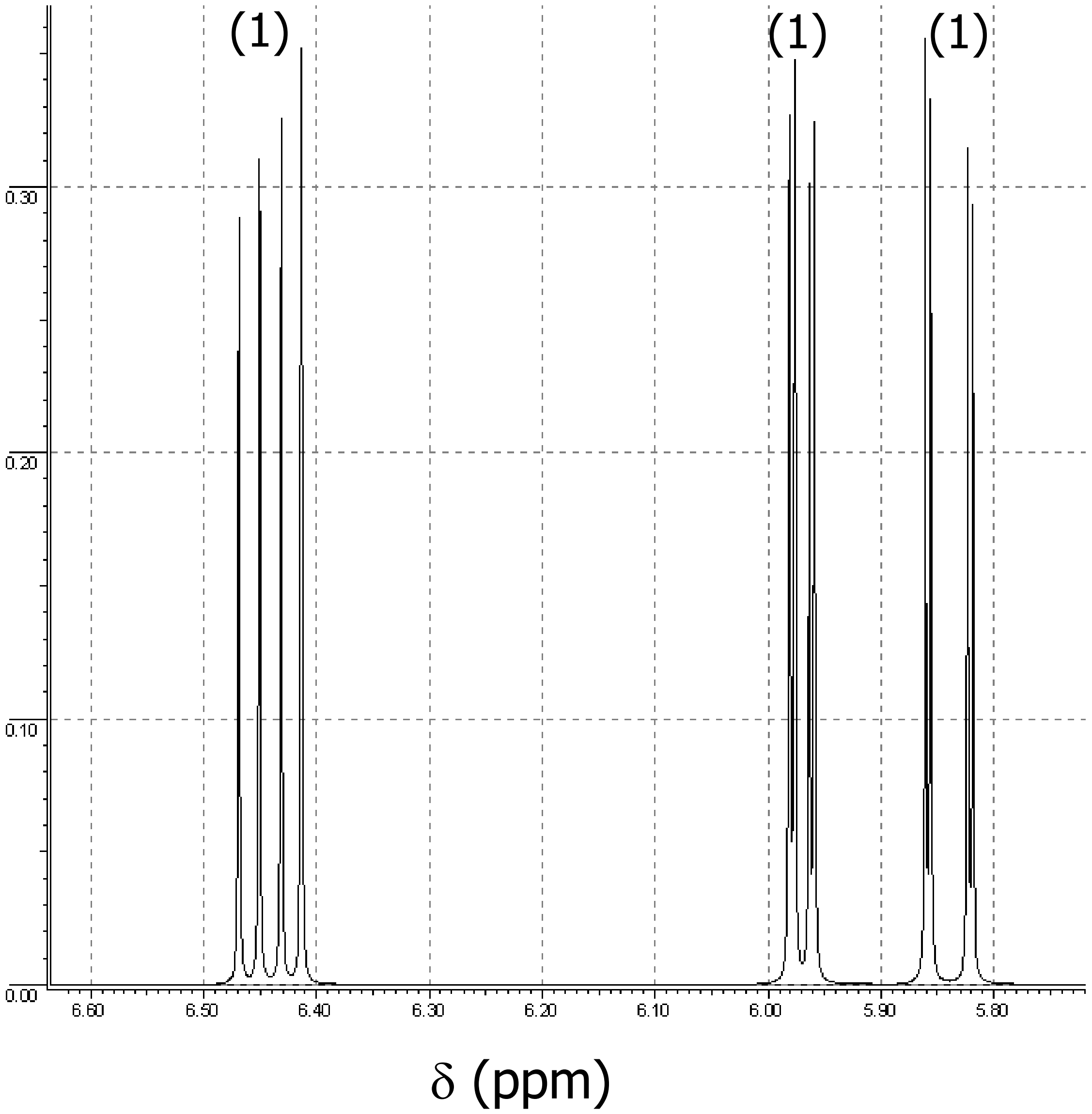
- For more complex splitting patterns (i.e. where more than one coupling constant is involved), we often use tree diagrams:

  e.g.



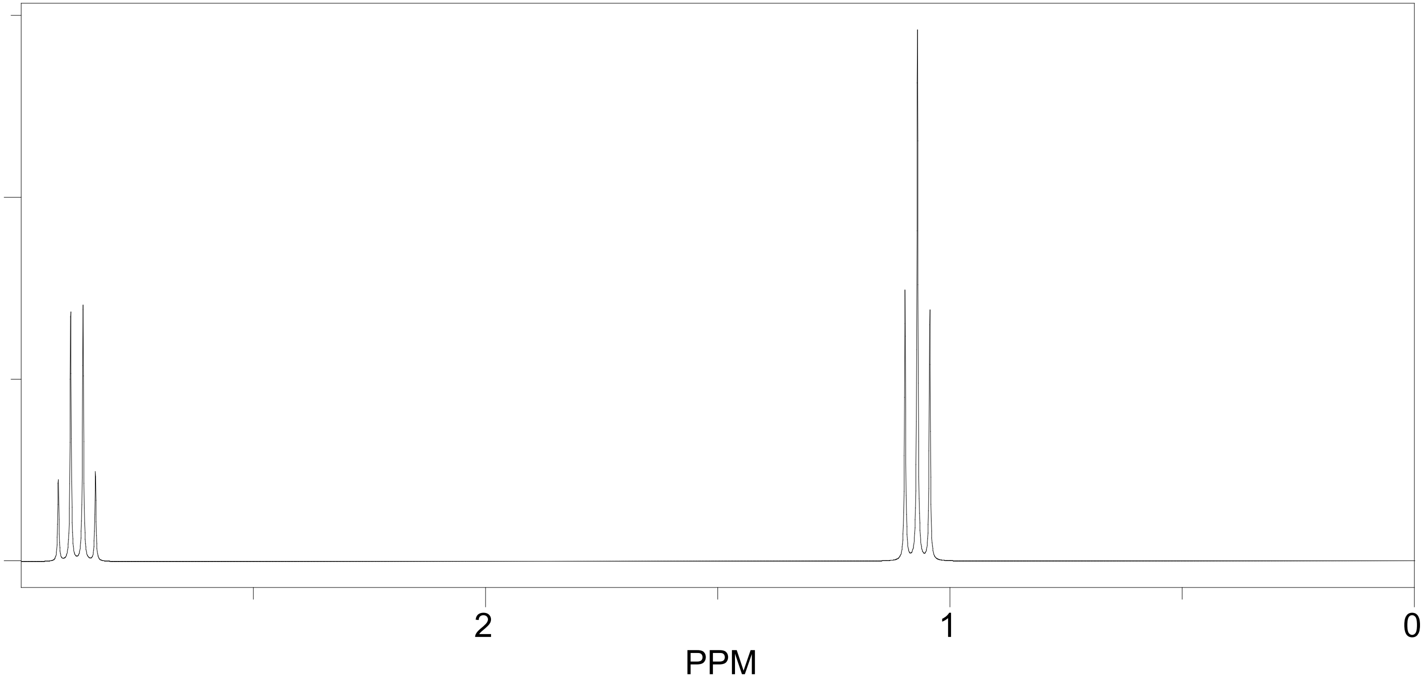
Multiplicity and Spin-Spin Coupling





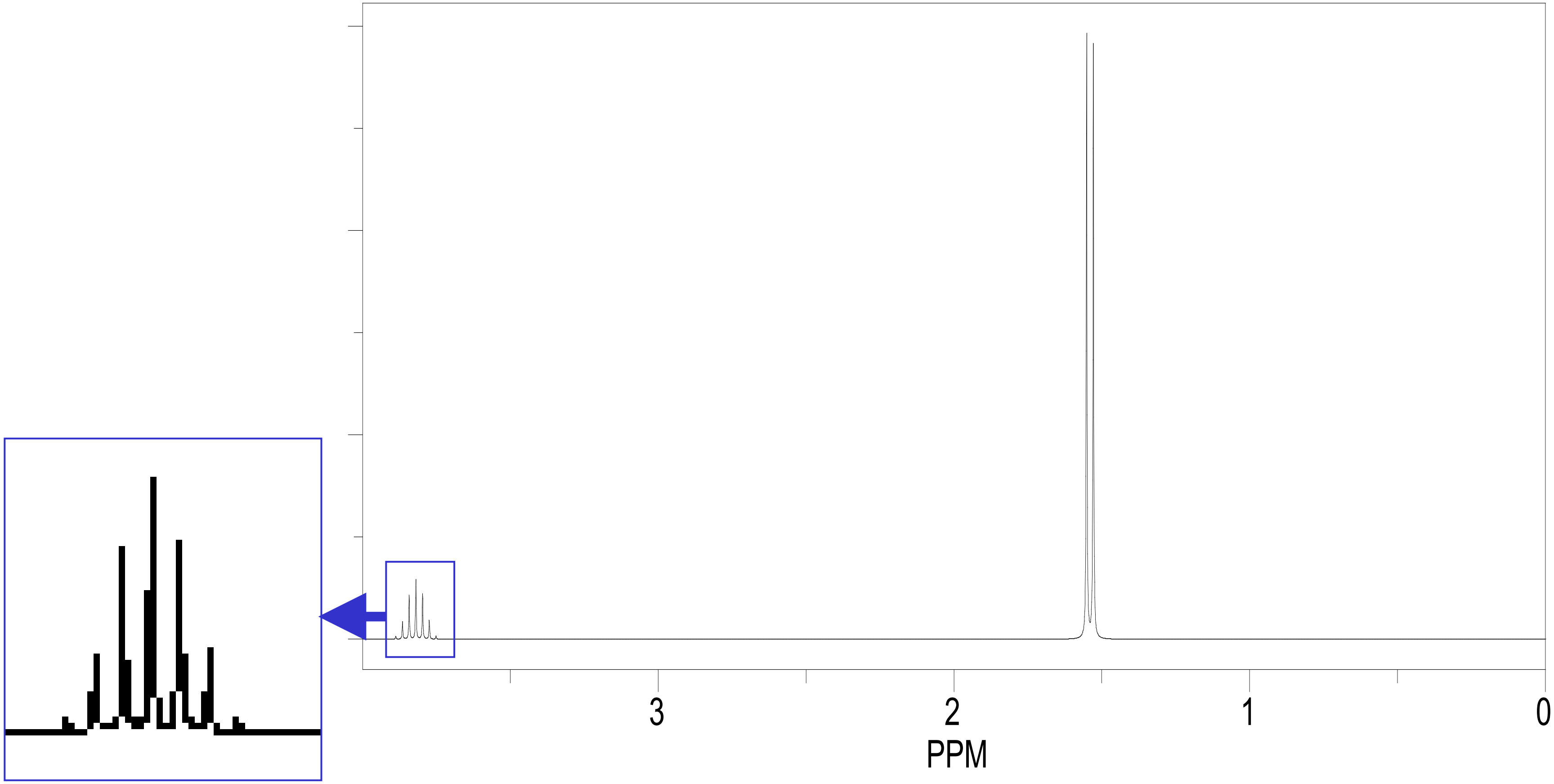
Multiplicity and Spin-Spin Coupling

- This set of three "doublet of doublet" peaks is indicative of a vinyl group (assuming the chemical shift is in the appropriate range). Other common substituents can be recognized by looking for the corresponding set of peaks:
  - An ethyl group gives a _______________ integrating to ___ and a ____________________ integrating to ___



