CHEM 210

Infrared Spectroscopy

IR Spectroscopy

I. Introduction

A. **Spectroscopy** is the study of the interaction of matter with the electromagnetic spectrum

1. Electromagnetic radiation displays the properties of both particles and waves
2. The particle component is called a ***photon***
3. The energy (E) component of a photon is proportional to the frequency . Where h is Planck's constant and n is the frequency in Hertz (cycles per second)

$$E = h\nu$$

4. The term "photon" is implied to mean a small, massless particle that contains a small wave-packet of EM radiation/light – we will use this terminology in the course

IR Spectroscopy

I. Introduction

5. Because the speed of light, ***c***, is constant, the ***frequency, ν***, (number of cycles of the wave per second) can complete in the same time, must be inversely proportional to how long the oscillation is, or ***wavelength***:

$$\nu = \frac{c}{\lambda} \qquad \therefore E = h\nu = \frac{hc}{\lambda}$$

$$c = 3 \times 10^{10} \text{ cm/s}$$

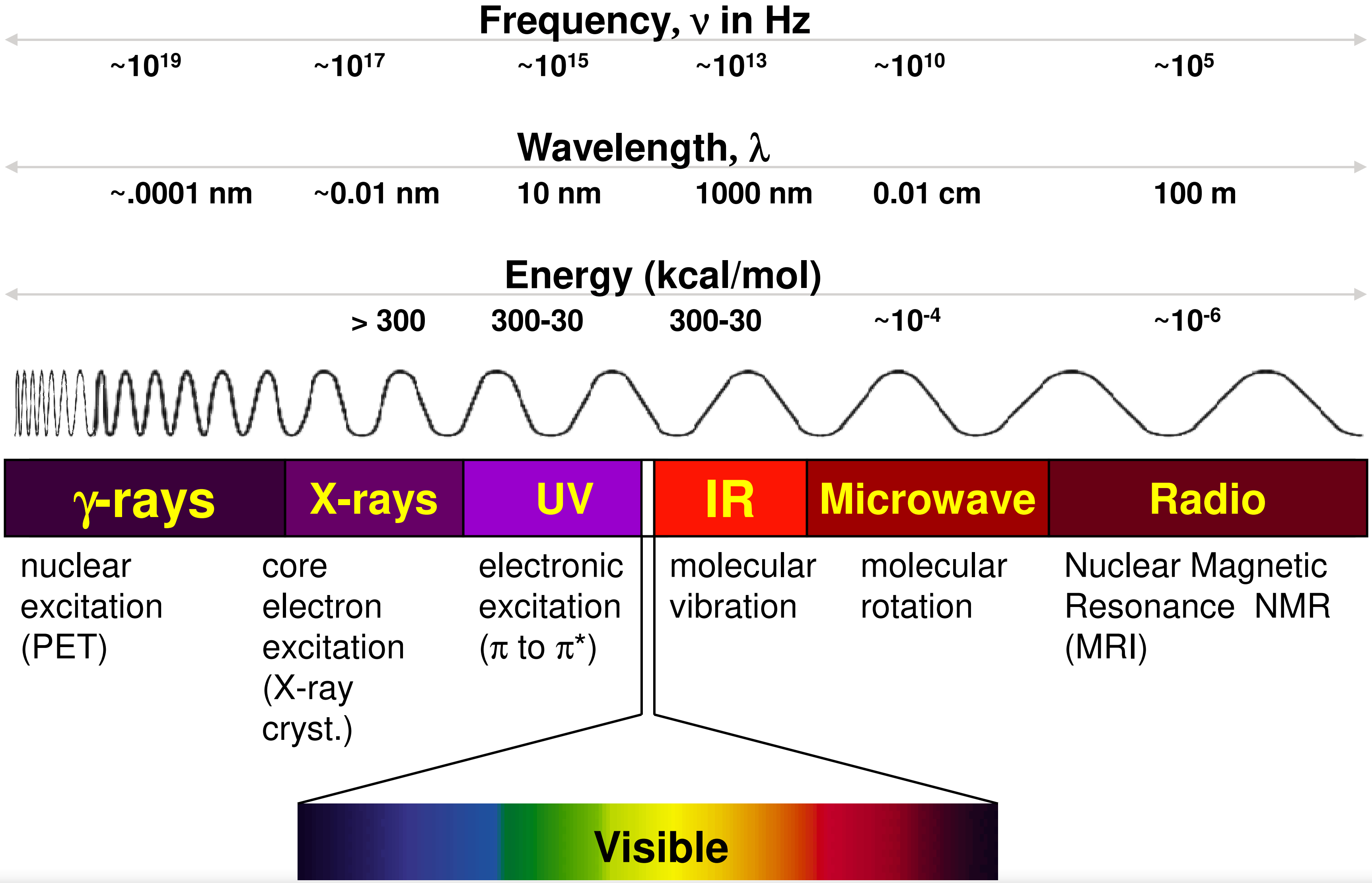
6. Amplitude, ***A***, describes the wave height, or strength of the oscillation

7. Because the atomic particles in matter also exhibit wave and particle properties (though opposite in how much) EM radiation can interact with matter in two ways:
   - Collision – particle-to-particle – energy is lost as heat and movement
   - Coupling – the wave property of the radiation matches the wave property of the particle and "couple" to the next higher quantum mechanical energy level

IR Spectroscopy

I. Introduction

8. The entire electromagnetic spectrum is used by chemists:



	γ-rays	X-rays	UV	IR	Microwave	Radio
Frequency, ν in Hz	~10^{19}	~10^{17}	~10^{15}	~10^{13}	~10^{10}	~10^{5}
Wavelength, λ	~.0001 nm	~0.01 nm	10 nm	1000 nm	0.01 cm	100 m
Energy (kcal/mol)		> 300	300-30	300-30	~10^{-4}	~10^{-6}
	nuclear excitation (PET)	core electron excitation (X-ray cryst.)	electronic excitation (π to π*)	molecular vibration	molecular rotation	Nuclear Magnetic Resonance NMR (MRI)

IR Spectroscopy

I. Introduction

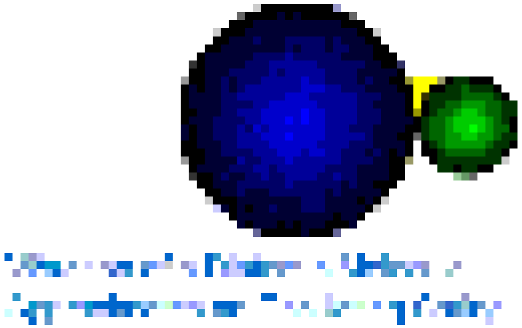
C. The IR Spectroscopic Process

1. The quantum mechanical energy levels observed in IR spectroscopy are those of ***molecular vibration***

2. We perceive this vibration as heat

3. When we say a ***covalent bond*** between two atoms is of a certain length, we are citing an average because the bond behaves as if it were a vibrating spring connecting the two atoms

4. For a simple diatomic molecule, this model is easy to visualize:



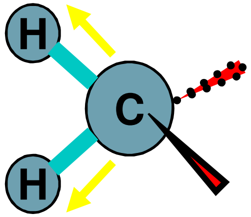
IR Spectroscopy

I. Introduction

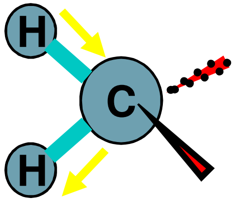
  C. The IR Spectroscopic Process

    5. There are two types of bond vibration:

- ***Stretch*** – Vibration or oscillation along the line of the bond

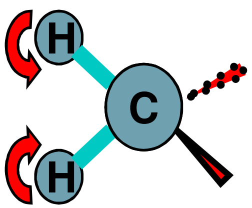


symmetric

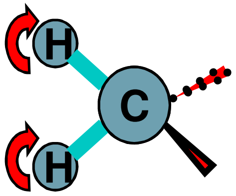


asymmetric

- ***Bend*** – Vibration or oscillation not along the line of the bond

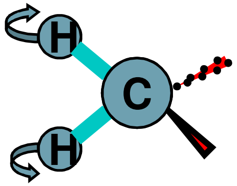


scissor

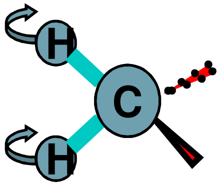


rock

in plane



twist

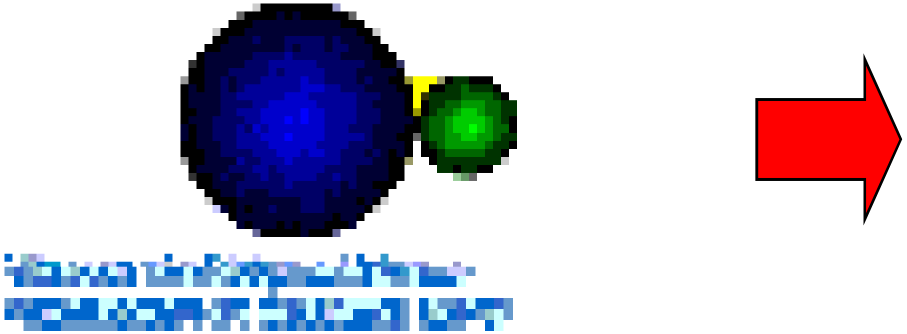


wag

out of plane

C. The IR Spectroscopic Process

6. As a covalent bond oscillates – due to the oscillation of the dipole of the molecule – a varying electromagnetic field is produced

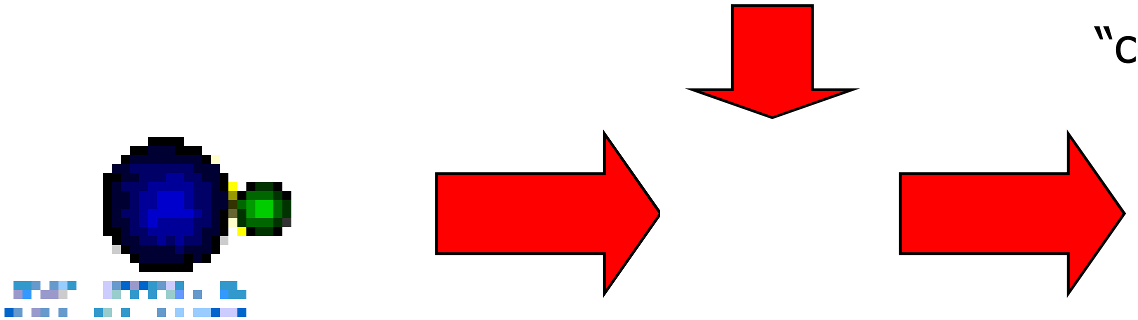


7. The greater the dipole moment change through the vibration, the more intense the EM field that is generated

C. The IR Spectroscopic Process

8. When a wave of infrared light encounters this oscillating EM field generated by the oscillating dipole of the same frequency, the two waves couple, and IR light is absorbed

9. The coupled wave now vibrates with twice the amplitude



IR beam from spectrometer

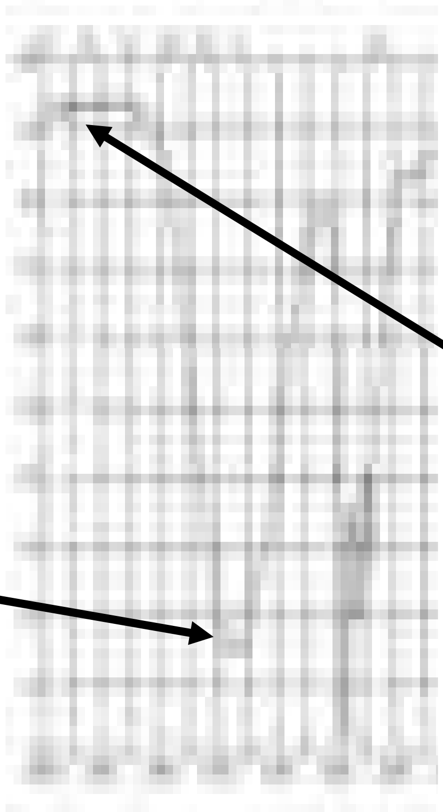
"coupled" wave

EM oscillating wave
from bond vibration

Infrared Spectroscopy

D. The IR Spectrum

  1. Each stretching and bending vibration occurs with a characteristic frequency as the atoms and charges involved are different for different bonds



