

# Introduction to Spectroscopy

## Infrared Absorption Spectroscopy

**Infrared radiation** - just below the red end of the visible light spectrum

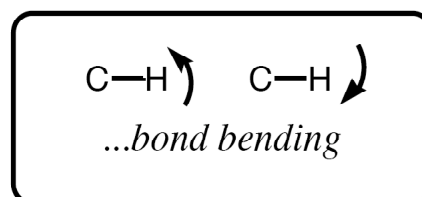
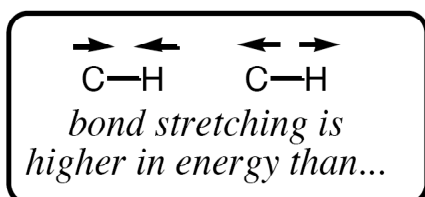
The energy of the radiation is approximately 1–20 kcal/mol

*This corresponds to the energy needed to induce bond vibrations*

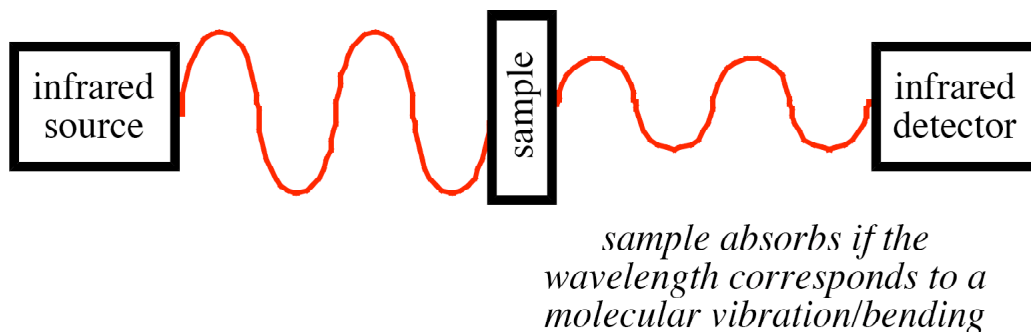
energy is related to frequency  $E = h\nu$

and energy is related to wavelength  $E = c/\lambda$

so **high energy vibrations** have **high frequency** and **short wavelength**



*If we provide the appropriate energy (wavelength or frequency) infrared radiation, the bonds will absorb it, and vibrate/bend more rapidly...*



**If we plot wavelength vs. absorption, we will obtain the infrared spectrum characteristic of our sample**

Infrared radiation frequency is reported in micrometers ( $10^{-6}$  meter)

**OR** in wavenumbers -  $\text{cm}^{-1}$  ( $10^4$  divided by wavelength in micrometers)

**We will use  $\text{cm}^{-1}$**

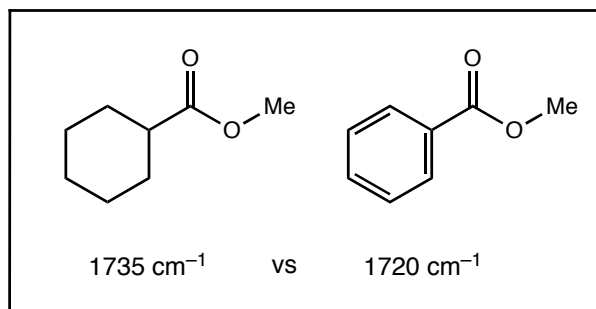
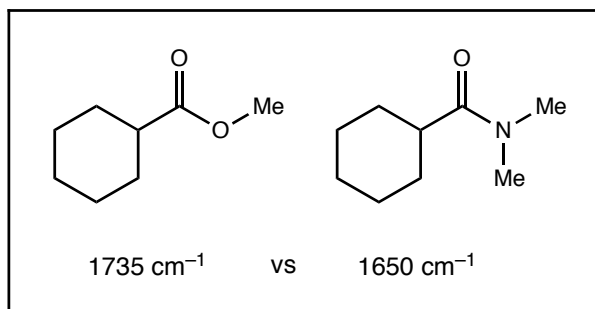
*Frequency is proportional to  $\text{cm}^{-1}$ , and "wavenumber" is often called "frequency"*