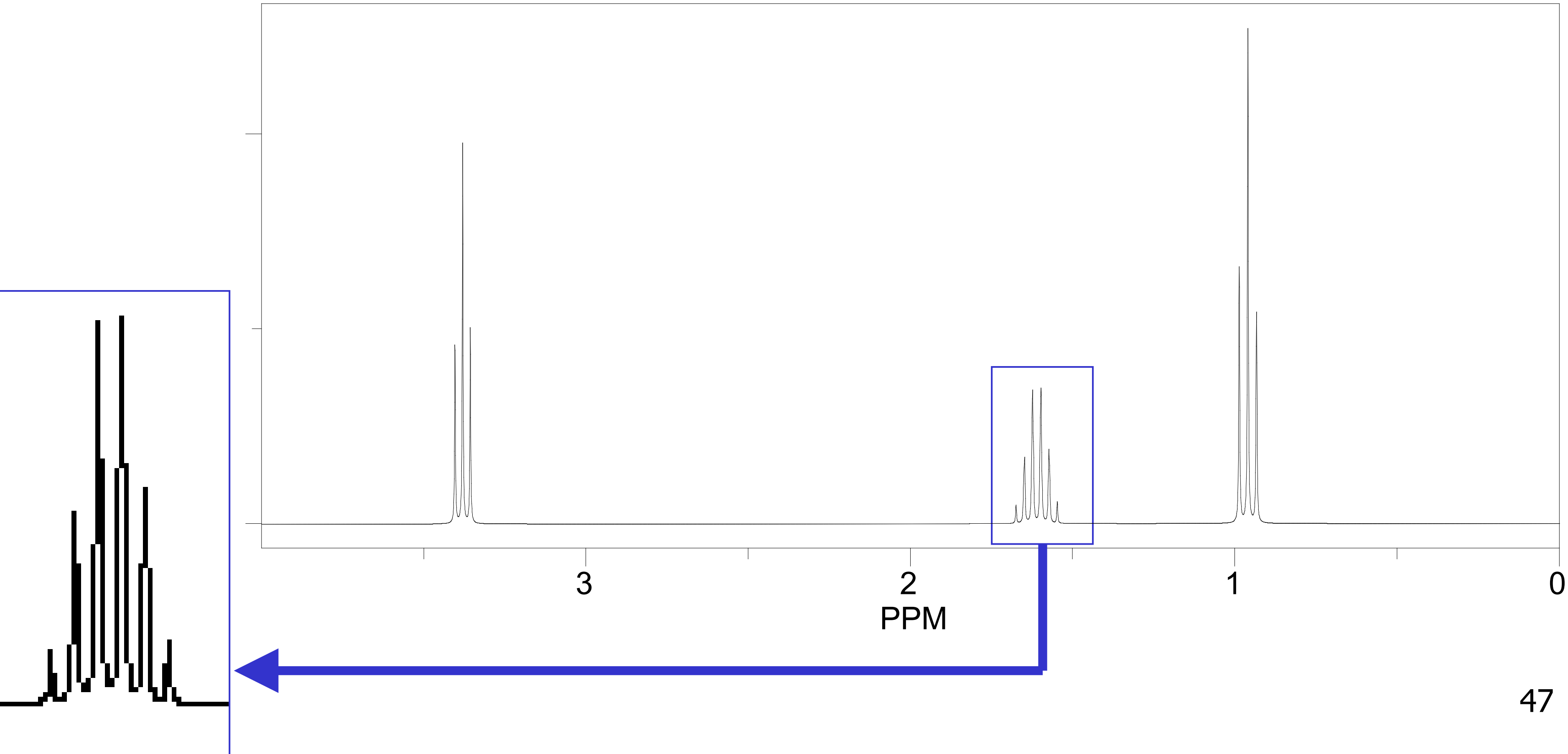
Multiplicity and Spin-Spin Coupling

- An isopropyl group gives a _______________ integrating to ___ and a ____________________ integrating to ___



Multiplicity and Spin-Spin Coupling

- A propyl group gives a ______________________ integrating to ___,
  a ________________________ integrating to ___ and
  a ________________________ integrating to ___.

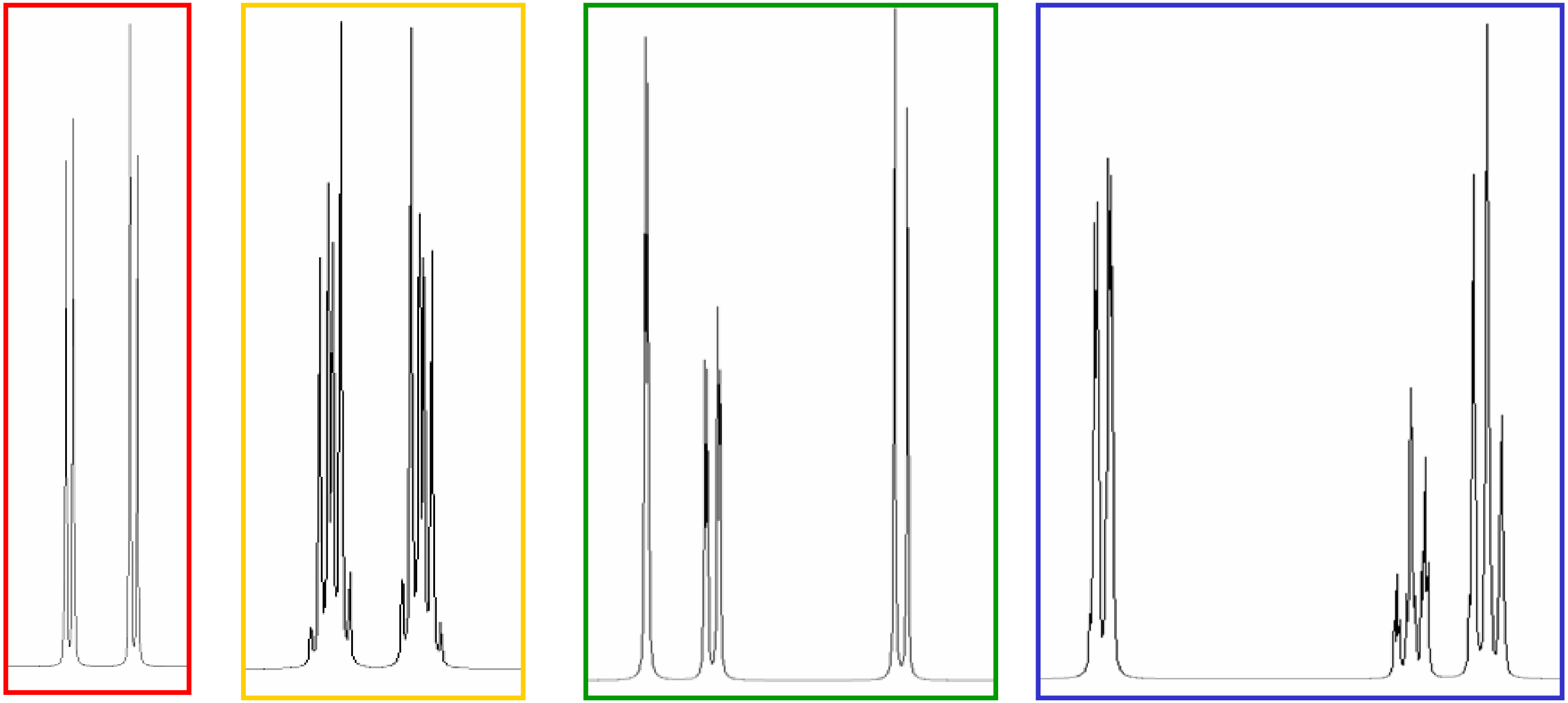


Multiplicity and Spin-Spin Coupling

- What patterns would you expect to see for a:
    - butyl group (e.g. chlorobutane)
    - *t*-butyl group
    - isobutyl group
    - *s*-butyl group

Multiplicity and Spin-Spin Coupling

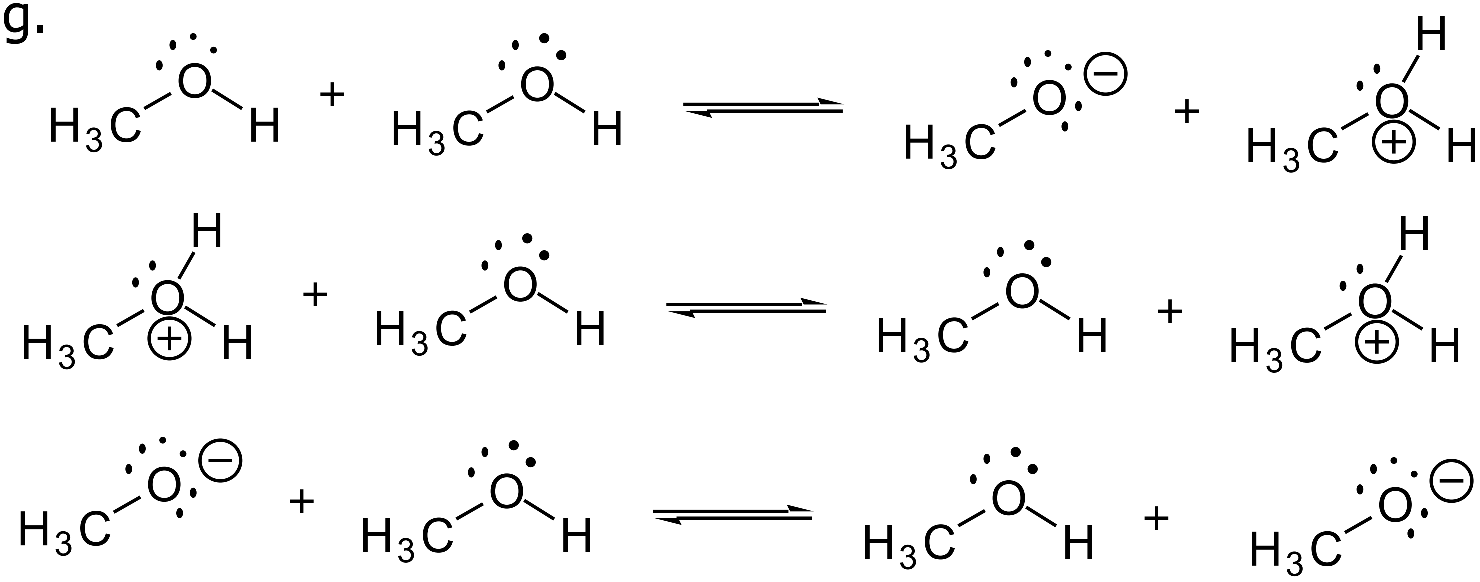
- Which of the patterns below represents a:
  - monosubstituted benzene ring?
  - 1,2-disubstituted benzene ring with both substituents the same?
  - 1,4-disubstituted benzene ring with two different substituents?
  - 1,2,4-trisubstituted benzene ring with three different substituents?