The y-axis on an IR spectrum is in units of % transmittance

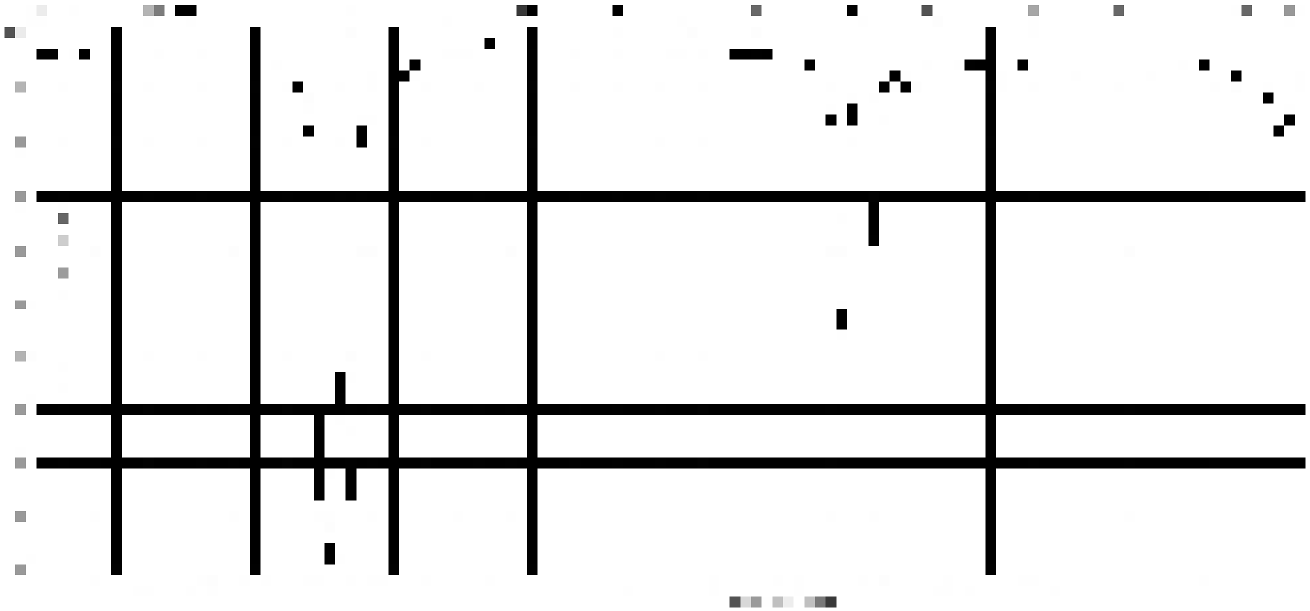
In regions where the EM field of an osc. bond interacts with IR light of the same ν – transmittance is low (light is absorbed)

In regions where no osc. bond is interacting with IR light, transmittance nears 100%

IR Spectroscopy

D. The IR Spectrum

2. The x-axis of the IR spectrum is in units of wavenumbers, ν, which is the number of waves per centimeter in units of cm^{-1} (Remember $E = h\nu$ or $E = hc/\lambda$)



IR Spectroscopy

D. The IR Spectrum

   3. This unit is used rather than wavelength (microns) because wavenumbers are directly proportional to the energy of transition being observed – *chemists like this, physicists hate it*

      High frequencies and high wavenumbers equate higher energy

      is quicker to understand than

      Short wavelengths equate higher energy

   4. This unit is used rather than frequency as the numbers are more "real" than the exponential units of frequency

   5. IR spectra are observed for what is called the mid-infrared: 400-4000 cm^{-1}

   6. The peaks are Gaussian distributions of the average energy of a transition

IR Spectroscopy

D. The IR Spectrum

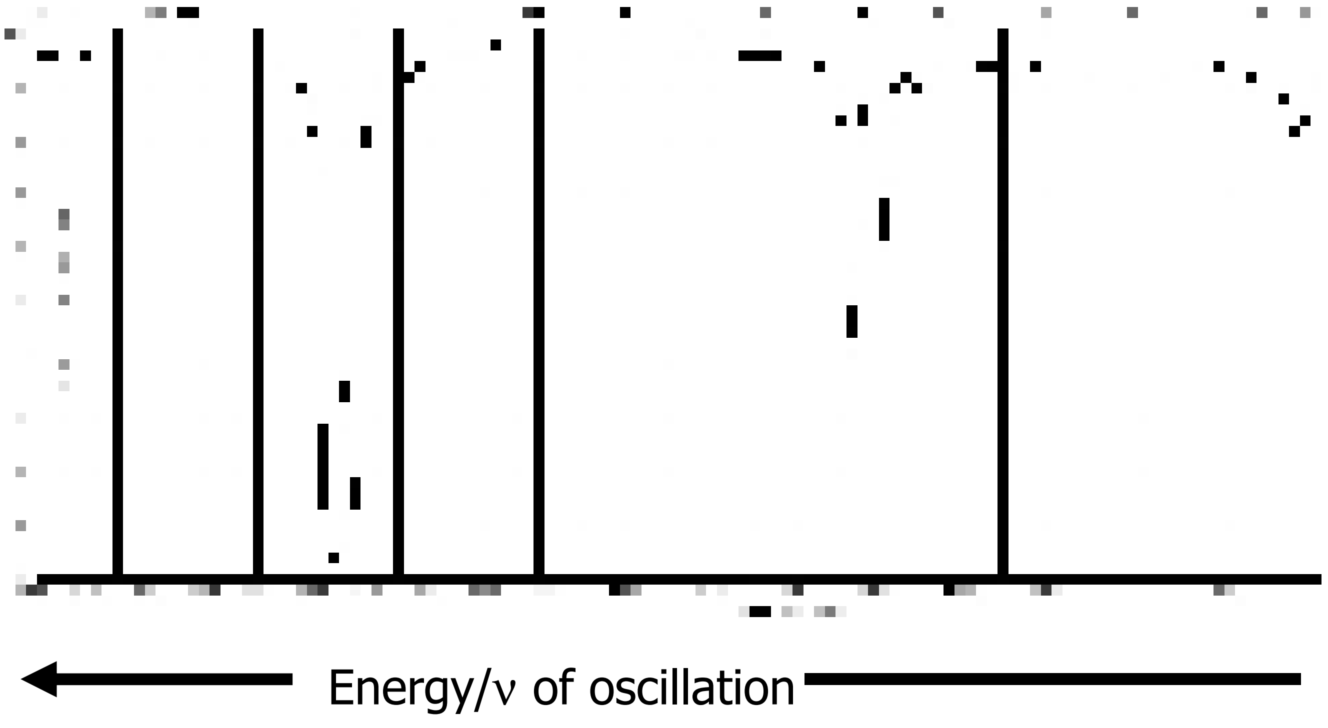
7. In general:

Lighter atoms will allow the oscillation to be faster – *higher energy*

This is especially true of bonds to hydrogen – C-H, N-H and O-H

Stronger bonds will have higher energy oscillations

Triple bonds > double bonds > single bonds in energy



Infrared Spectroscopy

E. The IR Spectrum – The detection of different bonds

7. As opposed to chromatography or other spectroscopic methods, the area of a IR band (or peak) is not ***directly*** proportional to concentration of the functional group producing the peak

8. The intensity of an IR band is affected by two primary factors:

   Whether the vibration is one of stretching or bending

   Electronegativity difference of the atoms involved in the bond

   - For both effects, the greater the change in dipole moment in a given vibration or bend, the larger the peak.

   - The greater the difference in electronegativity between the atoms involved in bonding, the larger the dipole moment

   - Typically, stretching will change dipole moment more than bending

Infrared Spectroscopy

E. The IR Spectrum – The detection of different bonds

9. It is important to make note of peak intensities to show the effect of these factors:

- [redacted]
- [redacted]
- [redacted]
- **** Broad (br)*** – if the Gaussian distribution is abnormally broad *(*this is more for describing a bond that spans many energies)*

Exact transmittance values are rarely recorded

II. Infrared Group Analysis

A. General

1. The primary use of the IR spectrometer is to ***detect functional groups***

2. Because the IR looks at the interaction of the EM spectrum with actual bonds, it provides a unique qualitative probe into the functionality of a molecule, as functional groups are merely different configurations of different types of bonds

3. Since most “types” of bonds in covalent molecules have roughly the same energy, i.e., C=C and C=O bonds, C-H and N-H bonds they show up in similar regions of the IR spectrum

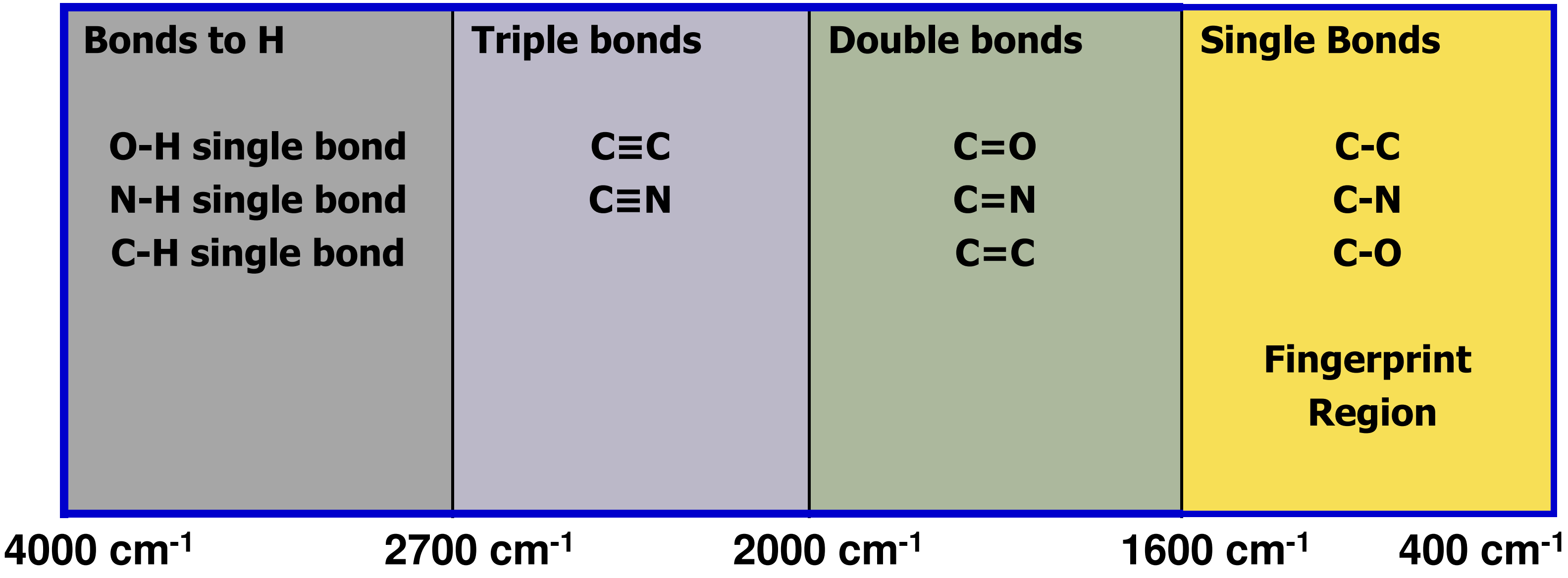
4. Remember all organic functional groups are made of multiple bonds and therefore show up as multiple IR bands (peaks)