*Reading: Sections 12.1 and 12.2*

## Factors That Determine IR Stretching Frequencies

- First, we should ask: why is it that the frequency of vibration is the same as the frequency of the IR light that is absorbed?
- Now, let's explore the two main factors that determine the frequencies of IR absorption:
  - the **mass** of the atoms
  - the **strength** of the bond

- Explain the following comparisons of C=O stretching frequencies:

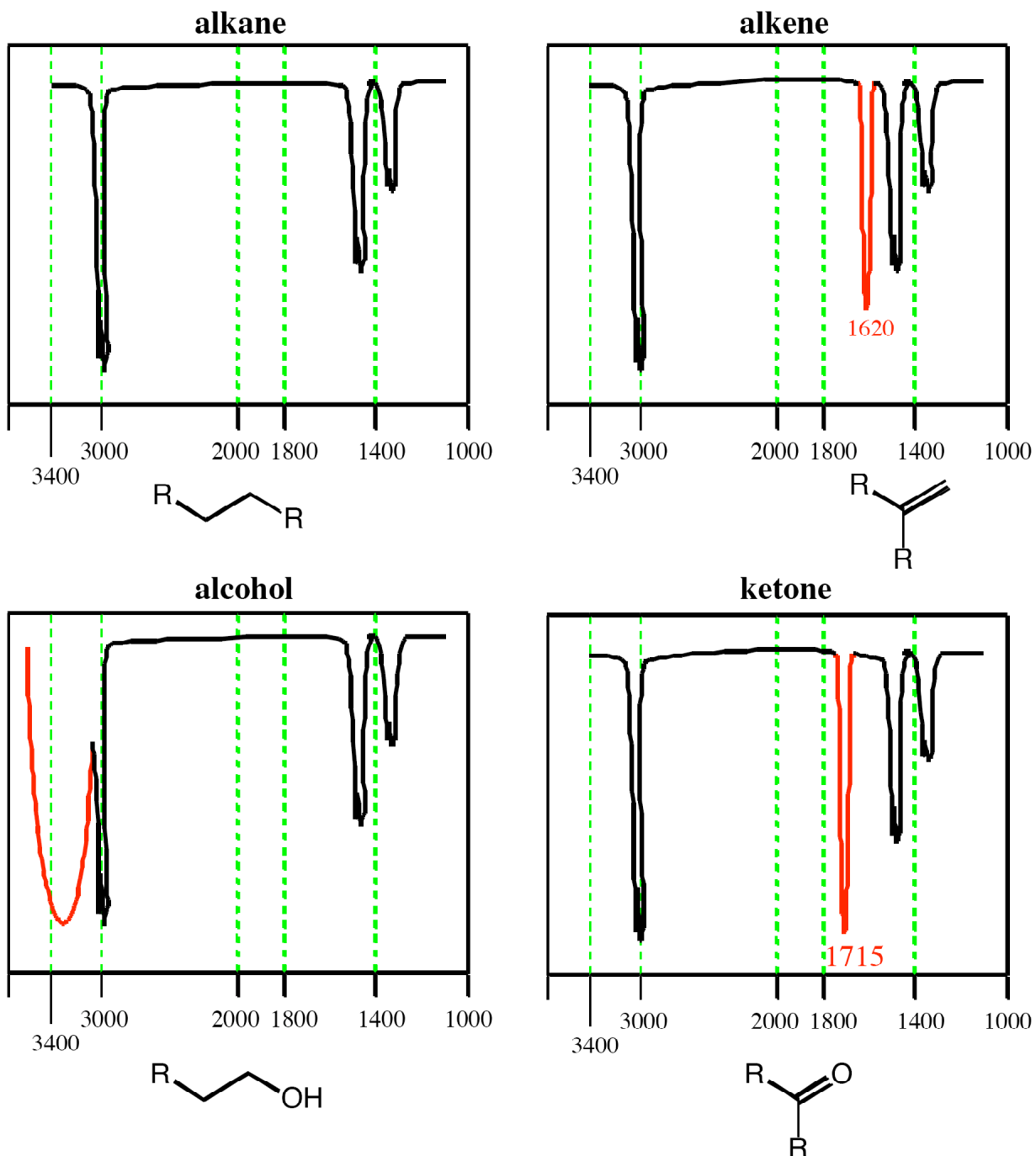


Reading: Section 12.2

## Identifying Functional Groups Using IR Spectroscopy

*idealized partial infrared spectra of some typical compound types*

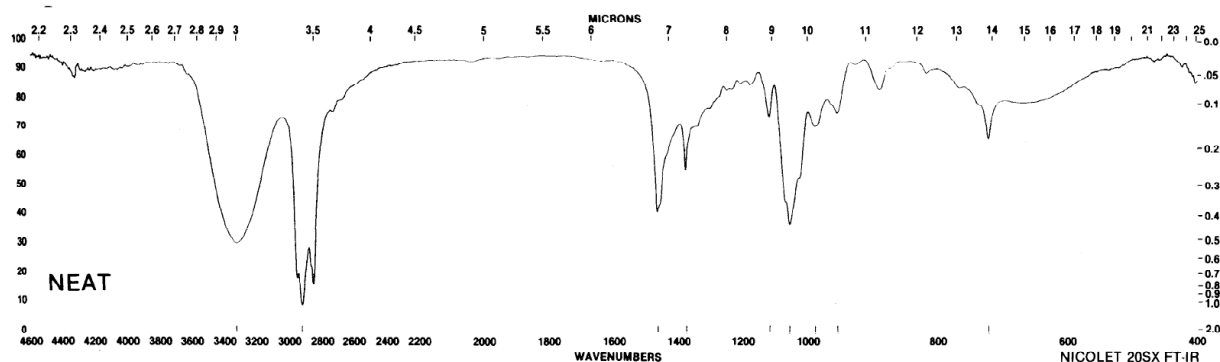
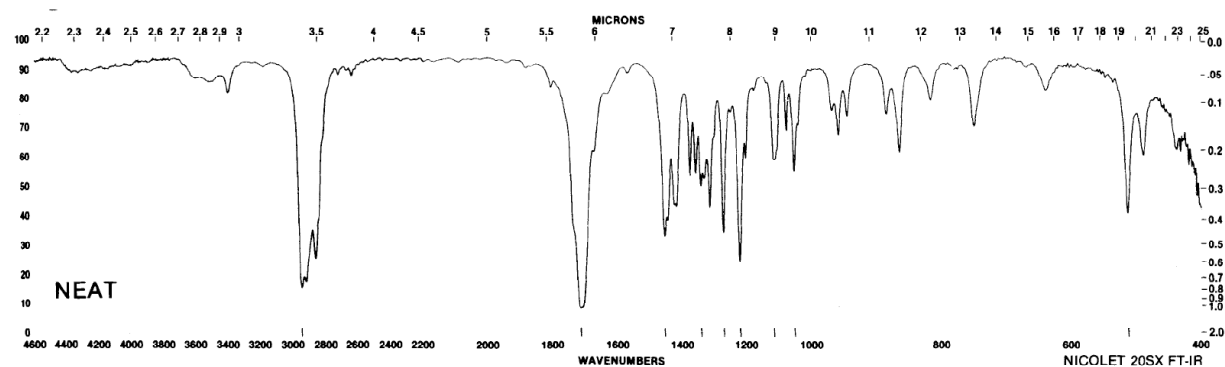
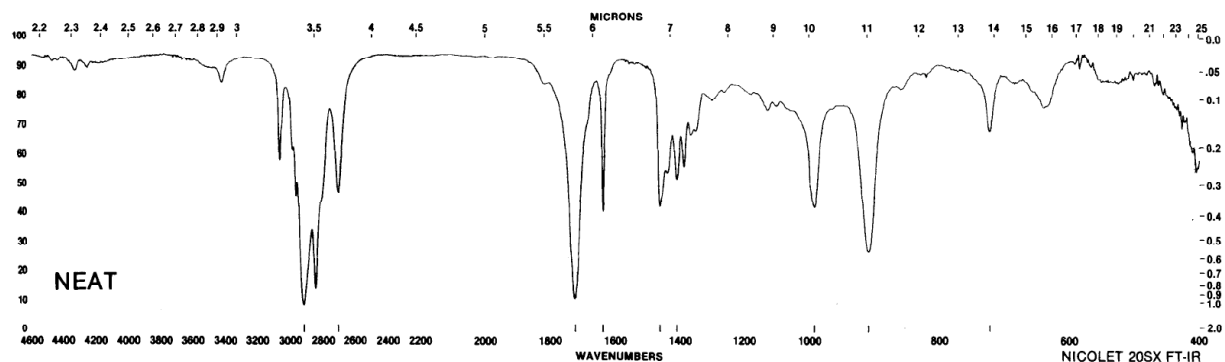
*In general terms, the infrared spectrum can identify certain functional groups which are present (or absent) in an organic compound*