Exchangeable ^1H (Alcohols, Amines, Acids)

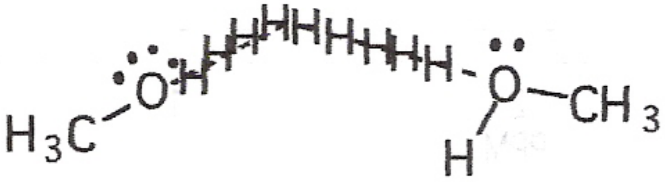
- NMR acquisition is much slower than other spectroscopic methods; it takes about 3 seconds to acquire a ^1H signal. As such, any ^1H whose chemical environment is changing more rapidly than that will give a broad signal. This is the case for ^1H bonded to oxygen or nitrogen since some of those ^1H are transferred from one molecule to another via autoionization at room temperature *(except in amides):*

  e.g.

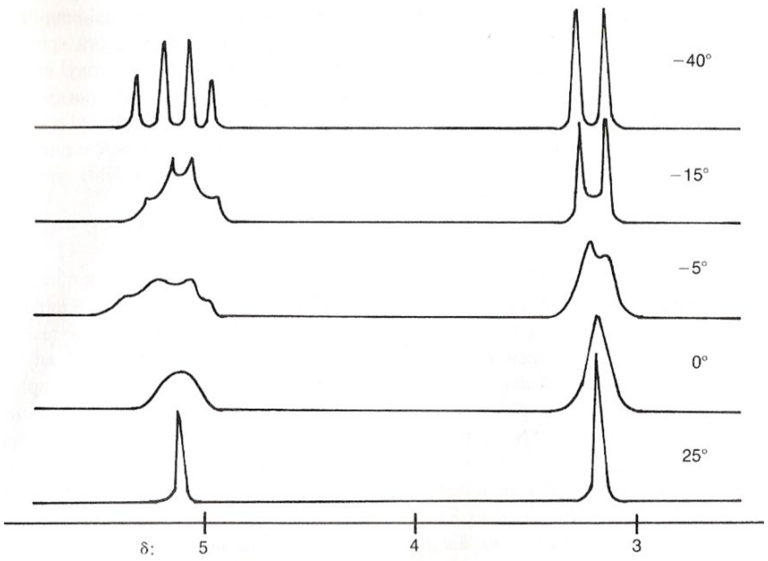


Exchangeable ^{1}H (Alcohols, Amines, Acids)

- Over the duration of the NMR experiment, the ^{1}H is therefore in many different environments:



- Under these conditions, the O-H peak is often broad and no coupling is observed.
  If the sample is cooled enough that the exchange becomes slower than the time required to acquire a signal, the peak sharpens and coupling becomes observable:



▸ **FIGURE 5.19** NMR spectra of methanol at various temperatures.

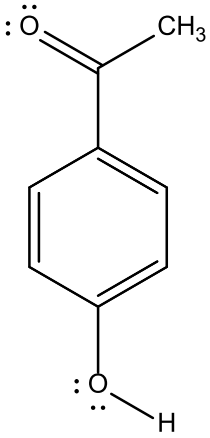
Figure from Pavia, Lampman & Kriz (1996) “Introduction to Spectroscopy” 2nd ed. p.206

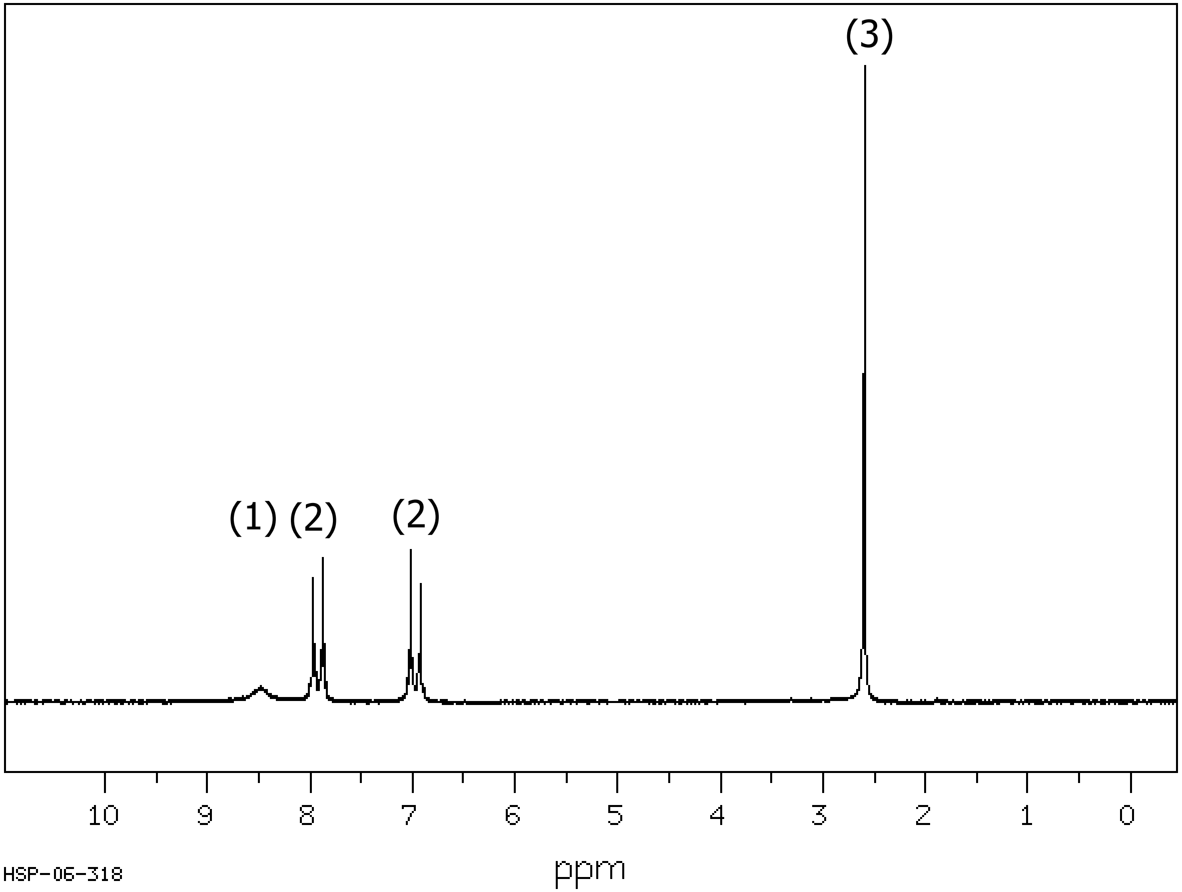
Exchangeable ^{1}H (Alcohols, Amines, Acids)

- Exchangeable ^{1}H can also exchange with the D in D_2O when it is added to the sample. This makes the peak disappear from the spectrum – and is a great way to confirm that a signal is from an alcohol or amine. *(Carboxylic acid signals are rarely in doubt.)*

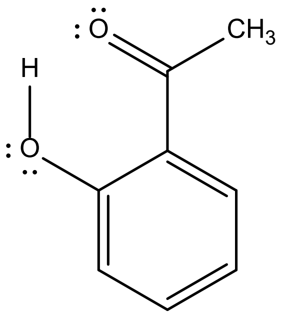
- In summary, exchangeable protons
  - Usually give broad peaks
  - Can be exchanged with D_2O (a new peak will appear for for HOD)
  - Only show coupling at low temperatures
  - Have chemical shifts that are difficult to predict and *very* solvent-dependent
    - Aliphatic OH usually 1 – 5 ppm in $CDCl_3$
    - Phenol OH usually 3.5 – 9 ppm in $CDCl_3$
    - Carboxylic acid OH usually 10 – 13 ppm in $CDCl_3$ (*very* broad)
    - Amine NH usually 0.5 – 5 ppm in $CDCl_3$
  - Hydrogen bonding will extend any of these ranges *significantly* farther downfield and sharpen the peak *(see next 2 pages)*