Infrared Spectroscopy

II. Infrared Group Analysis

A. General

5. The four primary regions of the IR spectrum



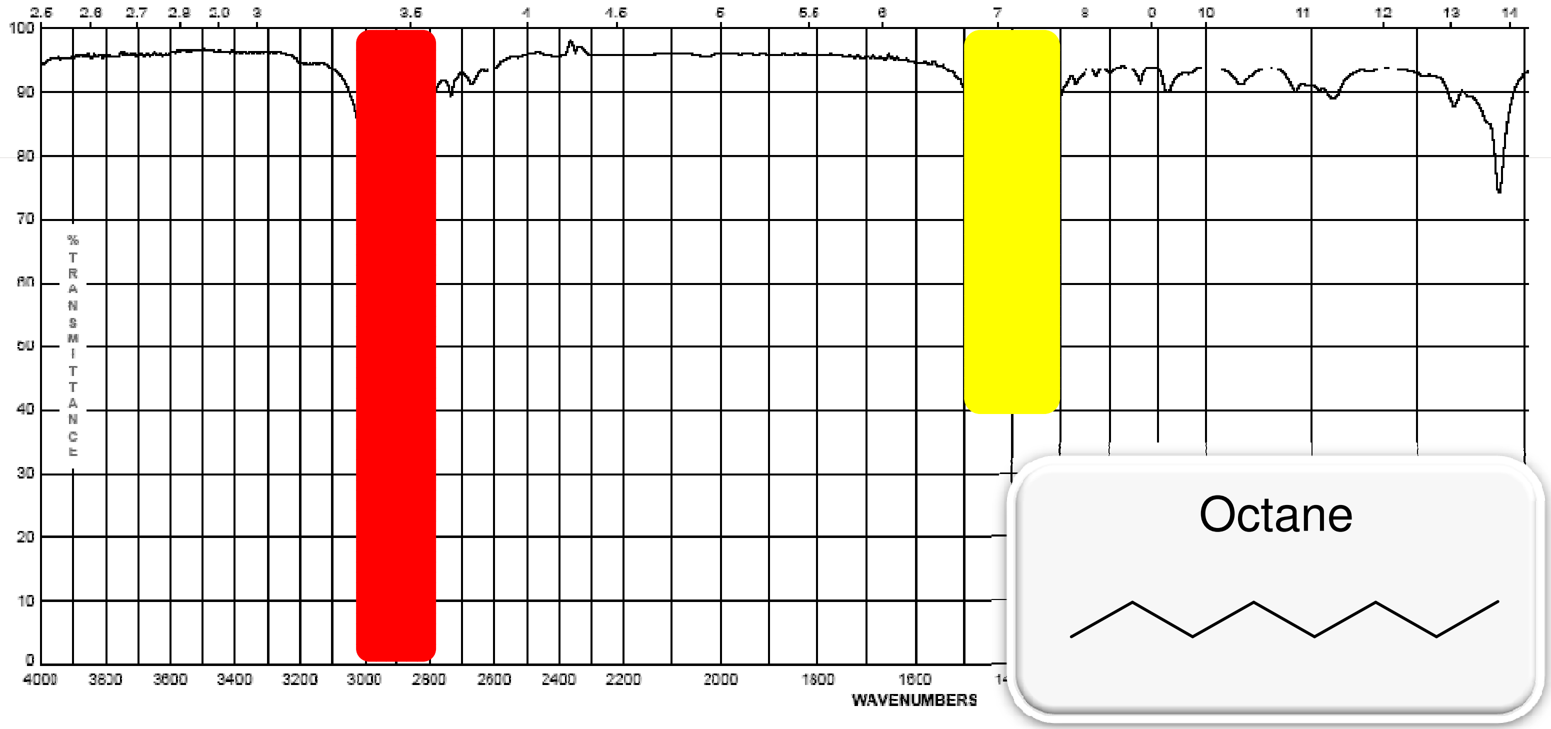
Bonds to H	Triple bonds	Double bonds	Single Bonds
O-H single bond	C≡C	C=O	C-C
N-H single bond	C≡N	C=N	C-N
C-H single bond		C=C	C-O
			Fingerprint Region

4000 cm^{-1} 2700 cm^{-1} 2000 cm^{-1} 1600 cm^{-1} 400 cm^{-1}

Infrared Spectroscopy

Specific groups

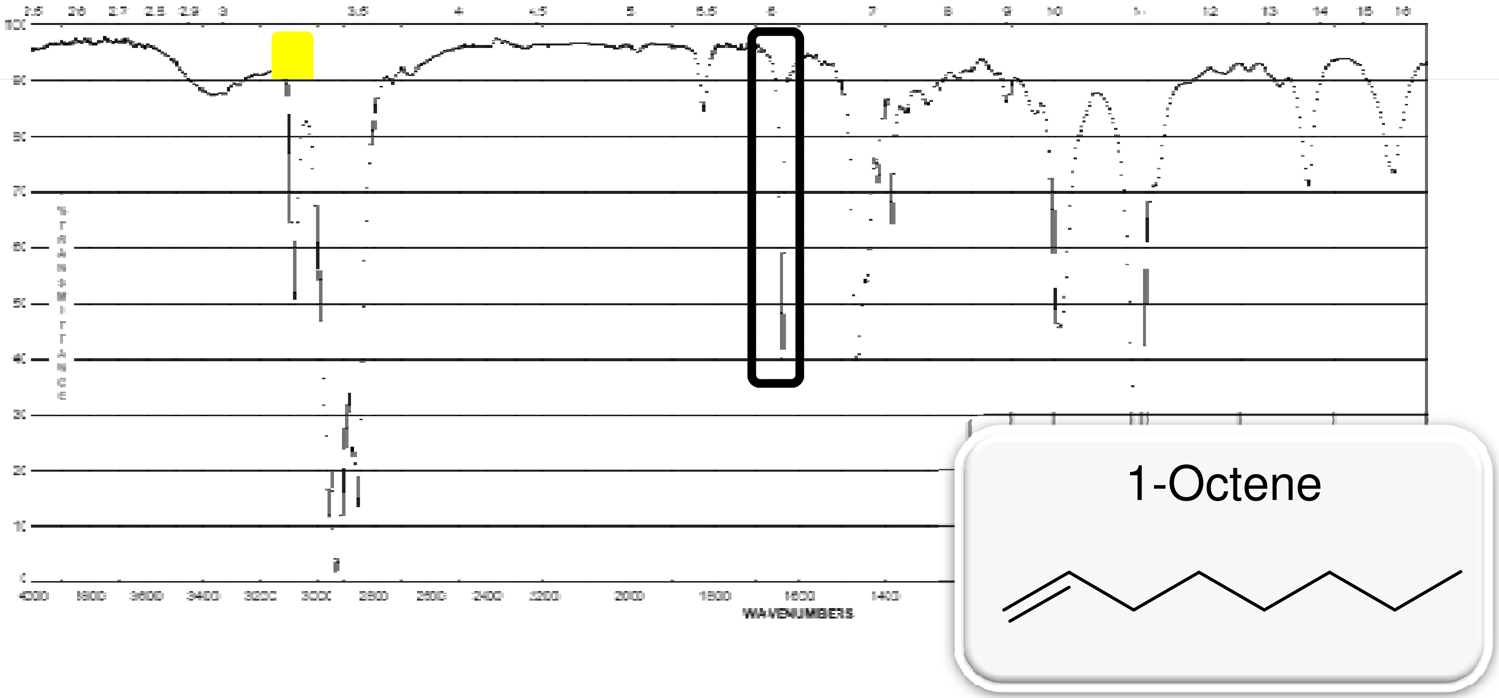
1. **Alkanes** – combination of C-C and C-H bonds
   - Show various C-C stretches and bends between 1360-1470 cm^{-1} (m)
   - C-C bond between methylene carbons (CH$_2$'s) 1450-1470 cm^{-1} (m)
   - C-C bond between methylene carbons (CH$_2$'s) and methyl (CH$_3$) 1360-1390 cm^{-1} (m)
   - Show sp^3 C-H between 2800-3000 cm^{-1} (s) cm $^{-1}$



Infrared Spectroscopy

Specific groups

2. **Alkenes** – addition of the C=C and vinyl C-H bonds
    - C=C stretch occurs at 1620-1680 cm^{-1} and becomes weaker as substitution increases
    - vinyl C-H stretch occurs at 3000-3100 cm^{-1}
    - **Note that the bonds of alkane are still present!**
    - The difference between alkane and alkene or alkynyl C-H is important! If the band is slightly above 3000 it is vinyl sp^2 C-H or alkynyl sp C-H if it is below it is alkyl sp^3 C-H

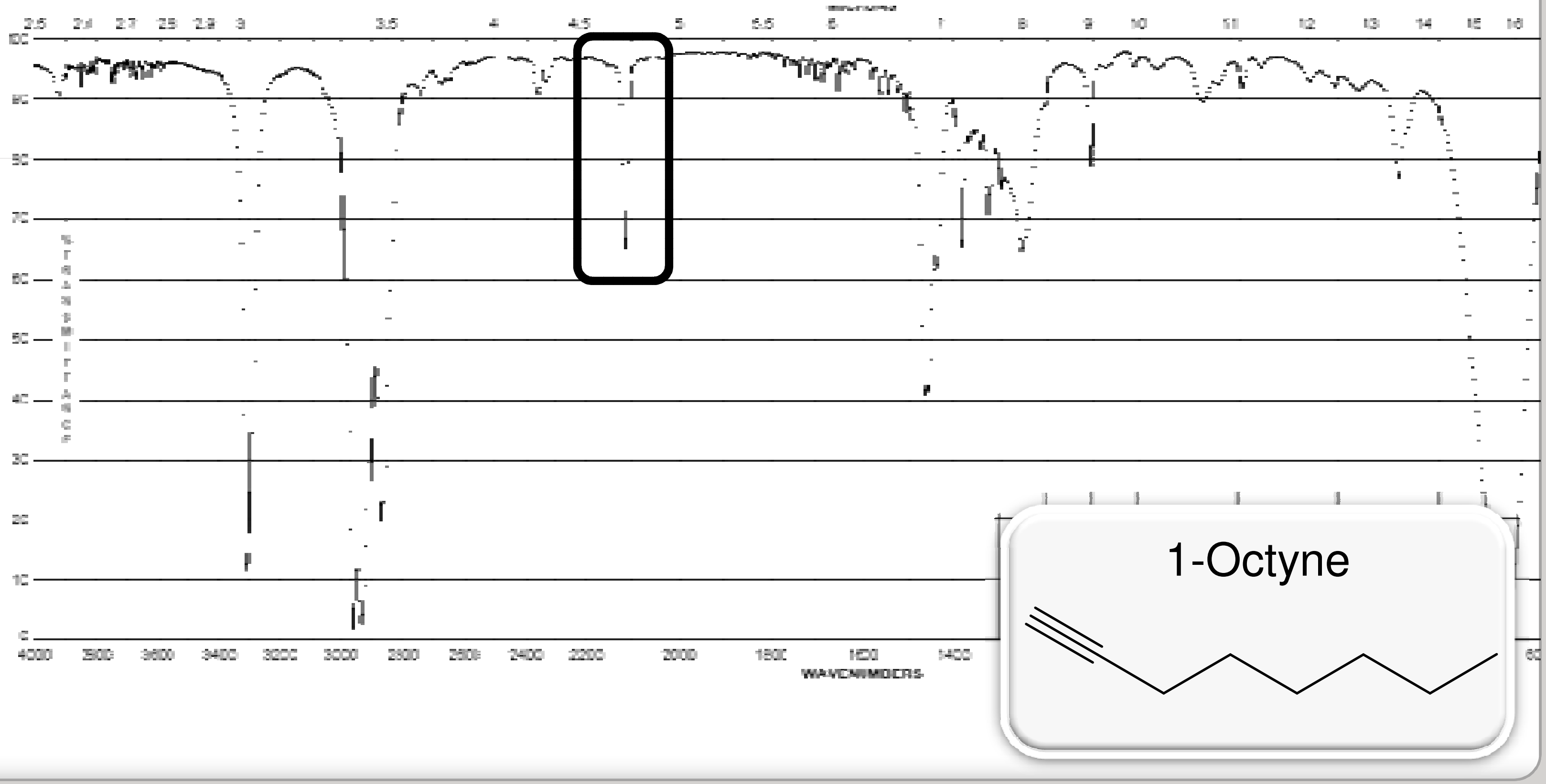


1-Octene

Infrared Spectroscopy

Specific groups

3. **Alkynes** – addition of the C=C and vinyl C-H bonds
   - C≡C stretch occurs between 2100-2260 cm^{-1}; the strength of this band depends on asymmetry of bond, strongest for terminal alkynes, weakest for symmetrical internal alkynes (w-m)
   - C-H for *terminal* alkynes occurs at 3200-3300 cm^{-1} (s)
   - Remember internal alkynes (R-C≡C-R) would not have this band!