Reading: Sections 12.3 and 12.4

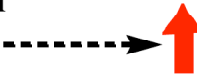
## Identifying Functional Groups Using IR Spectroscopy

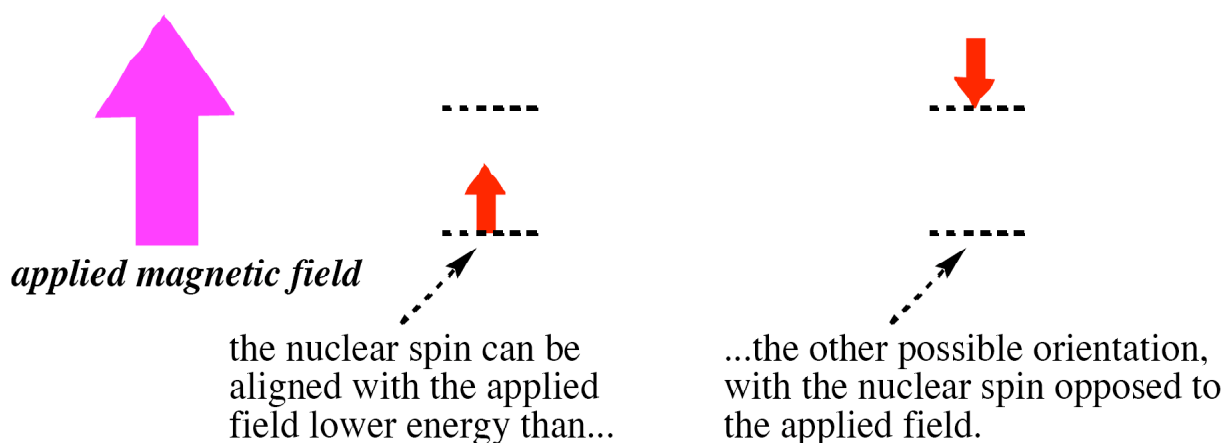
- Identify the functional groups in each of the following IR spectra:



Reading: Section 12.4 and Appendix II

## Nuclear Magnetic Resonance Spectroscopy

- Certain atomic nuclei possess a "nuclear spin"
- These nuclei behave like small "magnets" 
- Other nuclei ( $^{12}\text{C}$  and  $^{18}\text{O}$ ) have zero spin - they have no nmr spectra
- The nuclei which we will study are "spin  $1/2$  nuclei"
- They are  $^1\text{H}$  and  $^{13}\text{C}$
- When exposed to a strong magnetic field, there are 2 possible energy states



*The larger the applied field, the larger the energy difference*

even so, this energy is small (0.005 cal/mol)- corresponds to FM radio waves

This means that at room temperature both spin states will be populated...  
...with more (as usual) in the lower energy state