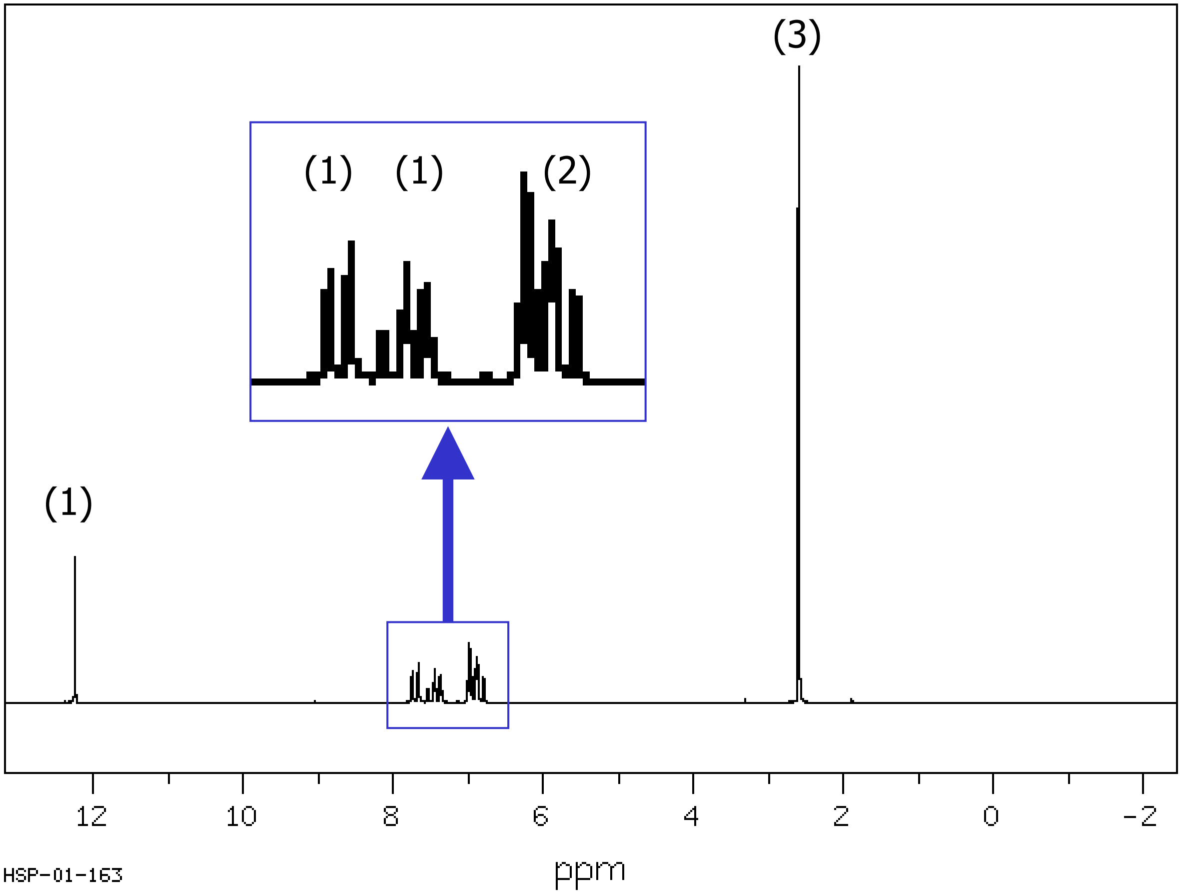
Exchangeable ^{1}H (Alcohols, Amines, Acids)



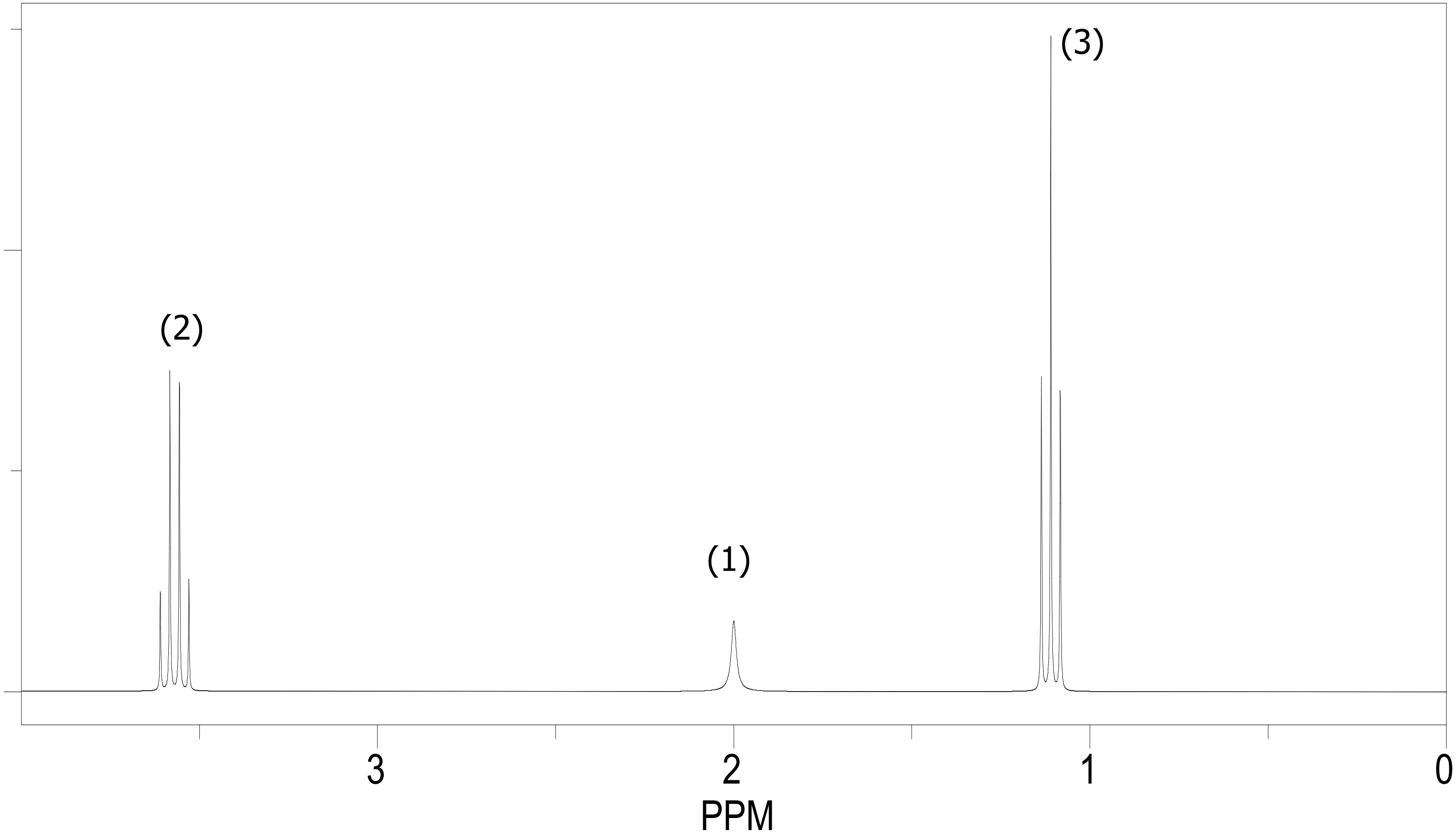


Exchangeable ^{1}H (Alcohols, Amines, Acids)