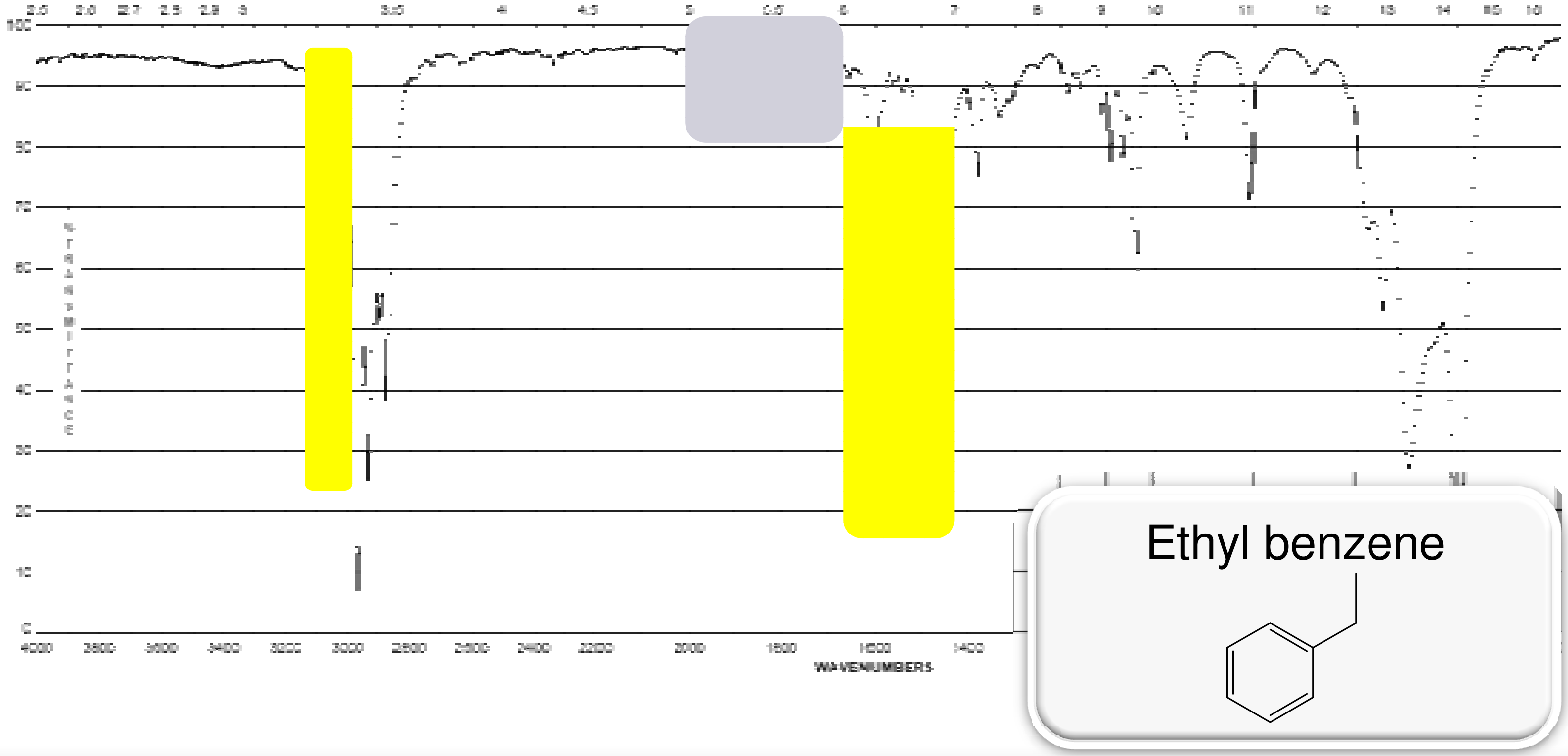


Infrared Spectroscopy

Specific groups

4. Aromatics

- Due to the delocalization of electrons in the ring, where the bond order between carbons is 1 ½, the stretching frequency for these bonds is slightly lower in energy than normal C=C
- These bonds show up as a *pair* of sharp bands, 1500 (s) & 1600 cm^{-1} (m), where the lower frequency band is stronger
- C-H bonds off the ring show up similar to vinyl C-H at 3000-3100 cm^{-1} (m)

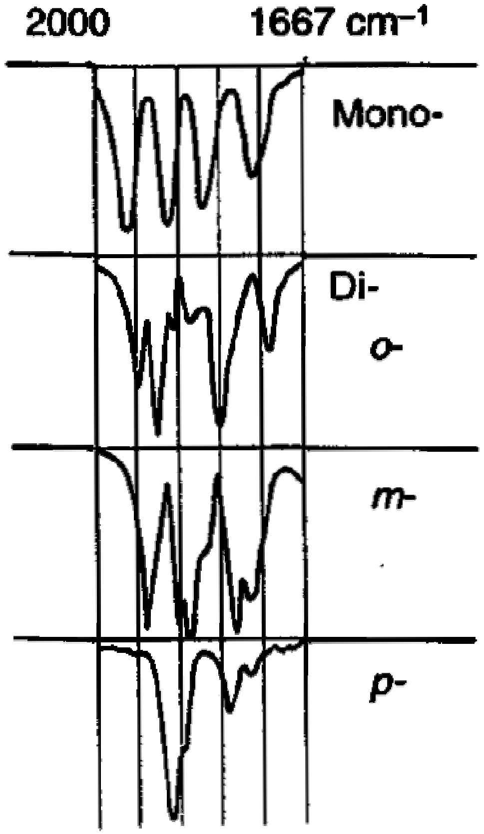


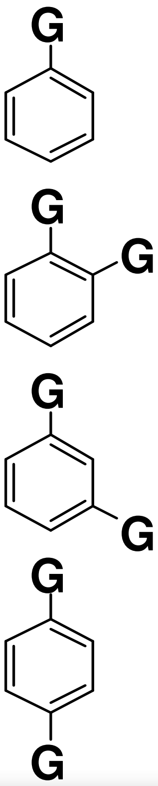
Infrared Spectroscopy

Specific groups

4. Aromatics

- If the region between 1667-2000 cm^{-1} (w) is free of interference (C=O stretching frequency is in this region) a weak grouping of peaks is observed for aromatic systems
- Analysis of this region, called the *overtone of bending* region, can lead to a determination of the substitution pattern on the aromatic ring





Monosubstituted

1,2 disubstituted (*ortho* or *o*-)

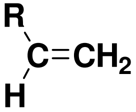
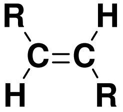
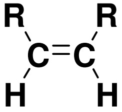
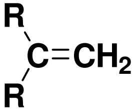
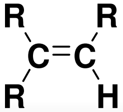
1,2 disubstituted (*meta* or *m*-)

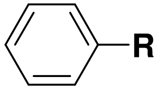
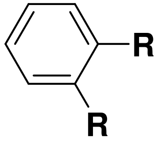
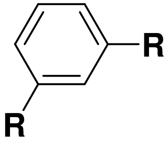
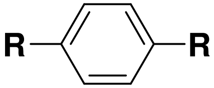
1,4 disubstituted (*para* or *p*-)

Infrared Spectroscopy

Specific groups

5. **Unsaturated Systems** – substitution patterns
   - The substitution of aromatics and alkenes can also be discerned through the out-of-plane bending vibration region
   - However, other peaks often are apparent in this region. *These peaks should only be used for reinforcement of what is known or for hypothesizing as to the functional pattern.*

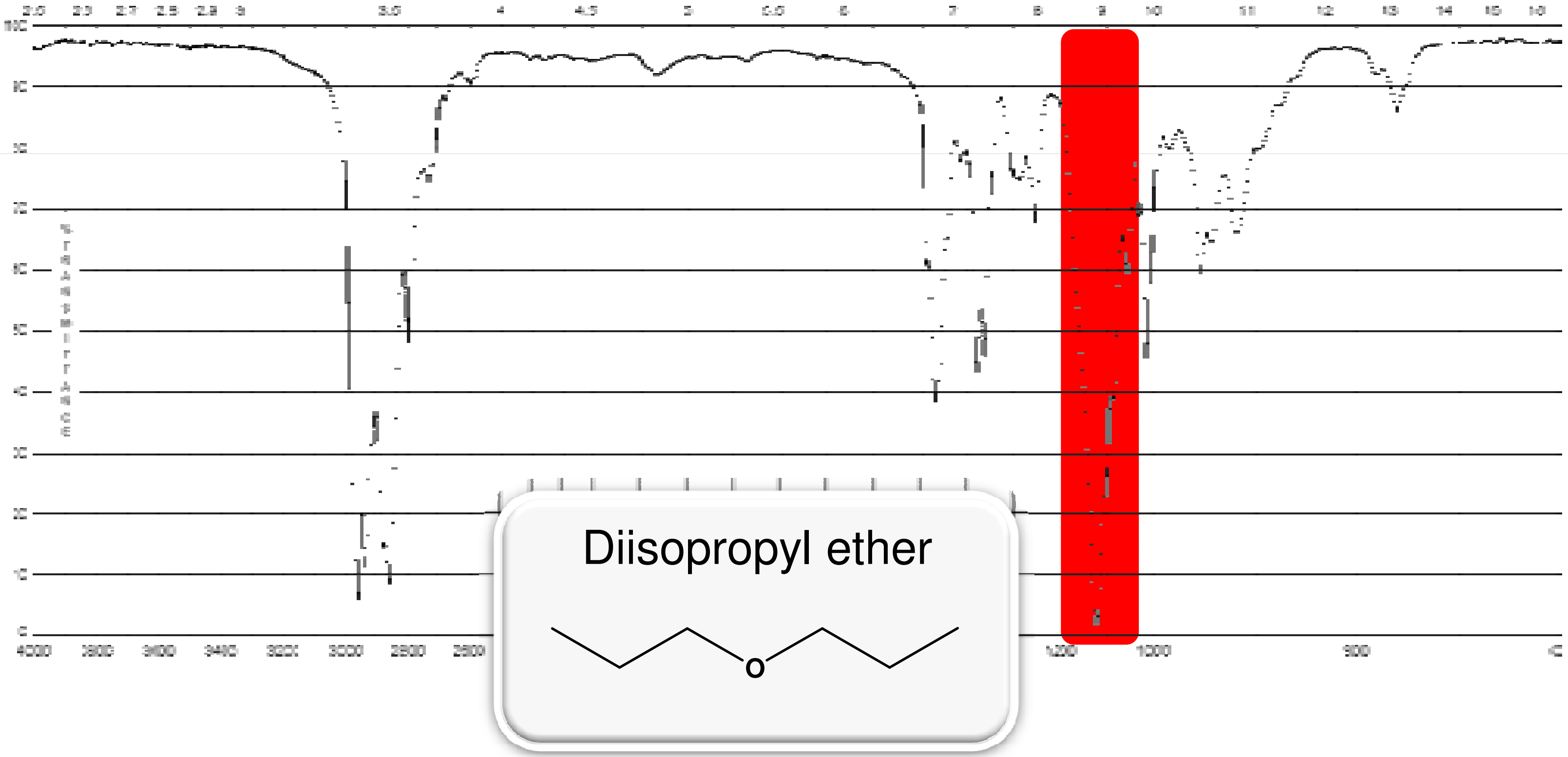
	cm^{-1}
	985-997 905-915
	960-980
	665-730
	885-895
	790-840

	cm^{-1}
	730-770 690-710
	735-770
	860-900 750-810 680-725
	800-860

Infrared Spectroscopy

Specific groups

6. **Ethers** – addition of the C-O-C asymmetric band and vinyl C-H bonds
    - Show a strong band for the antisymmetric C-O-C stretch at 1050-1150 cm^{-1}
    - Otherwise, dominated by the hydrocarbon component of the rest of the molecule



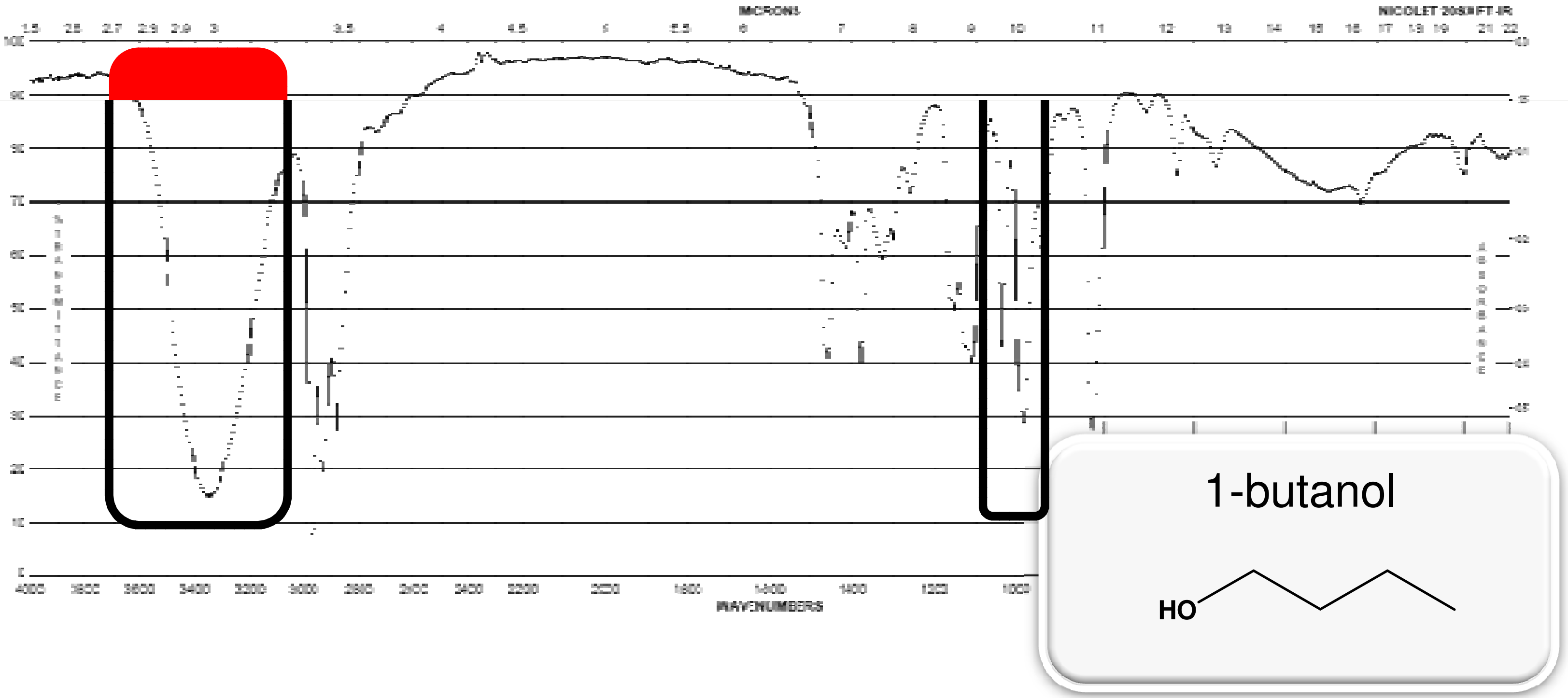
Diisopropyl ether

Infrared Spectroscopy

Specific groups

7. Alcohols

- Show a strong, broad band for the O-H stretch from 3200-3400 cm^{-1} (s, br) this is *one of the most recognizable IR bands*
- Like ethers, show a band for C-O stretch between 1050-1260 cm^{-1} (s)
- This band changes position depending on the substitution of the alcohol: 1° 1075-1000; 2°1075-1150; 3°1100-1200; phenol 1180-1260
- The shape is due to the presence of hydrogen bonding