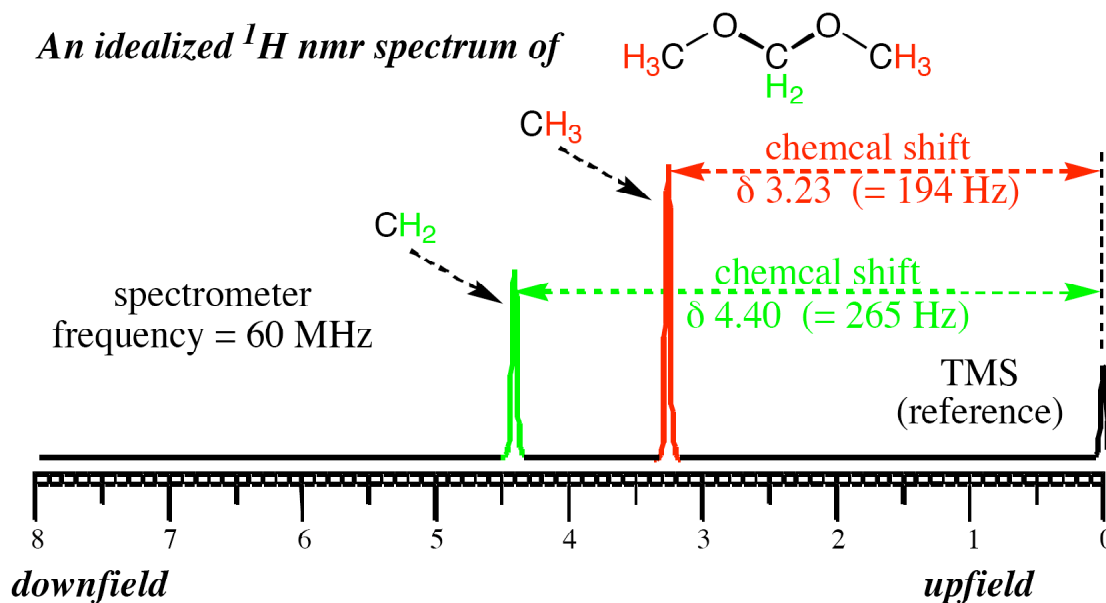
for every  $10^6$  protons in a sample, the low energy state contains an excess of no more than about 20 !!

If we apply radiation of the correct frequency -  
the "resonance" frequency -  
we will promote nuclei in the lower spin state to the  
higher - energy will be absorbed, so we can measure  
the **nuclear magnetic resonance spectrum**

*This is an immensely powerful and important technique in chemistry and biology - we can "see the protons in organic molecules"*

*Reading: Sections 13.1 and 13.2*

## The NMR Spectrum: Chemical Shifts



chemical shift ( $\delta$ ) is defined as: 
$$\frac{\nu - \nu_{\text{TMS}}}{\nu_0}$$
 operating frequency of spectrometer (MHz)

Example:  $\text{CH}_3$   $\frac{194 \text{ Hz}}{60 \text{ Mz}} = 3.23 \times 10^{-6}$   
 $= 3.23 \text{ ppm}$

The chemical shift is reported as **ppm** or read directly off the spectrum in **ppm**

### How many absorptions in the $^1\text{H}$ nmr spectrum?

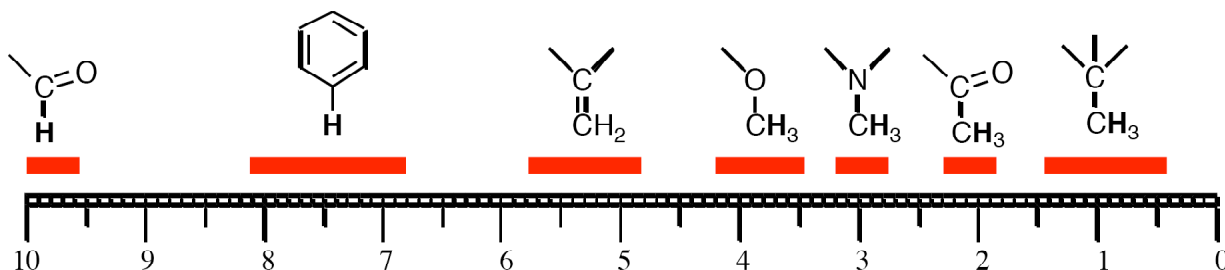
- In principle chemically nonequivalent protons have different shifts
- Chemically equivalent protons have identical shifts
- it follows that...*
- Homotopic protons have identical shifts
- Enantiotopic protons have identical shifts
- Diastereotopic protons have in principle different shifts