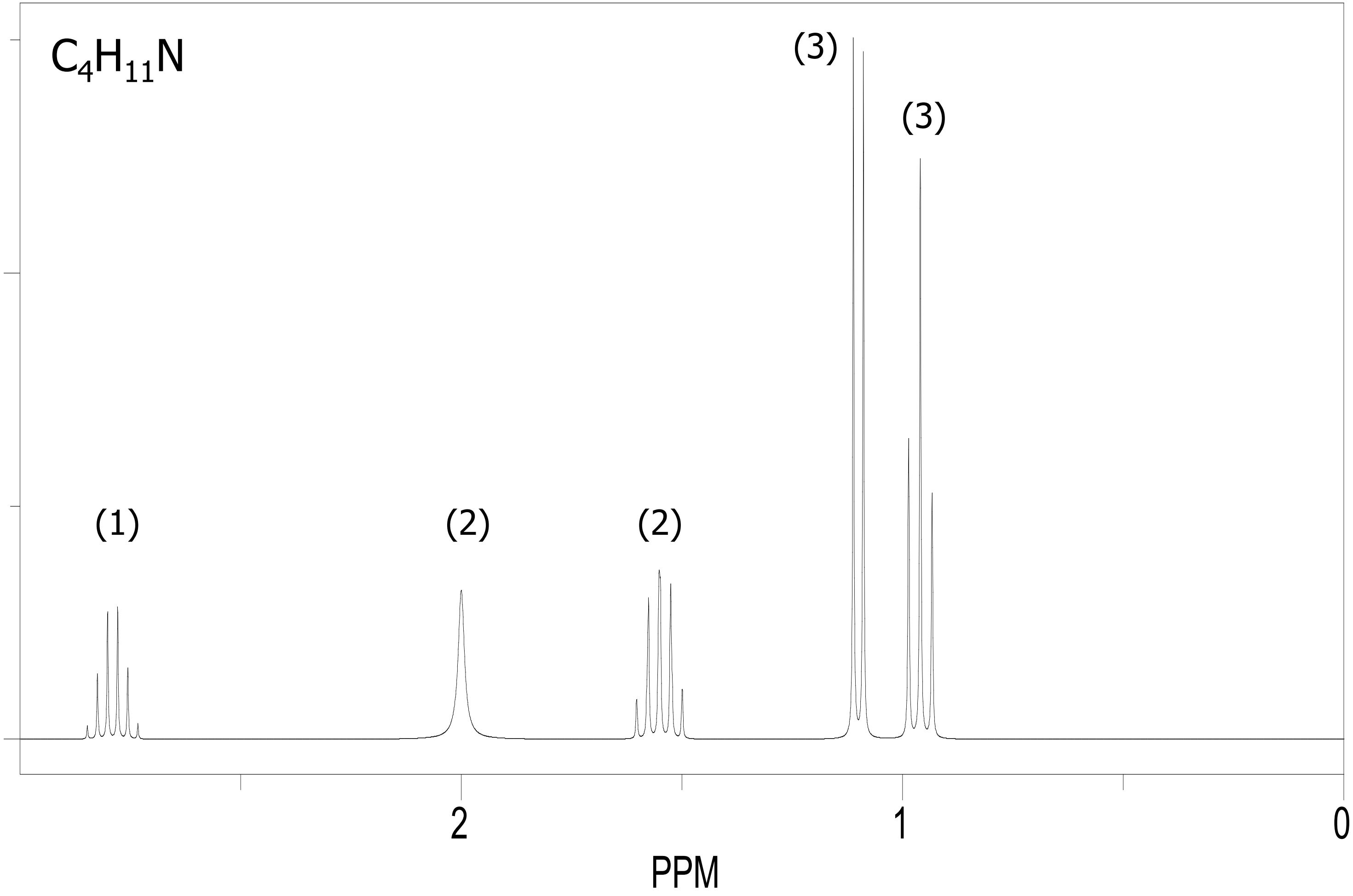


Analyzing Spectra



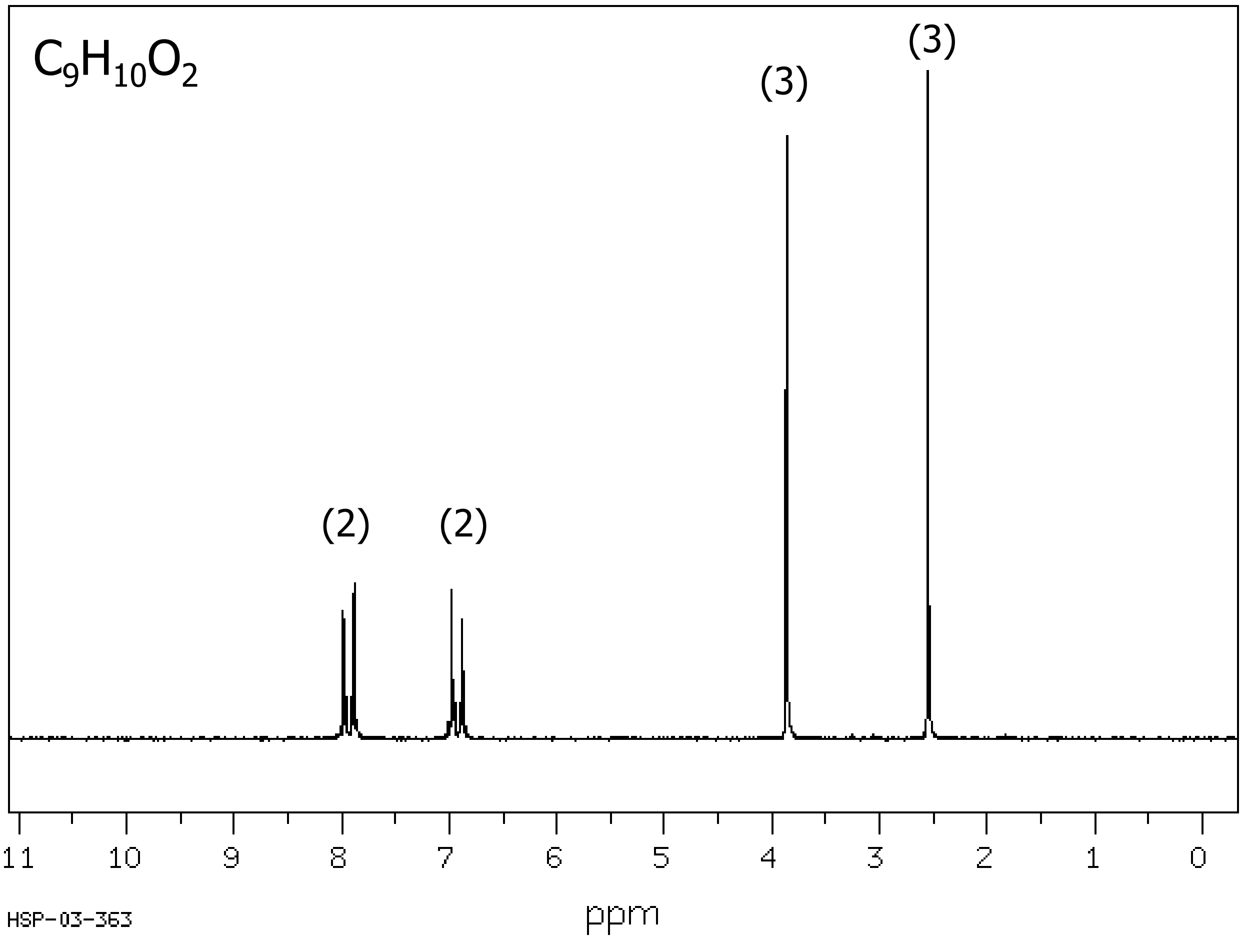
*Please note that "spectra" is the plural of "spectrum". "Spectrums" is not a word.