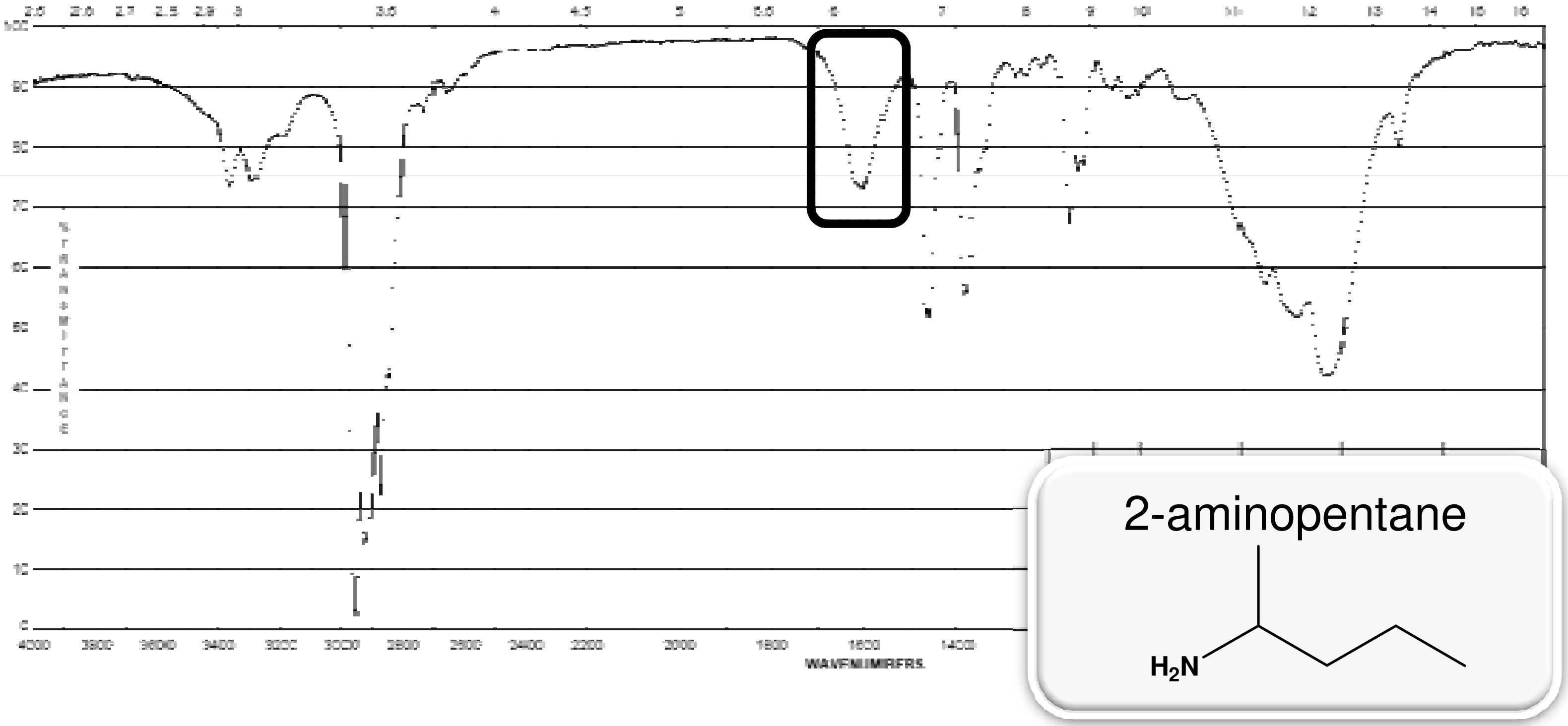


1-butanol

Infrared Spectroscopy

Specific groups

8. **Amines** - Primary
   - Shows the –N-H stretch for NH_2 as a ***doublet*** between 3200-3500 cm^{-1} (s-m); symmetric and anti-symmetric modes
   - -NH_2 group shows a deformation band from 1590-1650 cm^{-1} (w)
   - Additionally there is a “wag” band at 780-820 cm^{-1} that is not diagnostic

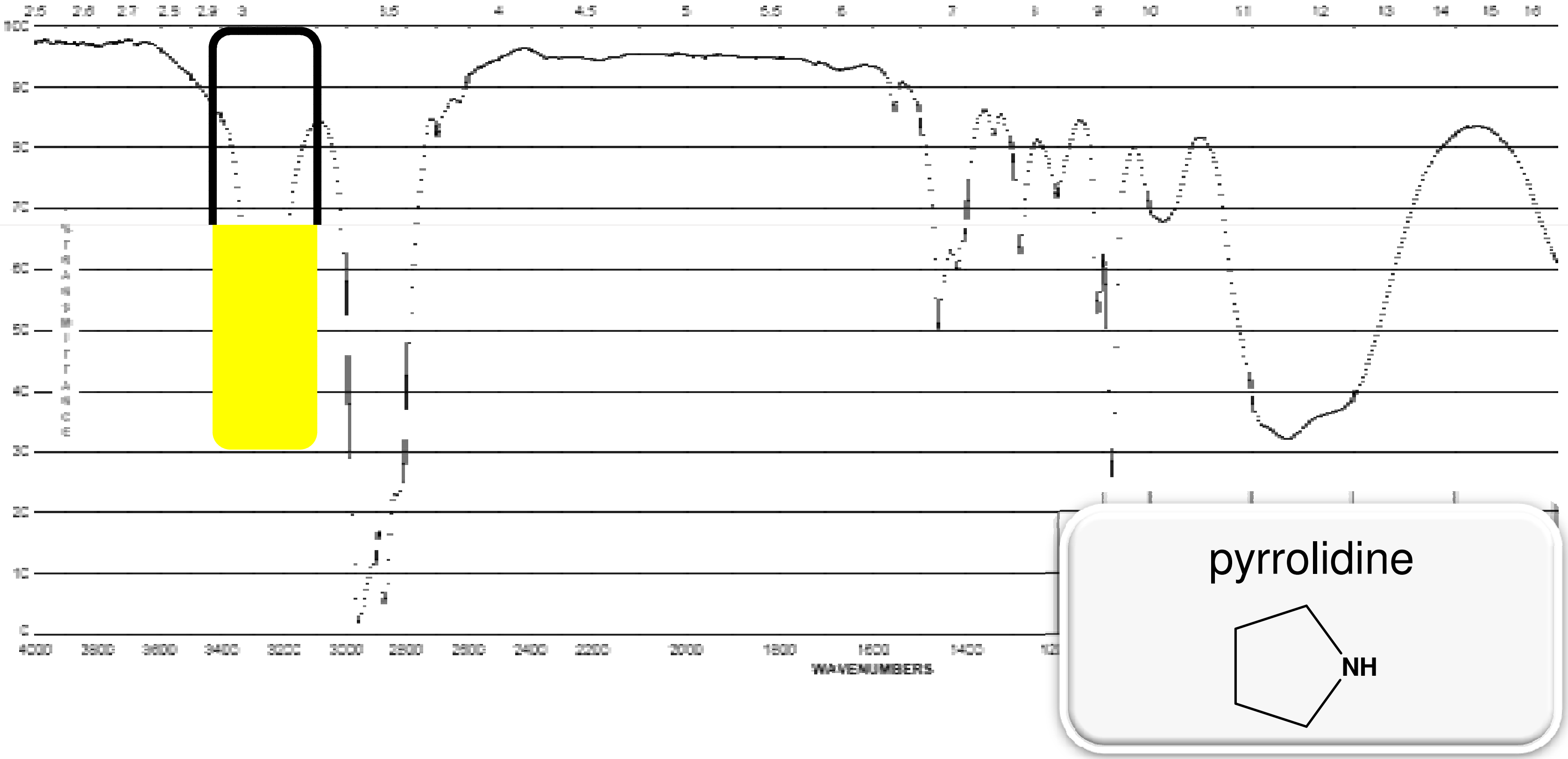


2-aminopentane

Infrared Spectroscopy

Specific groups

9. **Amines** – Secondary
    - -N-H band for R_2N-H occurs at 3200-3500 cm^{-1} (br, m) as a single sharp peak weaker than –O-H
    - Tertiary amines (R_3N) have no N-H bond and *will not* have a band in this region

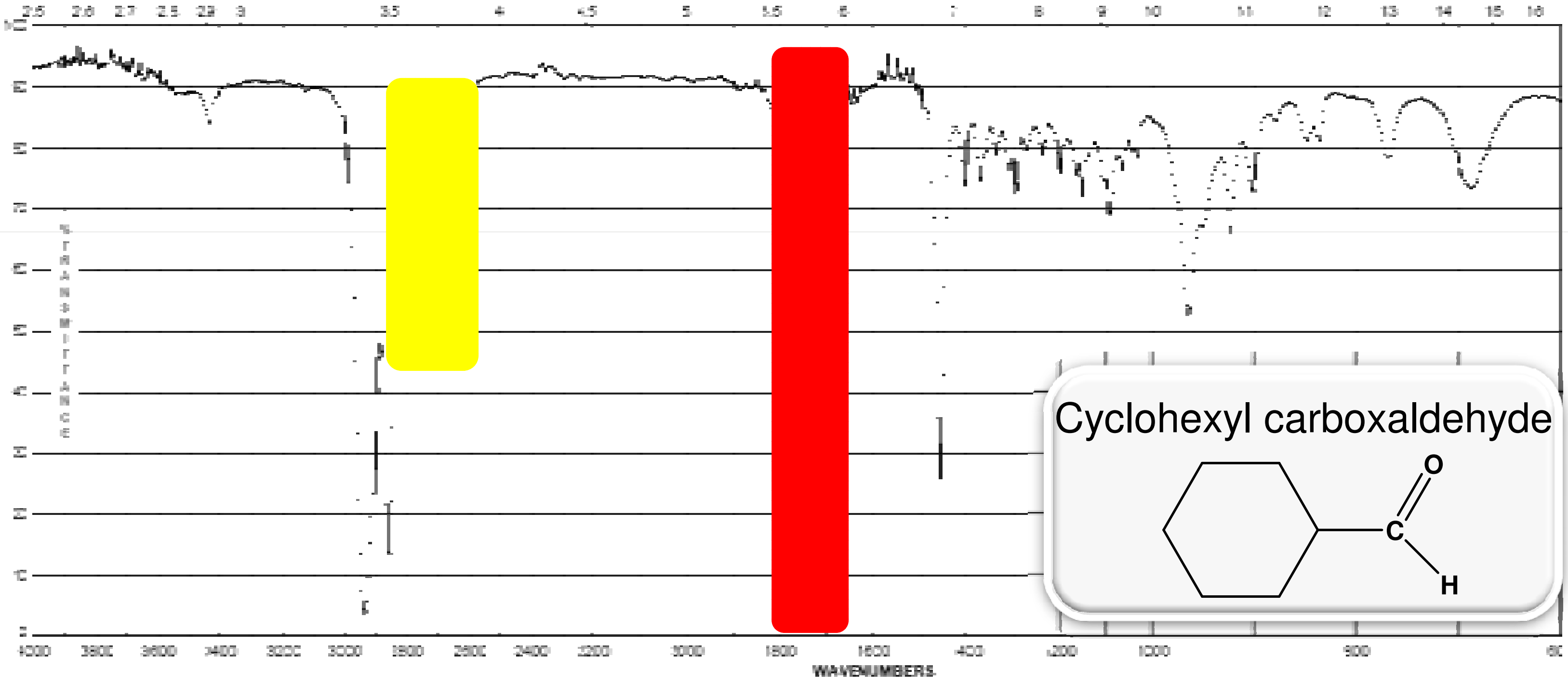


Infrared Spectroscopy

Specific groups

10. Aldehydes

- Show the C=O (carbonyl) stretch from 1720-1740 cm^{-1}(s)
- Band is sensitive to conjugation, as are all carbonyls (upcoming slide)
- Also displays a highly unique sp^2 C-H stretch as a doublet, 2720 & 2820 cm^{-1} (w) called a "*Fermi doublet*"