### Where do different types of protons absorb?

Reading: Section 13.3

## Chemical Shifts and Integrals

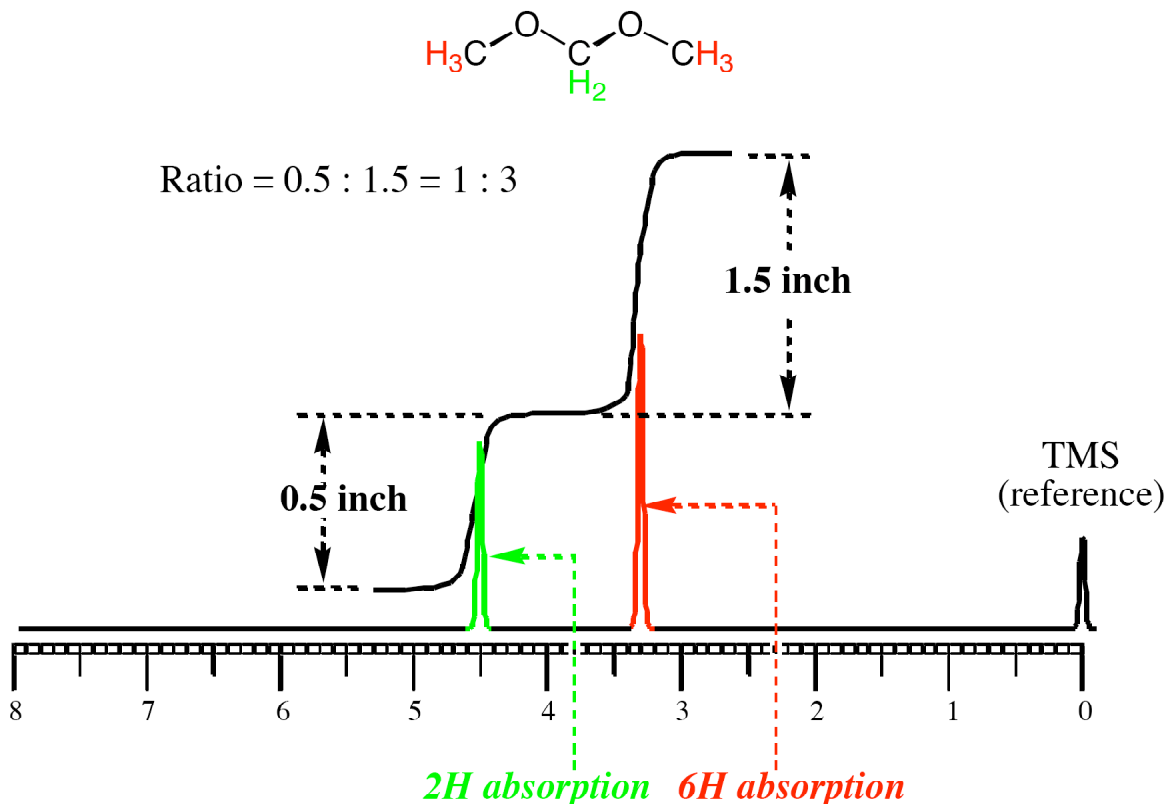
*Guidelines for selected chemical shifts:*



- Protons attached *directly* to  $\text{sp}^2$  C absorb at lower field
- Protons close to *electronegative groups* absorb at lower field

### Counting protons

- The "integral" (area) of the absorption is proportional to the number of protons
- The ratios of the "integrals" give the *relative* number of protons



Reading: Section 13.3

## Chemical and Stereochemical Equivalence

- The following molecule has many hydrogen atoms. Let's take a look at various pairs of hydrogen atoms and ask: are they *the same or not the same*? The best way to do so is to perform a *substitution test*.

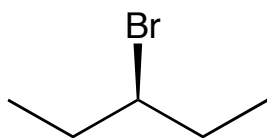
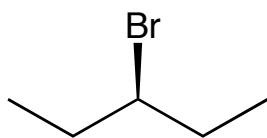
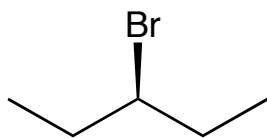
If the two compounds are entirely different, the groups are constitutionally inequivalent.