Analyzing Spectra



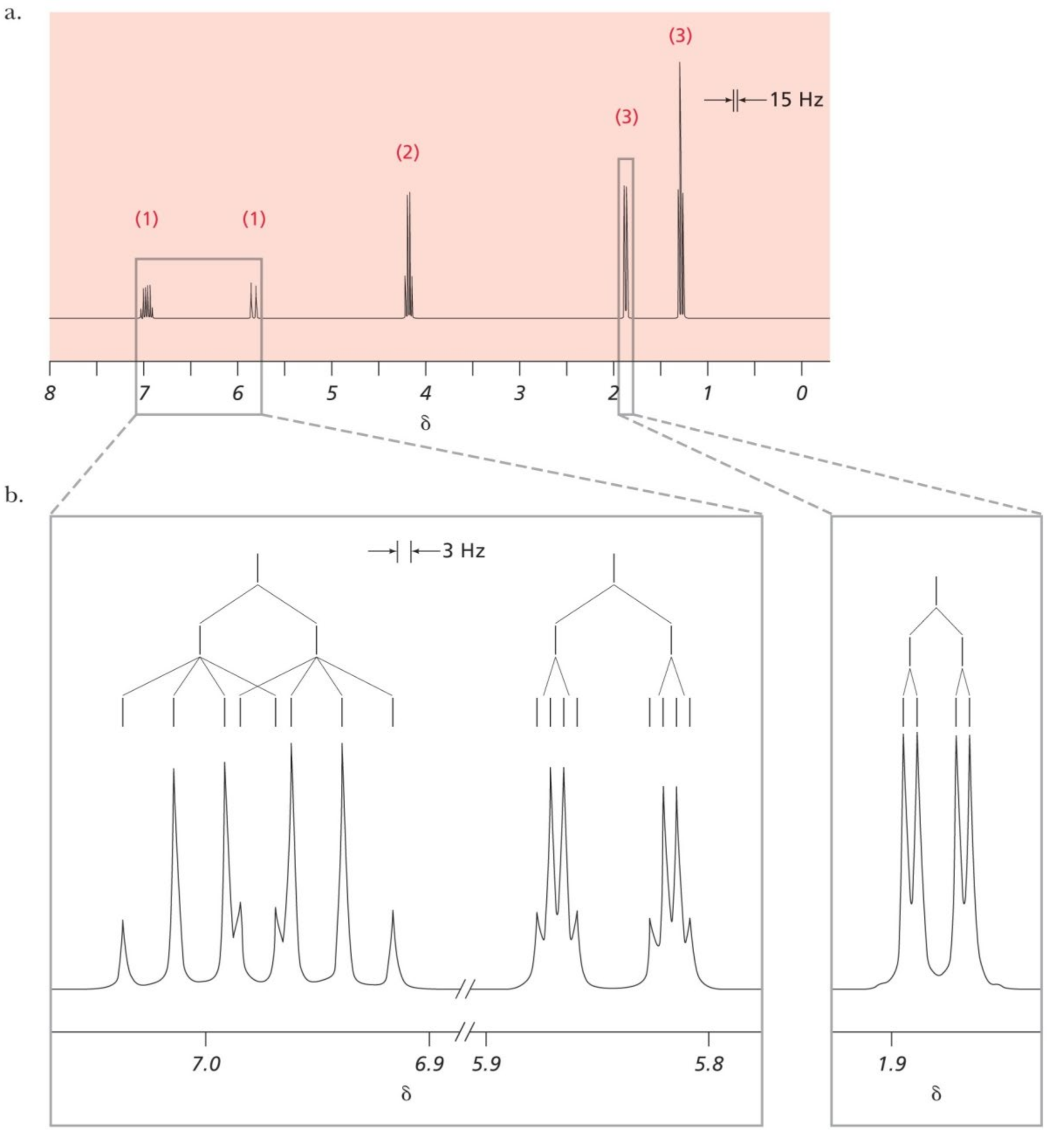
Analyzing Spectra

Analyzing Spectra

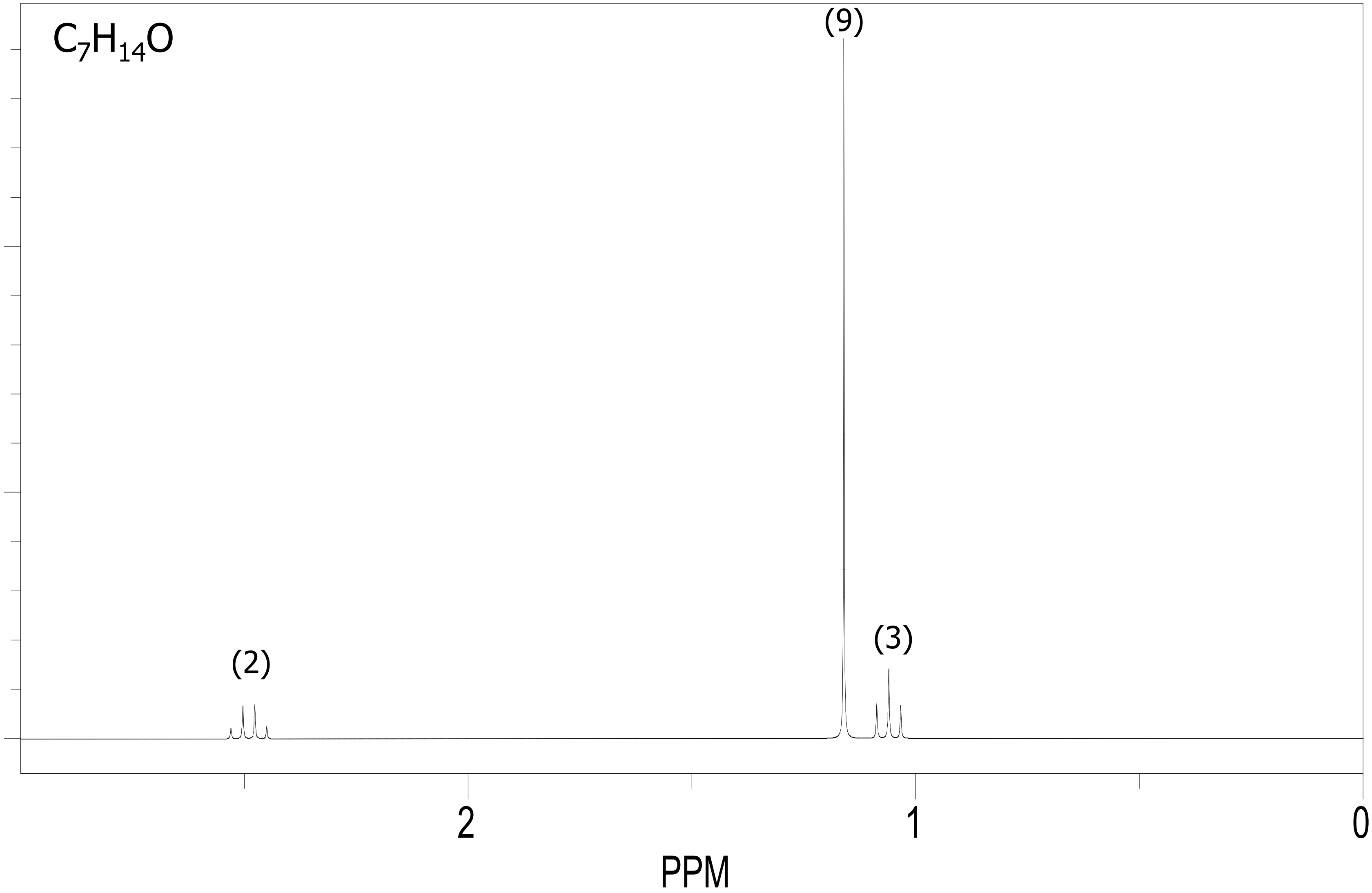


Analyzing Spectra

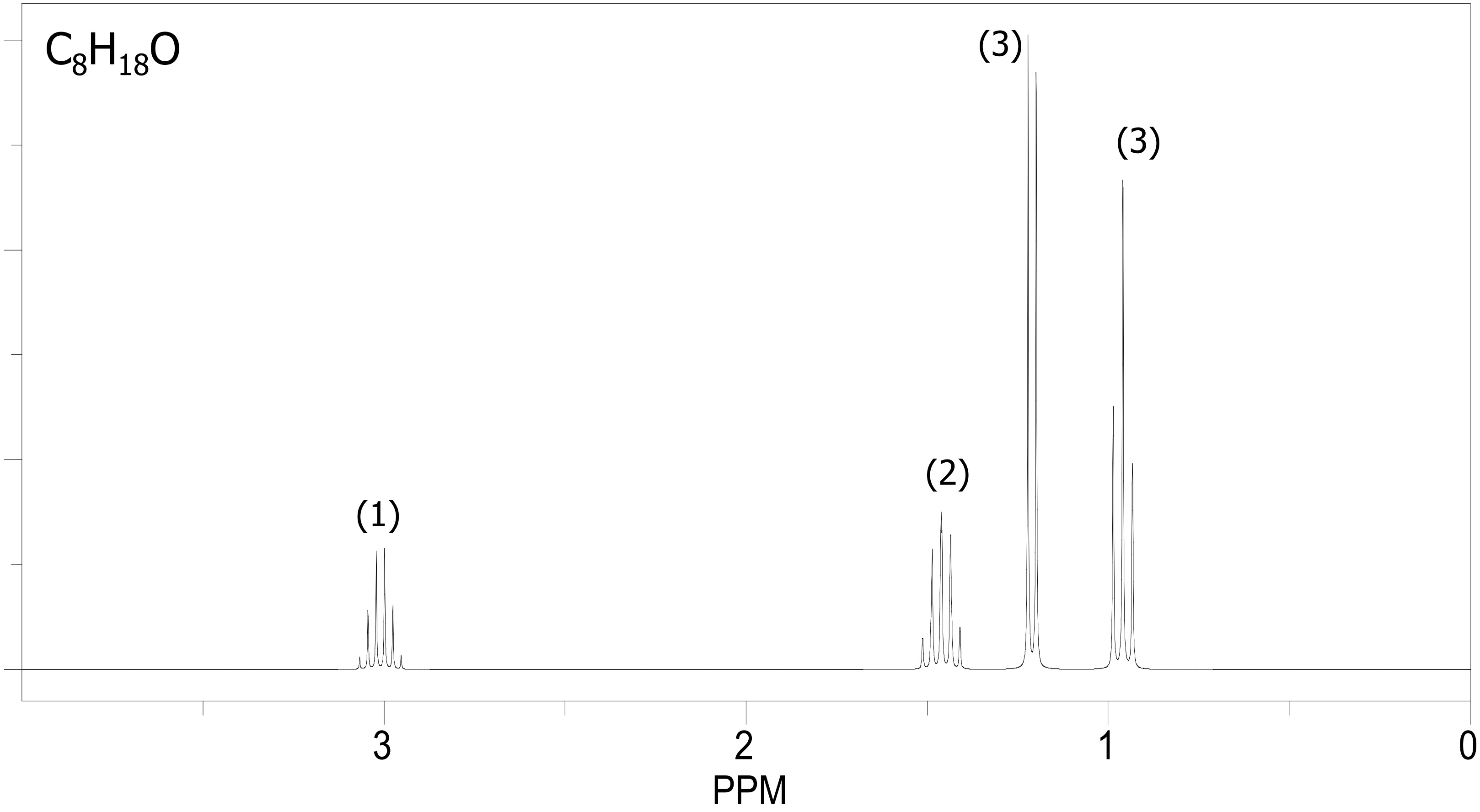
$C_6H_{10}O_2$



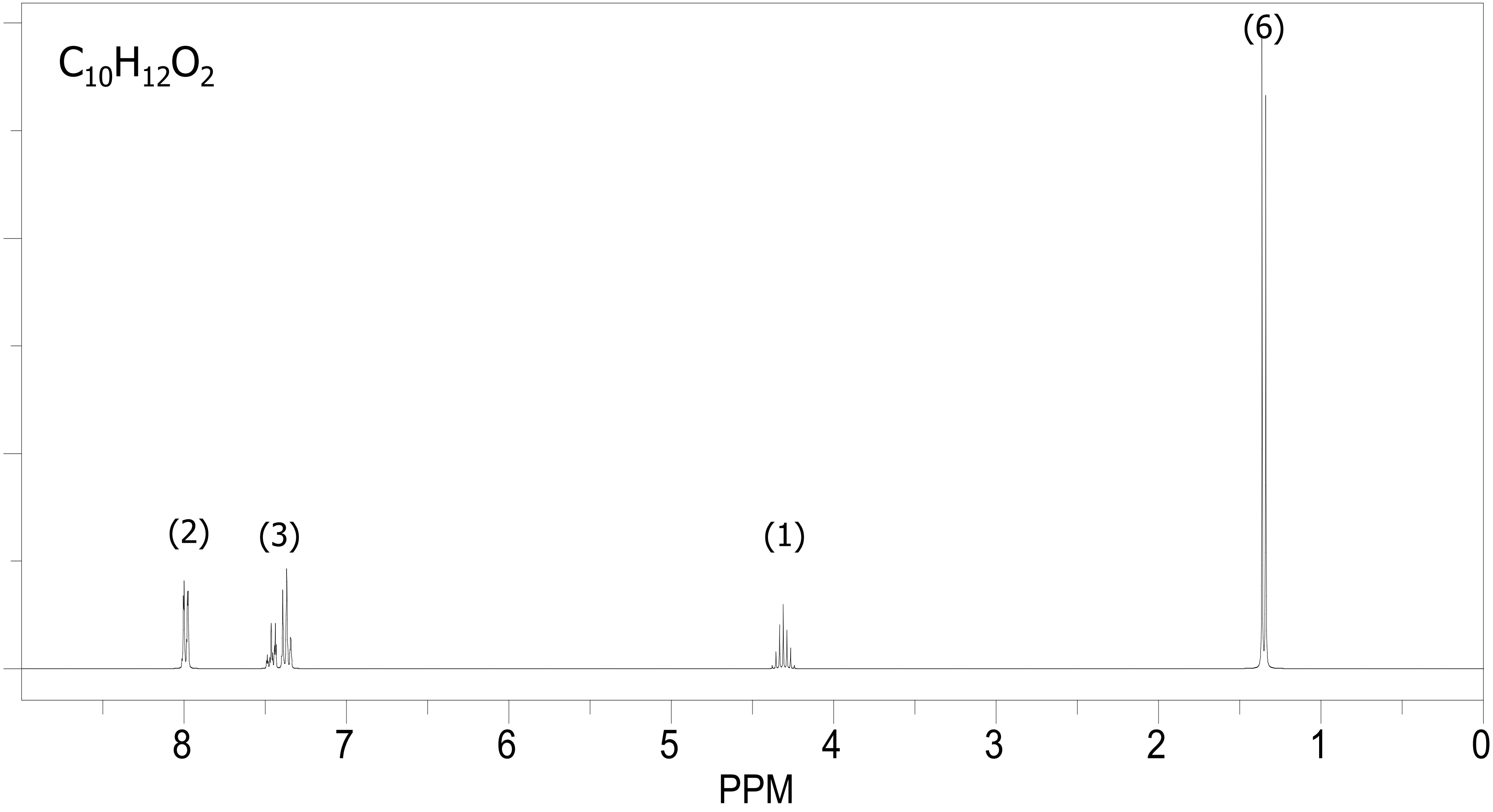
Analyzing Spectra



Analyzing Spectra



Analyzing Spectra



^{13}C NMR

- Organic molecules contain carbon by definition. It would be very helpful to get the same sort of information for the carbon atoms as we can get for the hydrogen atoms with ^{1}H NMR. Unfortunately, ^{12}C has no spin so can't be analyzed by NMR.

- 1% of all carbon atoms in a sample are ^{13}C – which has I = ½ so can be analyzed by NMR. The external magnetic field has only ¼ the effect on a ^{13}C nucleus as it has on a ^{1}H nucleus. Coupled with the low abundance of ^{13}C, this meant that ^{13}C NMR only became feasible with the development of FT-NMR.