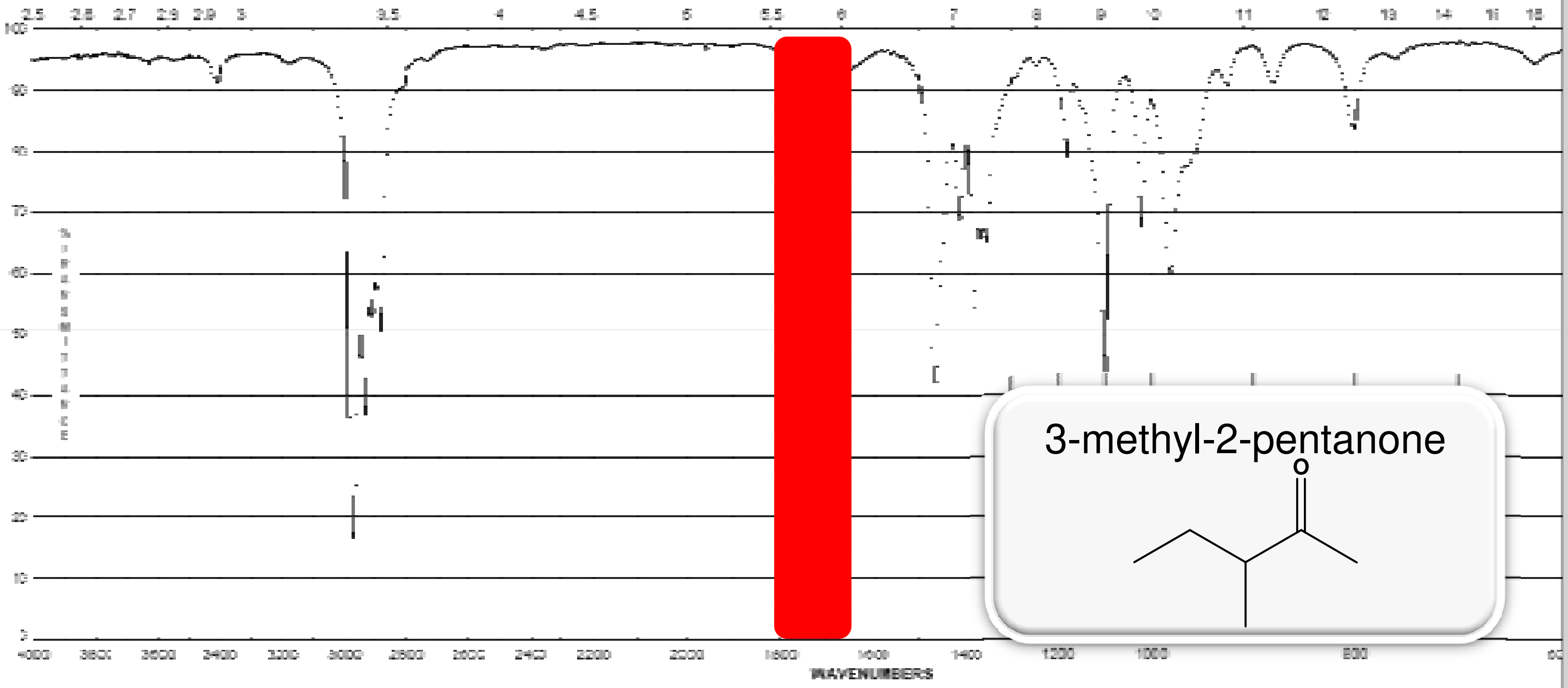


Cyclohexyl carboxaldehyde

Infrared Spectroscopy

Specific groups

11. **Ketones**
    - Simplest of the carbonyl compounds as far as IR spectrum – carbonyl only
    - C=O stretch occurs at 1705-1725 cm^{-1} (s)



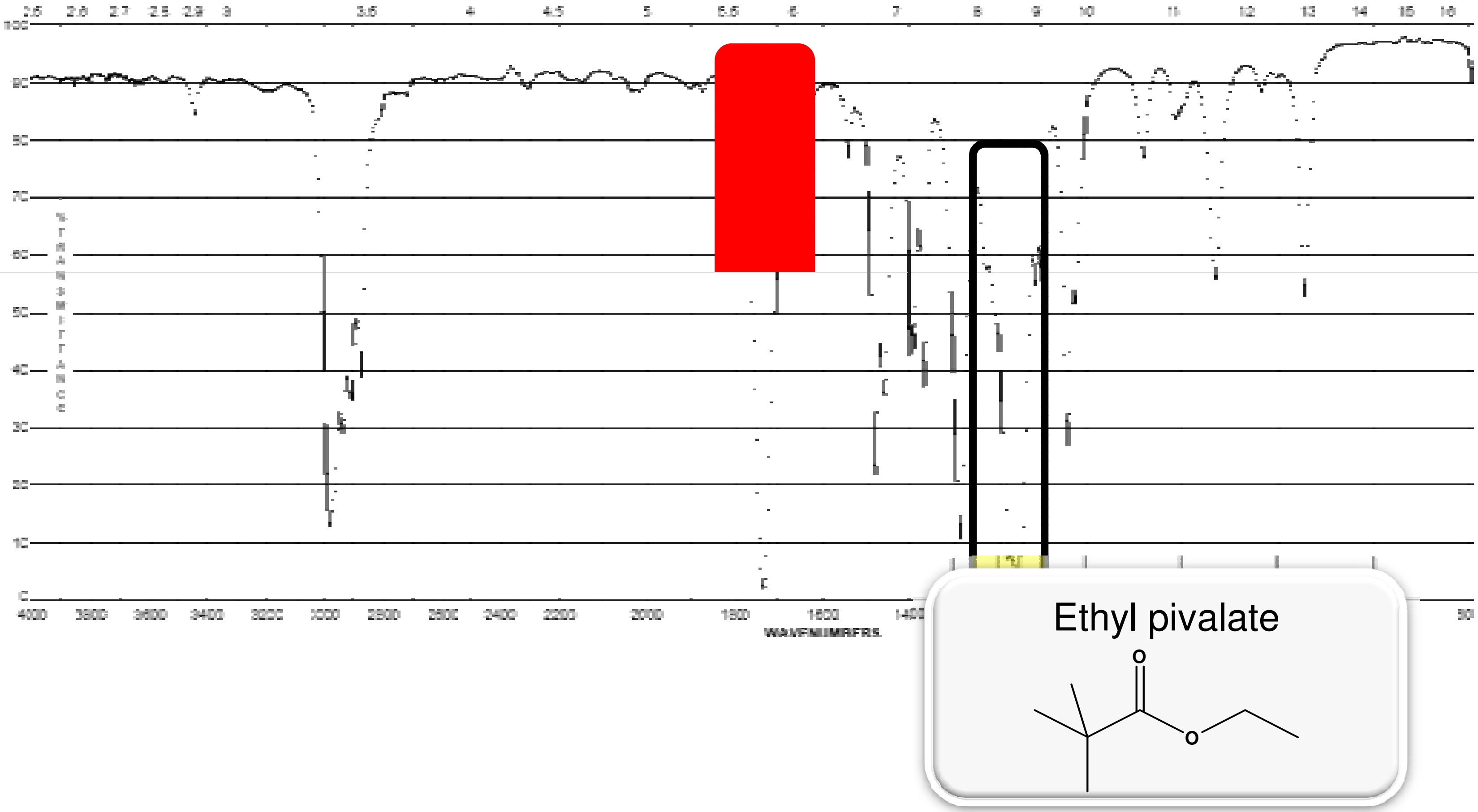
3-methyl-2-pentanone

Infrared Spectroscopy

Specific groups

12. Esters

1. C=O stretch occurs at 1735-1750 cm^{-1} (s)
2. Also displays a strong band for C-O at a higher frequency than ethers or alcohols at 1150-1250 cm^{-1} (s)



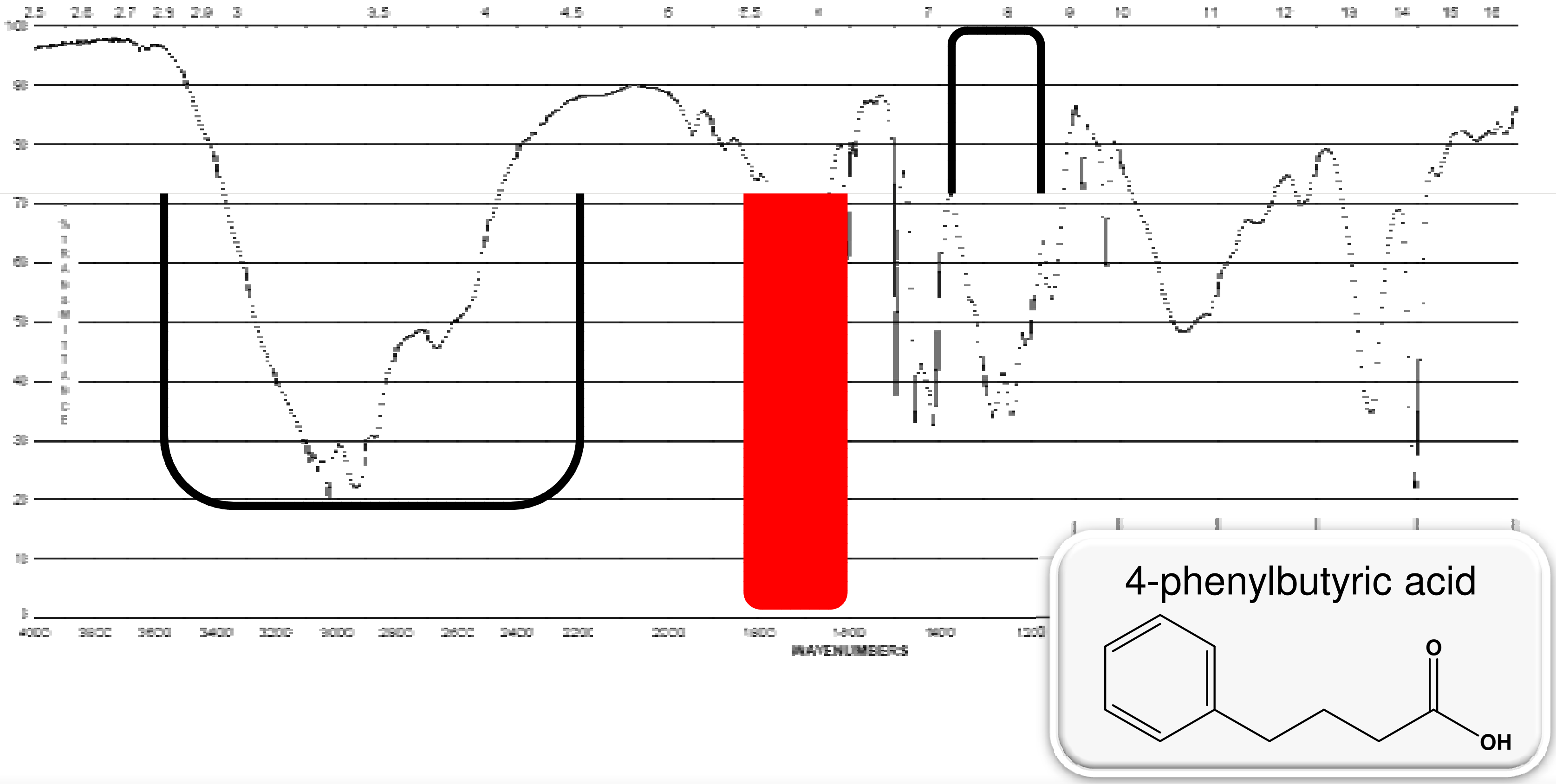
Ethyl pivalate

Infrared Spectroscopy

Specific groups

13. Carboxylic Acids:

- Gives the messiest of IR spectra
- C=O band occurs between 1700-1725 cm^{-1}
- The highly dissociated O-H bond has a broad band from 2400-3500 cm^{-1} (m, br) covering up to half the IR spectrum in some cases