If the two compounds are diastereomers, the groups are diastereotopic.

If the two compounds are enantiomers, the groups are enantiotopic.

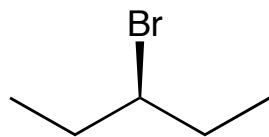
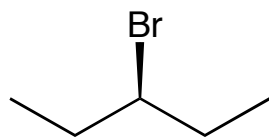
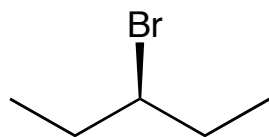
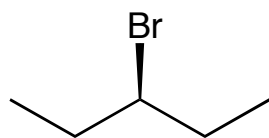
If the two compounds are identical, the groups are homotopic.

Let's look at some examples:



*Reading:* Section 10.8

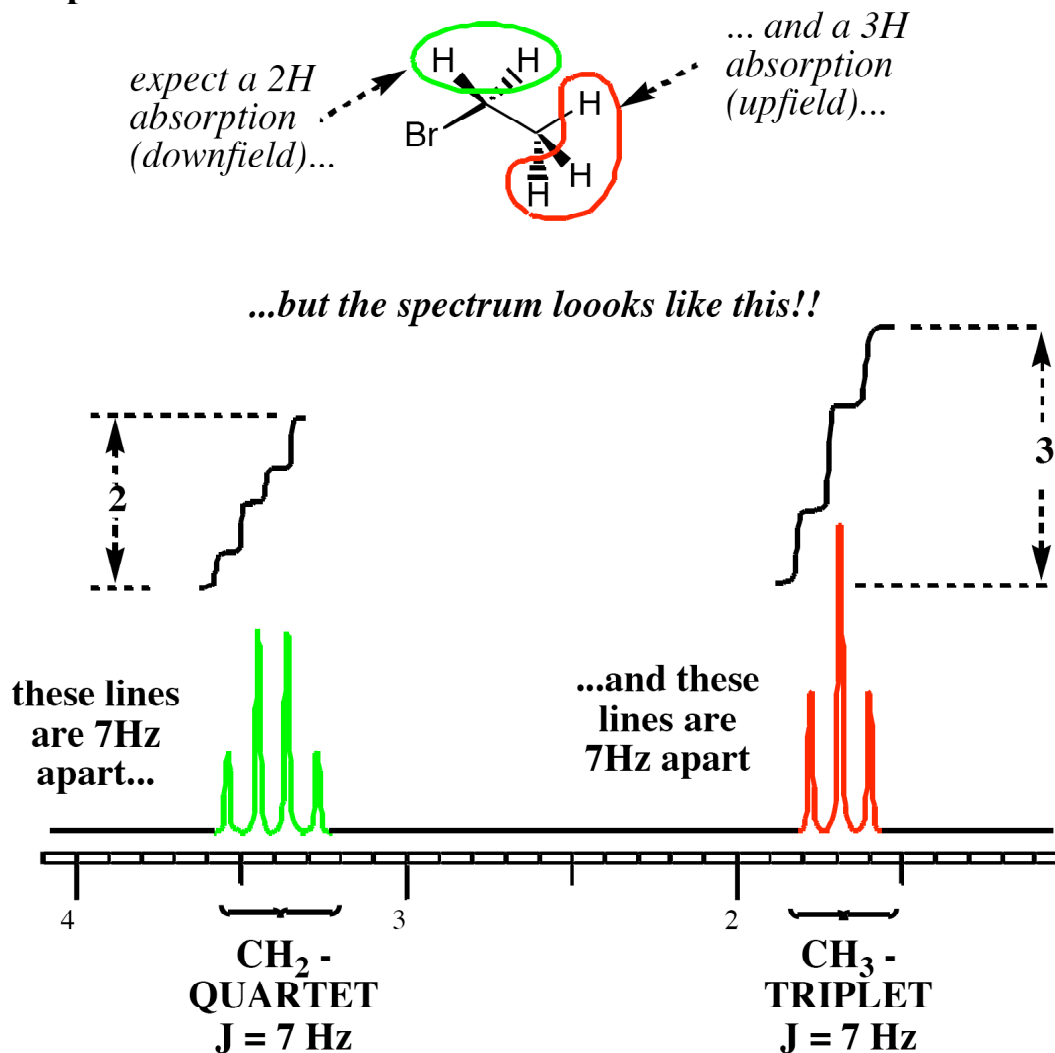




*Reading:* Section 10.8

## Spin-Spin Splitting

### Example:



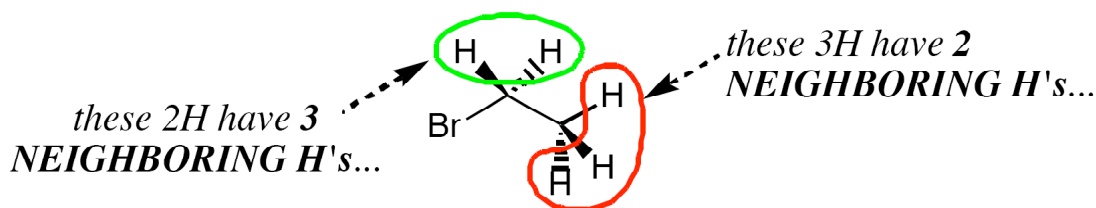
- The CH<sub>3</sub> and CH<sub>2</sub> protons are **coupled**
- The adjacent nuclear spins cause **splitting**