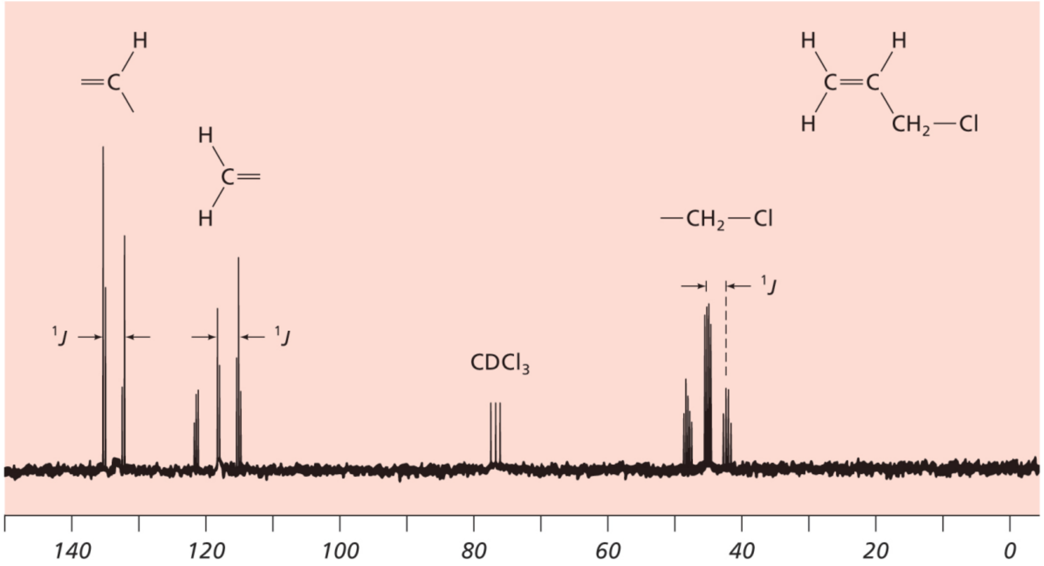
- The theory behind ^{13}C NMR is the same as the theory behind ^{1}H NMR; however, a wider range of chemical shifts is observed in ^{13}C NMR. Peaks usually appear from 0 to 220 ppm in $CDCl_3$.

^{13}C NMR

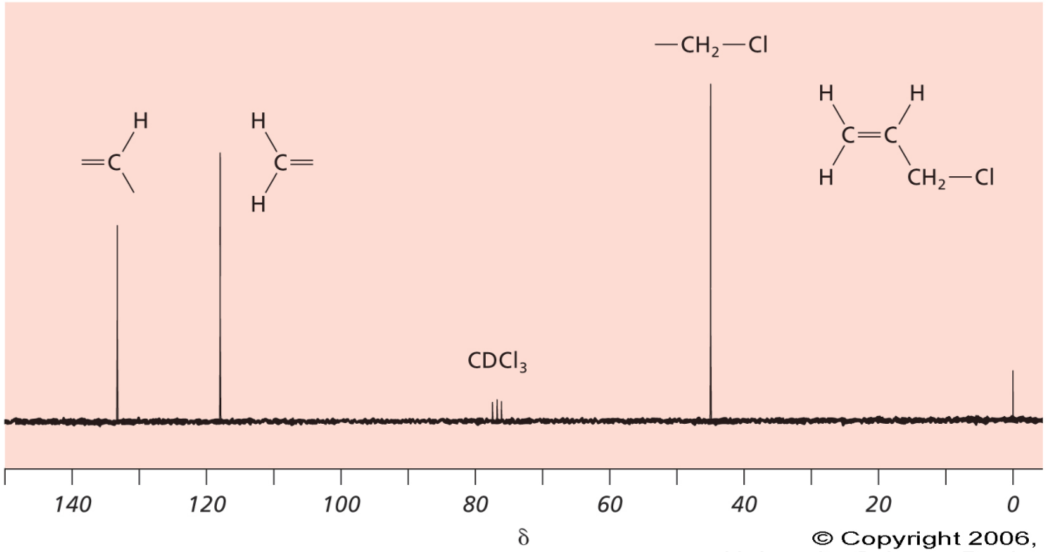
- Important things to realize about ^{13}C NMR:
  - Most of the time, integrations are meaningless. Similarly, don't look to peak height for information about number of carbon atoms. Unless an unusually long relaxation period is used between pulses, peak height will be as dependent on whether the carbon is primary, secondary, tertiary or quaternary as on the number of carbon atoms of that type. (Quaternary carbon atoms tend to give very short peaks.)
  - Coupling is not observed
    - No ^{13}C-^{13}C coupling because only a tiny fraction of molecules will have neighbouring carbon atoms [(1%)^2 = 0.01%]
    - Experimental parameters deliberately prevent ^{13}C-^{1}H coupling to give "cleaner", easier to read spectra
    - Special techniques are required to get information about the number of hydrogen atoms bonded to a carbon atom. These will not be discussed in CHEM 2600 but, if you're interested, look up DEPT 90 and DEPT 135.

^{13}C NMR

Coupling Allowed:

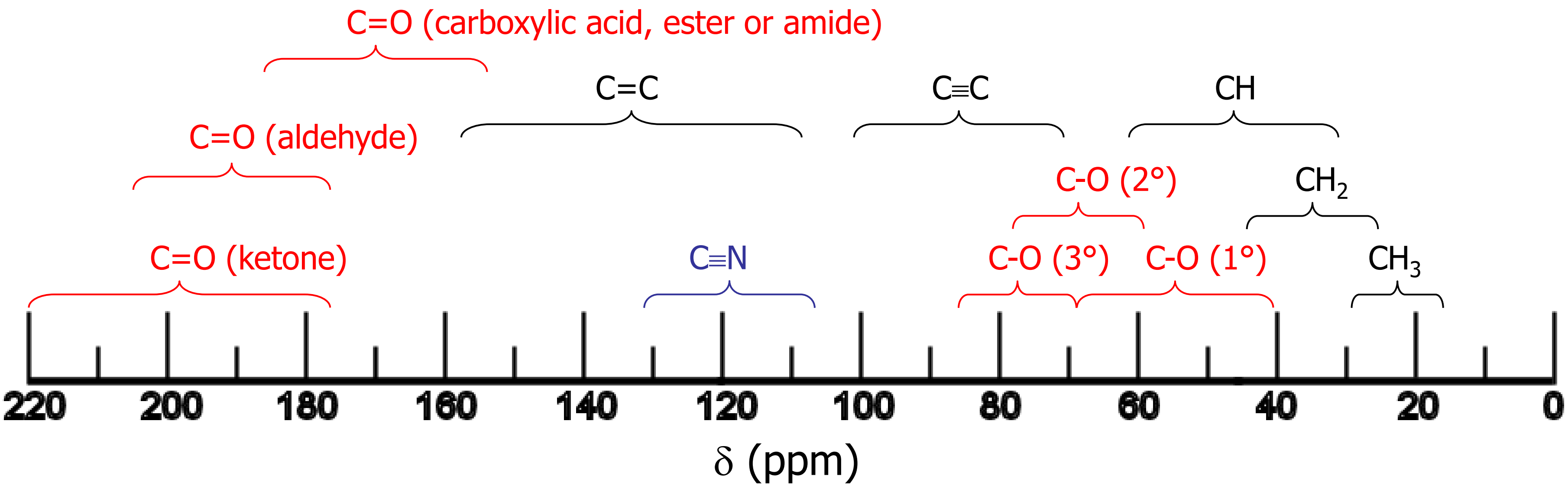


"Broadband Decoupled":



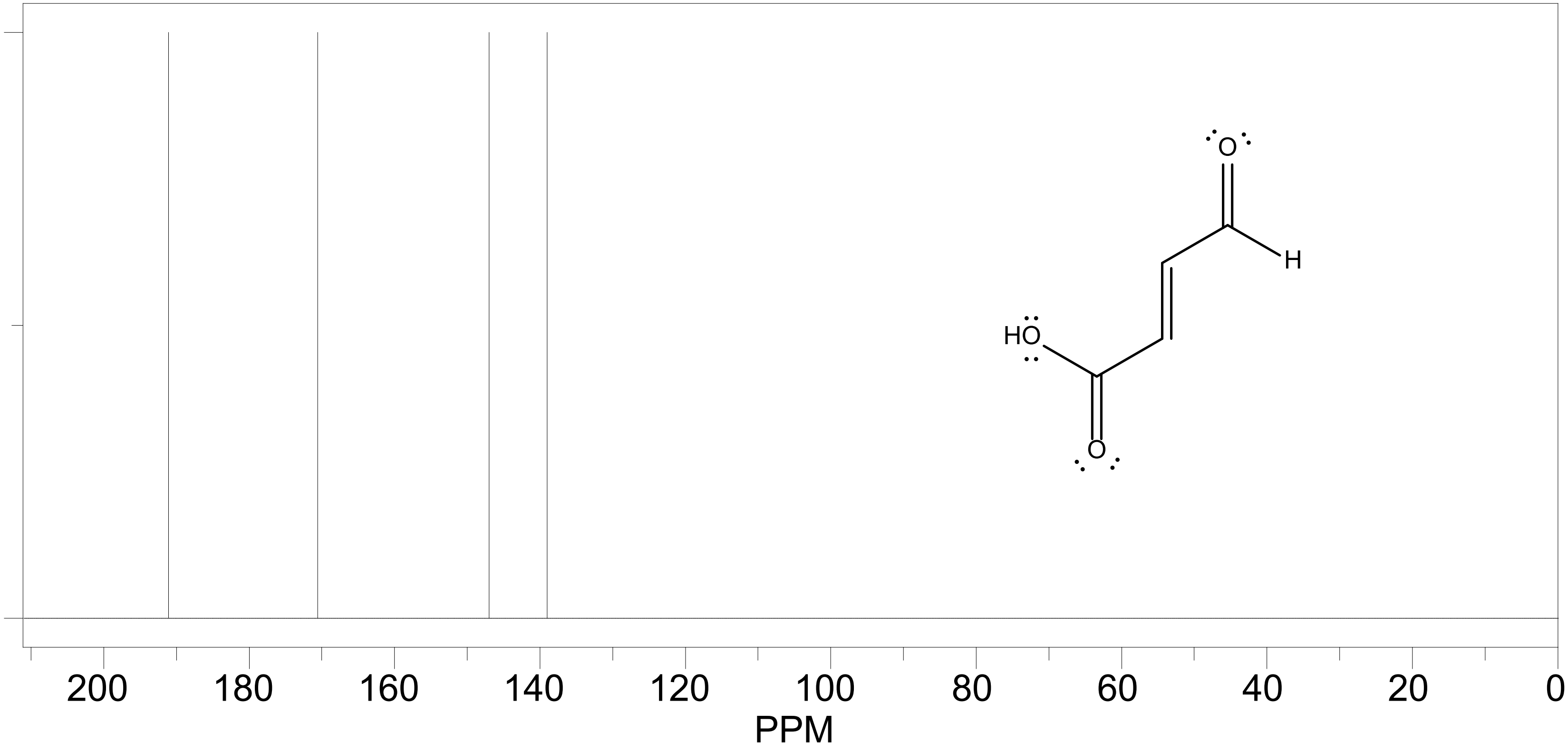
^{13}C NMR

- The main utility of ^{13}C NMR is to tell us how many unique carbon atoms are in a molecule and tell us whether each of those carbon atoms is *sp*^{3}, *sp*^{2} or *sp*-hybridized.