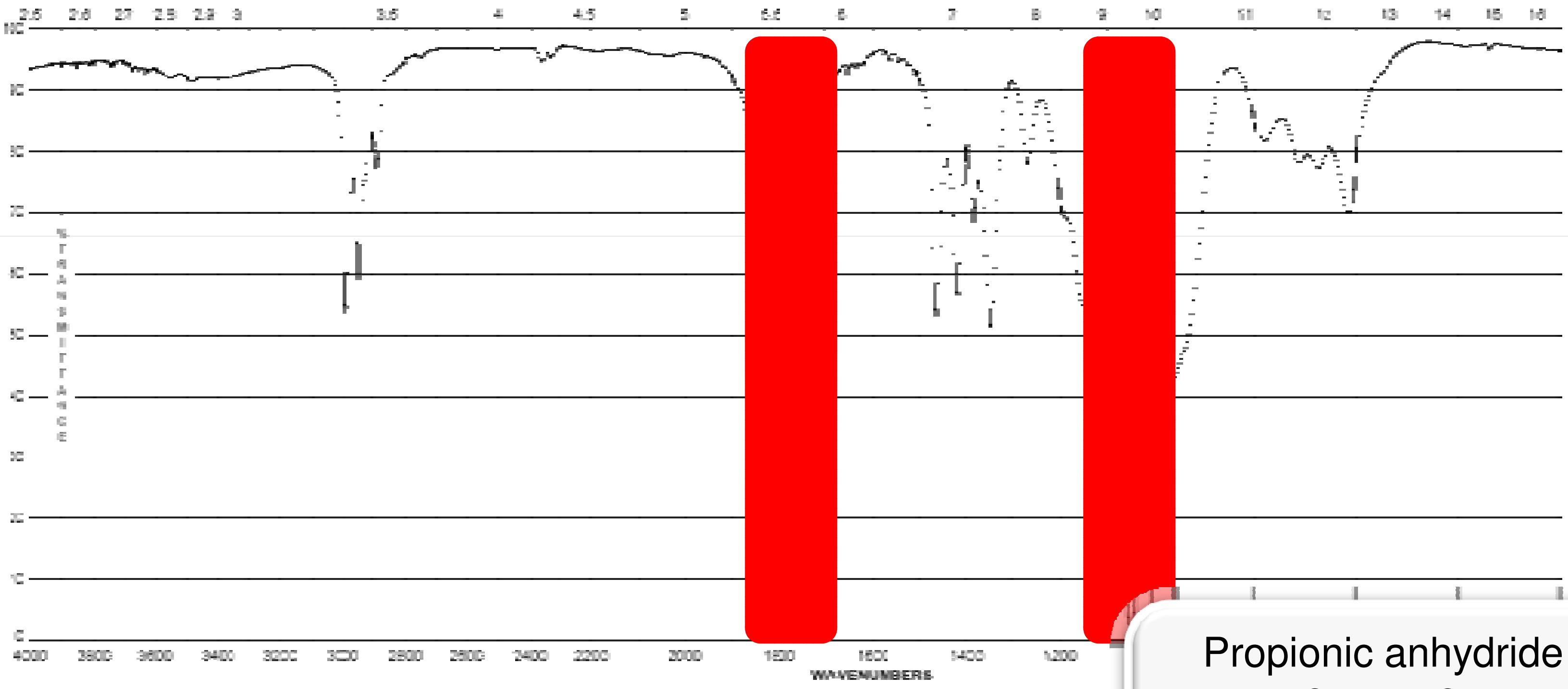
4-phenylbutyric acid

Infrared Spectroscopy

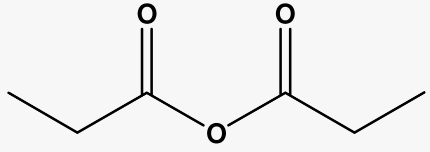
B. Specific groups

14. Acid anhydrides

- Coupling of the anhydride though the ether oxygen splits the carbonyl band into two with a separation of 70 cm^{-1}.
- Bands are at 1740-1770 cm-1 and 1810-1840 cm^{-1} (s)
- Mixed mode C-O stretch at 1000-1100 cm^{-1} (s)



Propionic anhydride

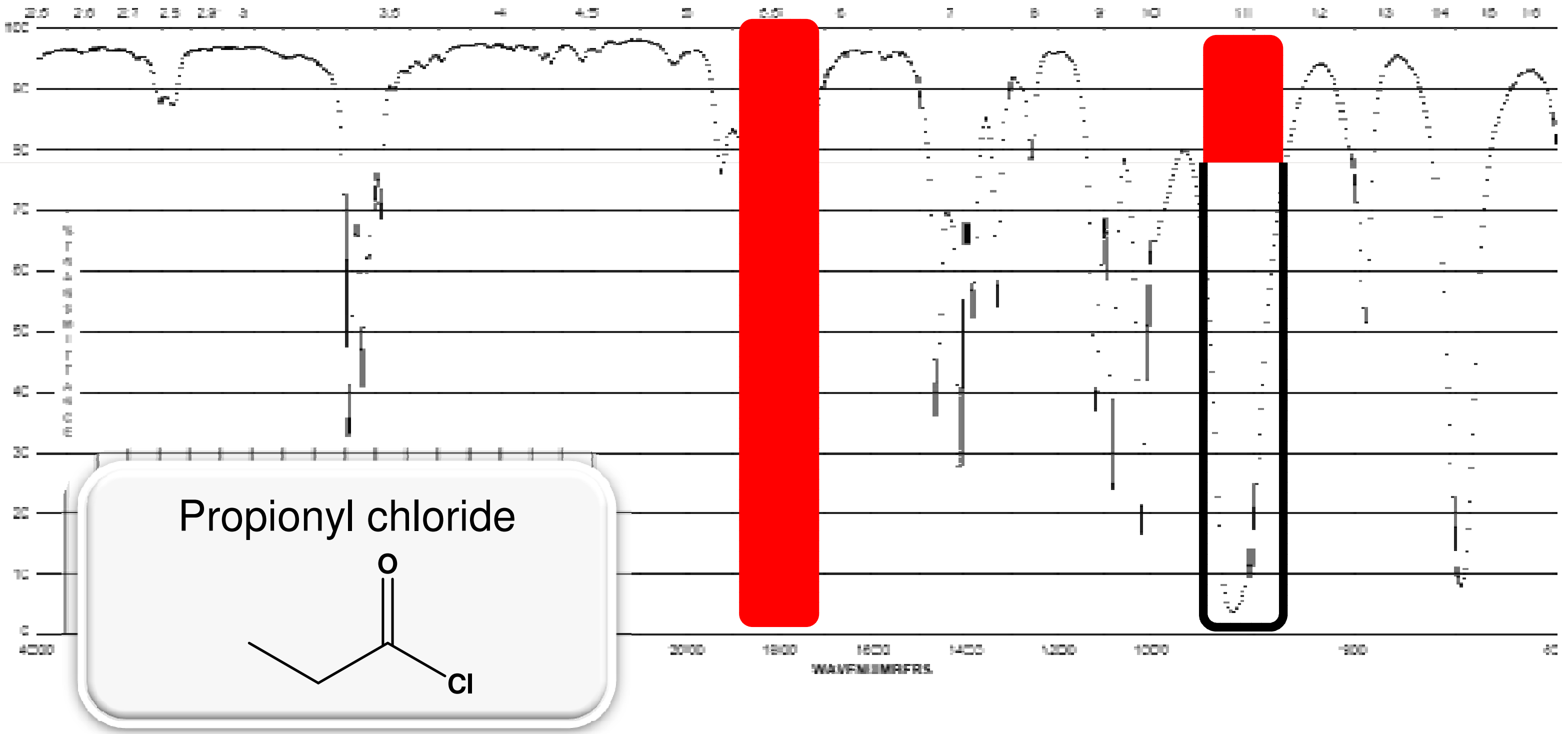


Infrared Spectroscopy

Specific groups

15. Acid halides

- Dominant band at 1770-1820 cm^{-1} for C=O (s)
- Bonds to halogens, due to their size (see Hooke's Law derivation) occur at low frequencies, where their presence should be used to reinforce rather than be used for diagnosis, C-Cl is at 600-800 cm^{-1} (m)