- The size of the splitting is equal for each coupled absorption
- It is described by the **coupling constant J**

**THE SPLITTING OF ONE ABSORPTION IS CAUSED BY THE ADJACENT PROTONS**

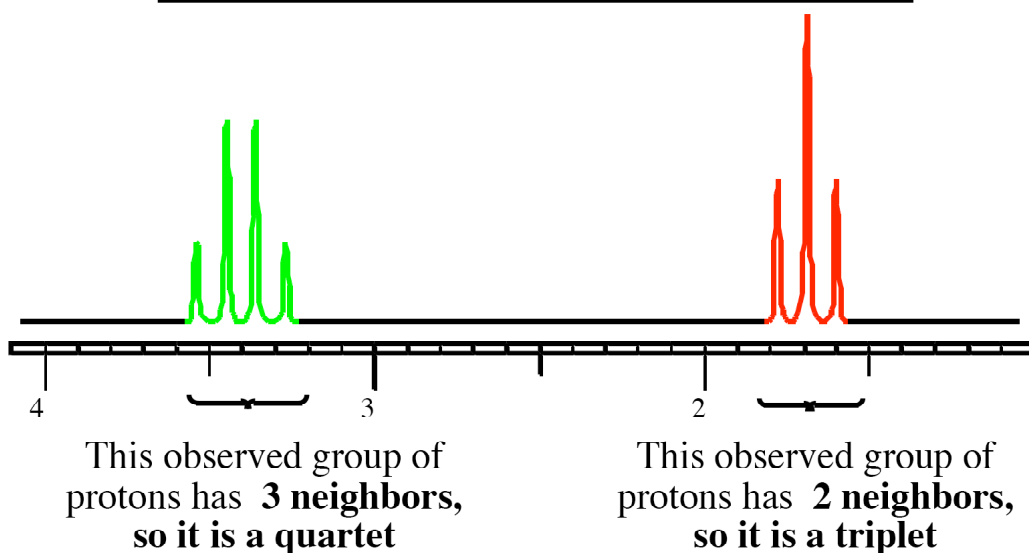
Reading: Section 13.4

## Spin-Spin Splitting: Counting Neighbors

Spin-spin splitting the "n + 1 rule"



If an observed proton has **n adjacent protons...**  
the absorption is split into **n + 1 lines**



**THE SPLITTING OF ONE ABSORPTION IS CAUSED BY THE ADJACENT PROTONS**

number of equivalent adjacent H's	splitting pattern	relative intensity of lines
0	1 - singlet	1
1	2 - doublet	1 1
2	3 - triplet	1 2 1
3	4 - quartet	1 3 3 1
4	5 - quintet	1 4 6 4 1
5	6 - sextet	1 5 10 10 5 1

Reading: Section 13.4