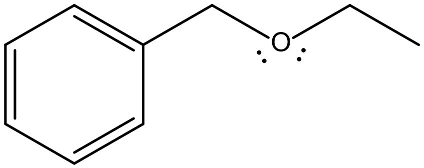


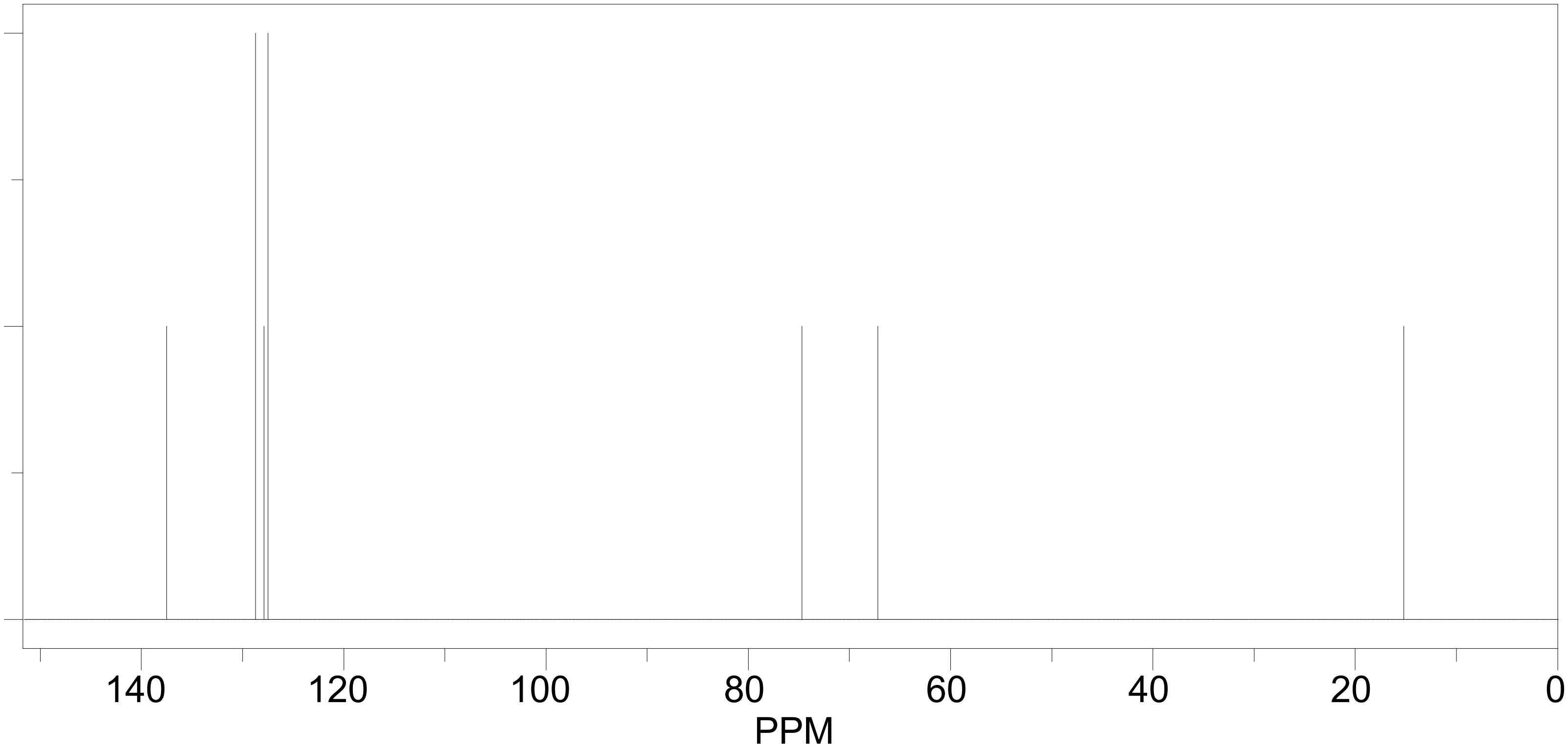
- ^{13}C NMR is particularly useful for identifying carbonyl and nitrile groups which don't show up directly on a ^{1}H NMR. What other analytical technique is an excellent way to look for these functional groups?

^{13}C NMR

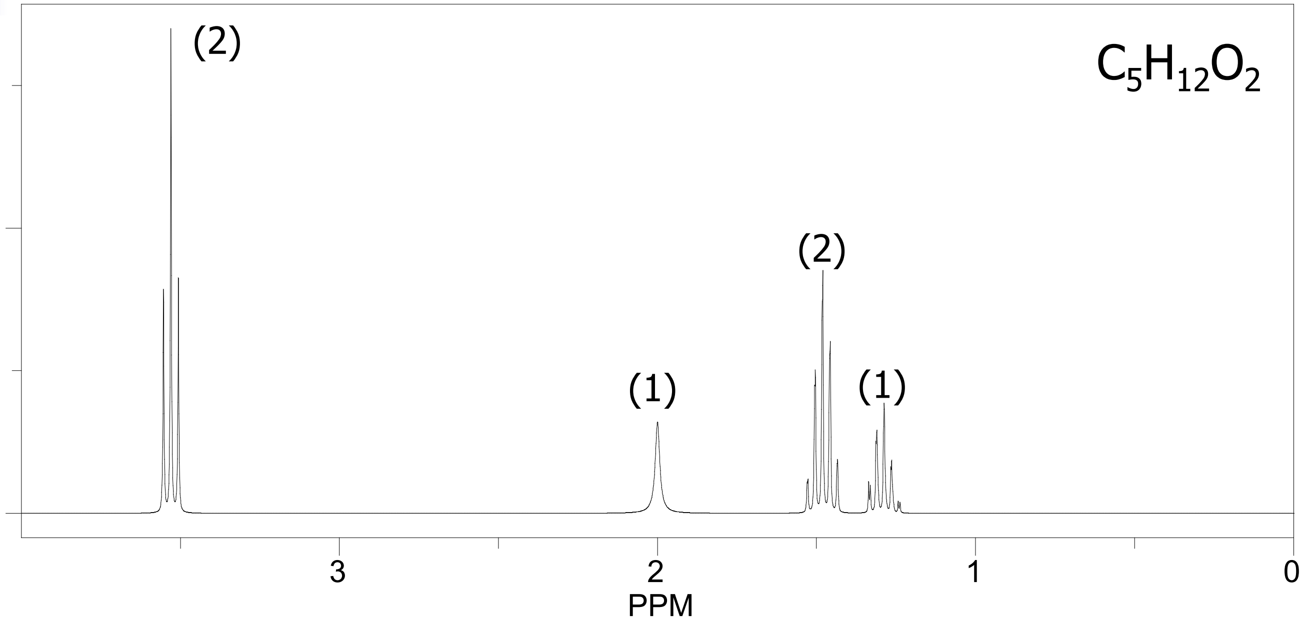


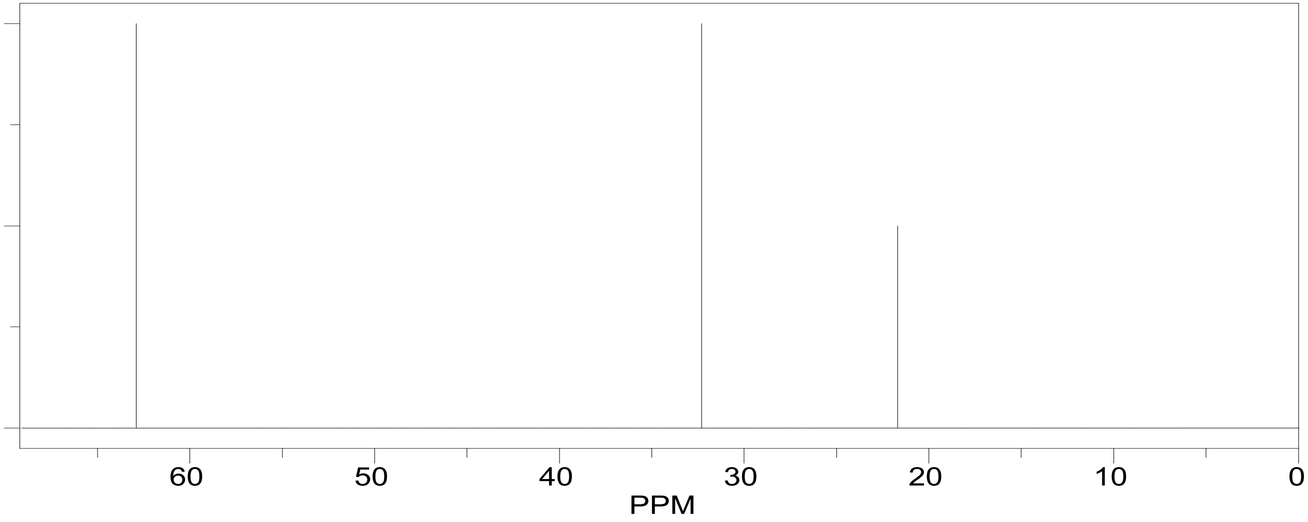
^{13}C NMR





^{13}C NMR (Solve Given ^{1}H and ^{13}C NMR)





Appendix: Calculating Unsaturation Index

- The molecular formula tells us how many rings and/or pi bonds a molecule contains. This is referred to as the Index of Hydrogen Deficiency, or Unsaturation Index (UI), because it tells us how many pairs of hydrogen atoms could theoretically be added to the molecule before it became saturated with them.
- Picture a chain of CH_2 groups with an extra H at each end (a saturated linear alkane).
  - There are 2C+2 hydrogen atoms.
  - Adding an O or S to the middle of the chain does not add any H.
  - Adding an N to the middle of the chain requires one extra H.
  - Adding any halogen (X) replaces one H.
  - Adding a ring or pi bond reduces the number of H by two.
  - So, the UI can be found by subtracting the actual number of H from the number that would be present if the molecule was fully saturated <u>then</u> dividing by two.
- Combine these factors to get $UI = \dfrac{2C + 2 + N - X - H}{2}$