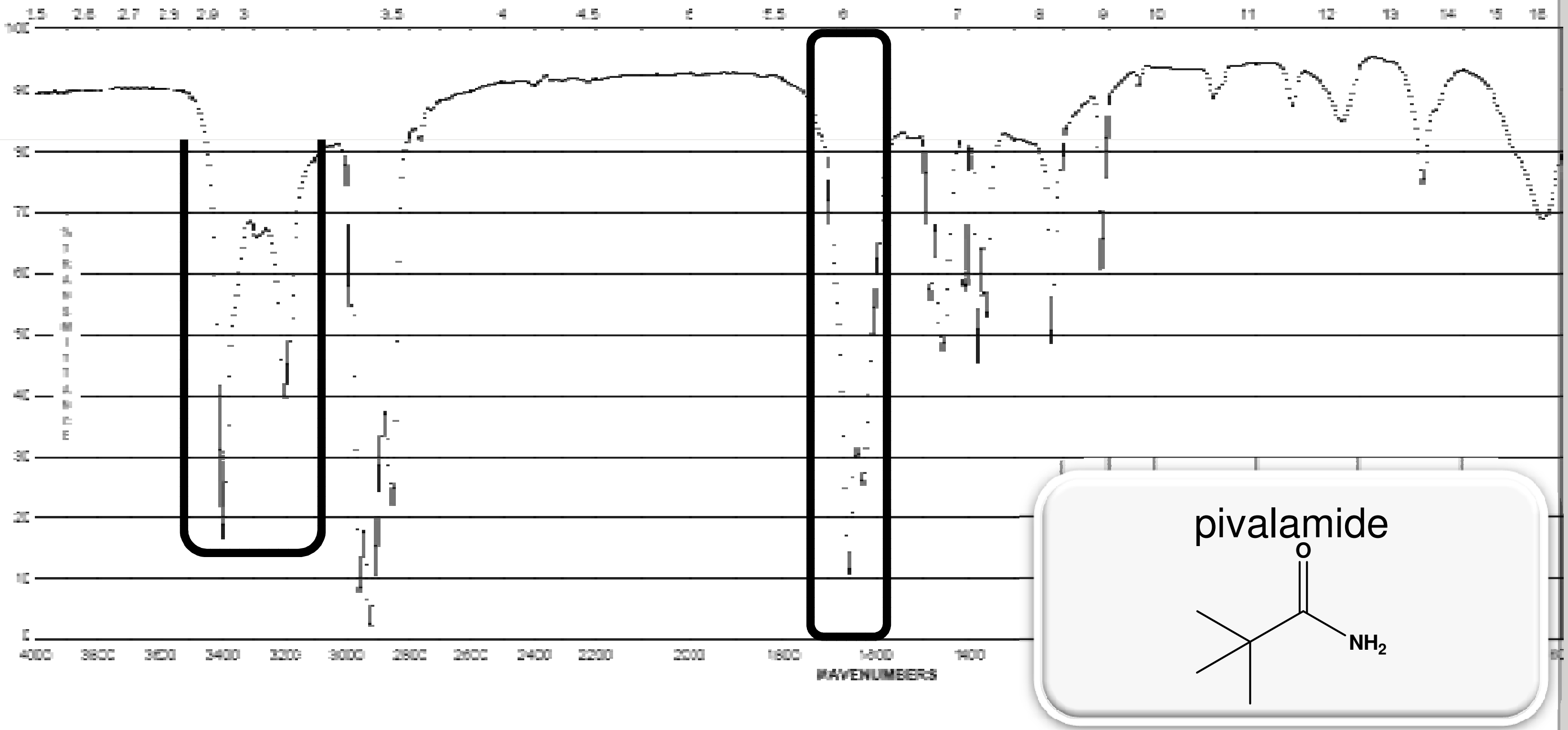

Propionyl chloride

Infrared Spectroscopy

Specific groups

16. Amides

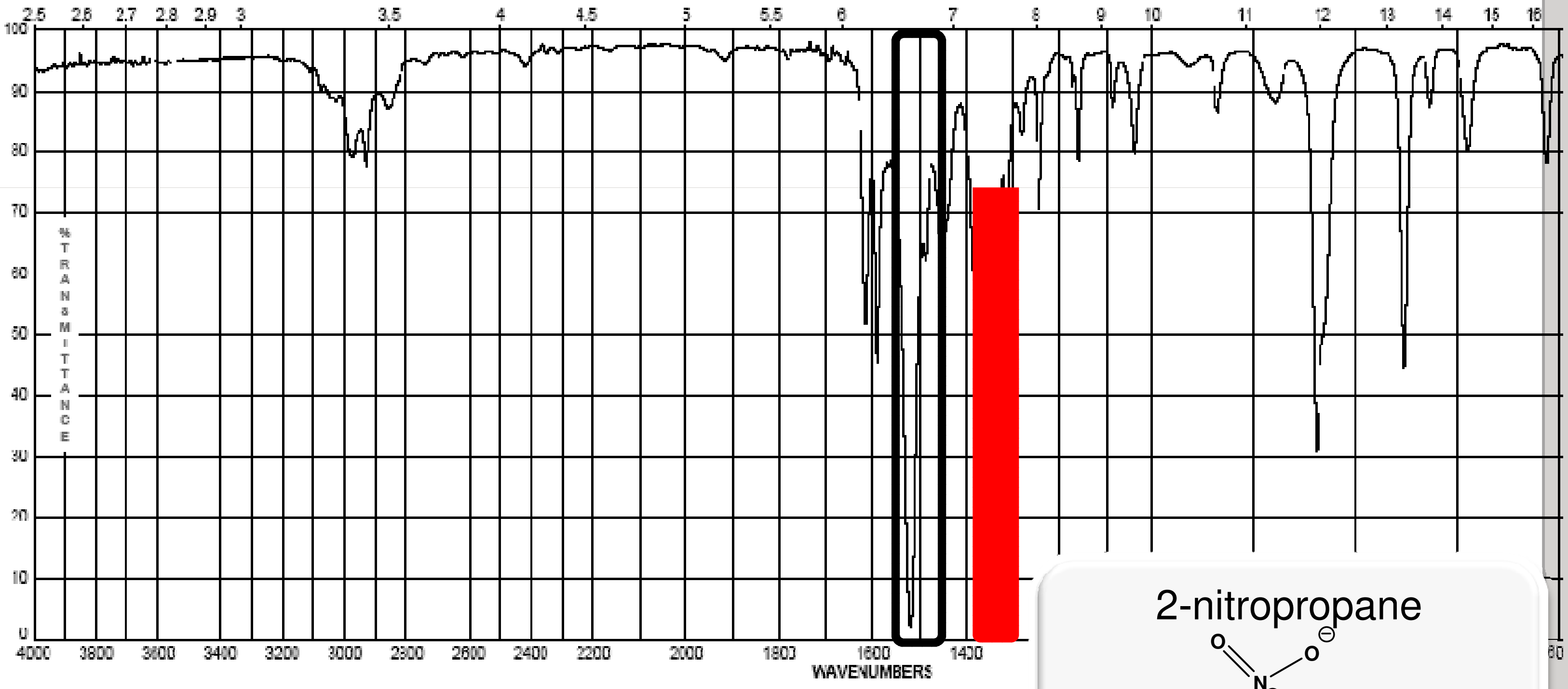
- Display features of amines and carbonyl compounds
- C=O stretch occurs from 1640-1680 cm^{-1}
- If the amide is primary (-NH$_2$) the N-H stretch occurs from 3200-3500 cm^{-1} as a doublet
- If the amide is secondary (-NHR) the N-H stretch occurs at 3200-3500 cm^{-1} as a sharp singlet



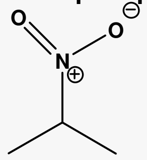
Infrared Spectroscopy

Specific groups

17. **Nitro group (-NO_2)**
    - Proper Lewis structure gives a bond order of 1.5 from nitrogen to each oxygen
    - Two bands are seen (symmetric and asymmetric) at 1300-1380 cm^{-1} (m-s) and 1500-1570 cm^{-1} (m-s)
    - This group is a strong resonance withdrawing group and is itself vulnerable to resonance effects



2-nitropropane

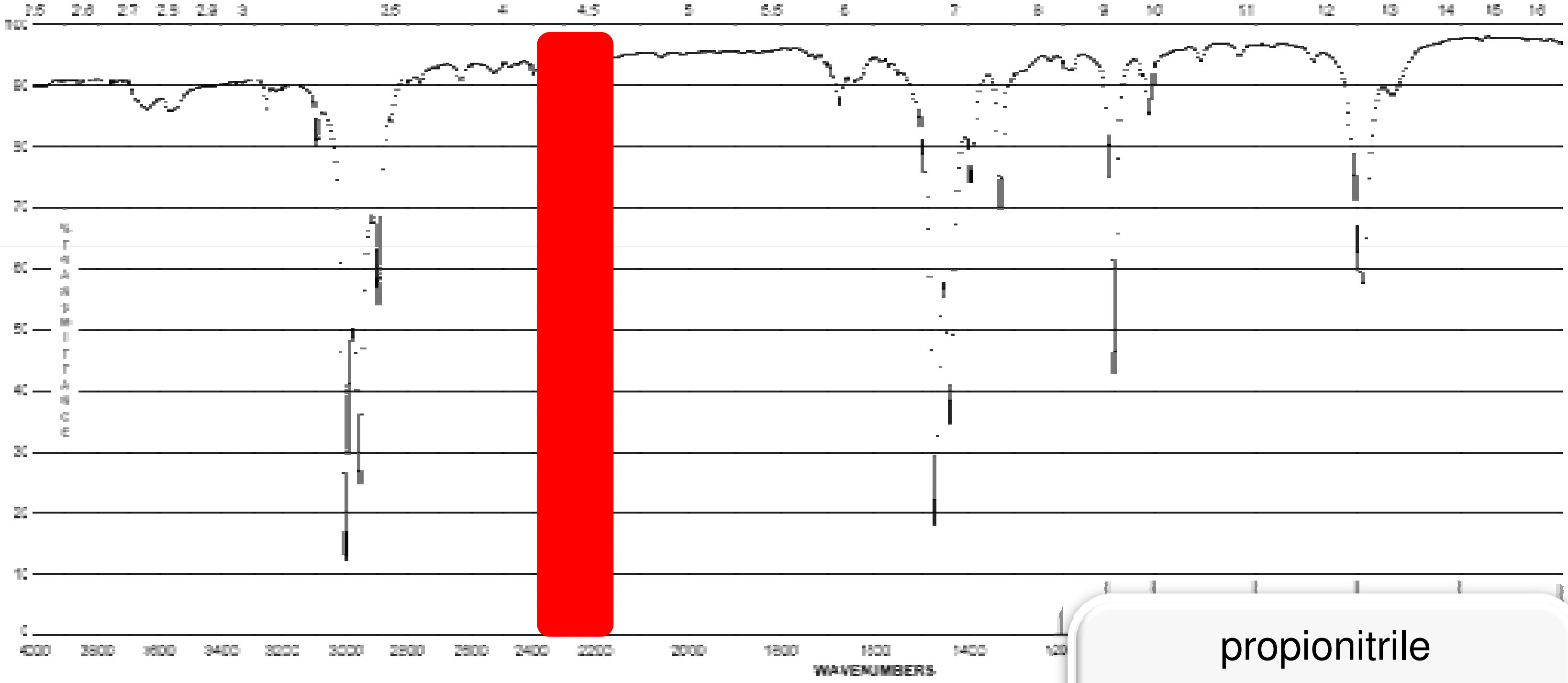


Infrared Spectroscopy

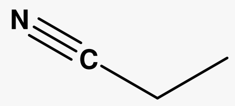
Specific groups – Hydrocarbons

18. Nitriles (the cyano- or –C≡N group)

- Principle group is the carbon nitrogen triple bond at 2100-2280 cm^{-1} (s)
- This peak is usually much more intense than that of the alkyne due to the electronegativity difference between carbon and nitrogen



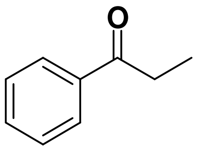
propionitrile



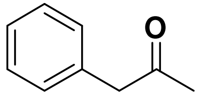
Infrared Spectroscopy

Effects on IR bands

1. Conjugation – by resonance, conjugation lowers the energy of a double or triple bond. The effect of this is readily observed in the IR spectrum:

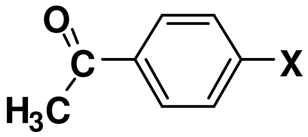


1684 cm^{-1}
C=O

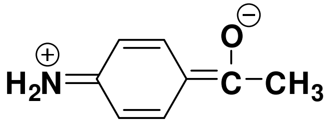


1715 cm^{-1}
C=O

- Conjugation will lower the observed IR band for a carbonyl from 20-40 cm^{-1} provided conjugation gives a strong resonance contributor

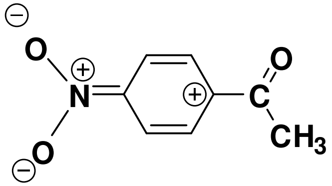


X =	NH_2	CH_3	Cl	NO_2	
	1677	1687	1692	1700	cm^{-1}



Strong resonance contributor

vs.



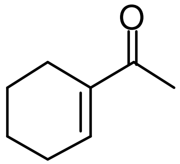
Poor resonance contributor
(cannot resonate with C=O)

- Inductive effects are usually small, unless coupled with a resonance contributor (note –CH_3 and –Cl above)

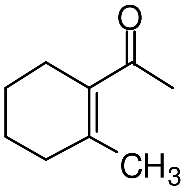
Infrared Spectroscopy

Effects on IR bands

1. Steric effects – usually not important in IR spectroscopy, unless they reduce the strength of a bond (usually π) by interfering with proper orbital overlap:



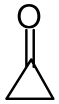
C=O: 1686 cm^{-1}



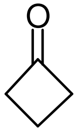
C=O: 1693 cm^{-1}

- Here the methyl group in the structure at the right causes the carbonyl group to be slightly out of plane, interfering with resonance

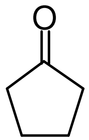
2. Strain effects – changes in bond angle forced by the constraints of a ring will cause a slight change in hybridization, and therefore, bond strength



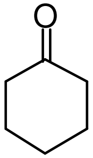
1815 cm^{-1}



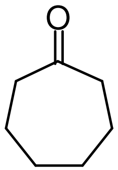
1775 cm^{-1}



1750 cm^{-1}



1715 cm^{-1}



1705 cm^{-1}

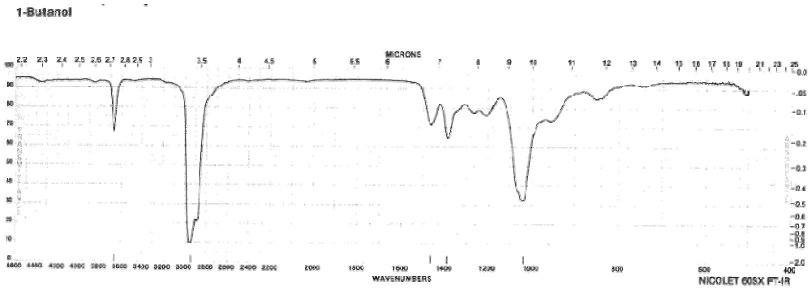
- As bond angle decreases, carbon becomes more electronegative, as well as less sp^2 hybridized (bond angle < 120°)

Infrared Spectroscopy

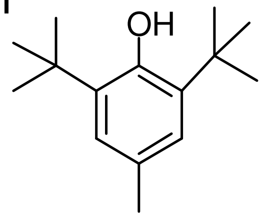
Effects on IR bands

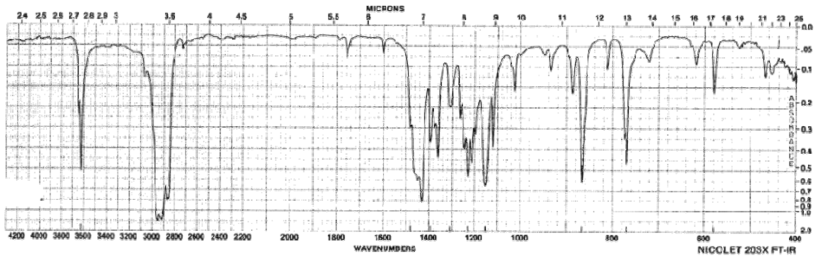
1. Hydrogen bonding
   - Hydrogen bonding causes a broadening in the band due to the creation of a continuum of bond energies associated with it
   - In the solution phase these effects are readily apparent; in the gas phase where these effects disappear or in lieu of steric effects, the band appears as sharp as all other IR bands:

Gas phase spectrum of 1-butanol

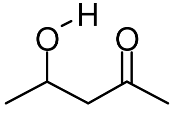


Steric hindrance to H-bonding in a di-*tert*-butylphenol





   - H-bonding can interact with other functional groups to lower frequencies



C=O; 1701 cm^{-1}