Topic 2 - Index of slides on IR
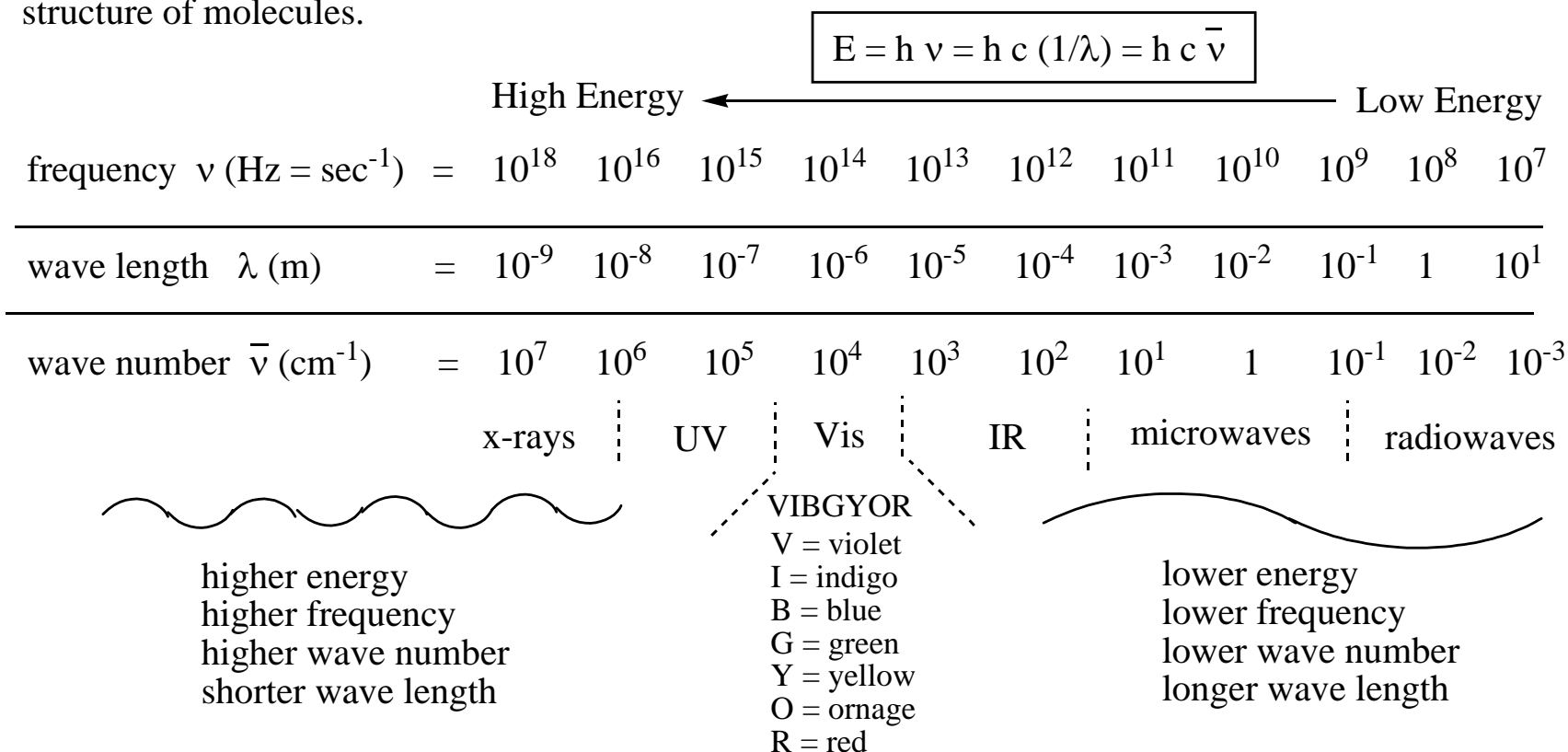
(link to copies of slides: http://www.cpp.edu/~psbeauchamp/pdf_videos/lecture_2_IR.pdf)

1

Common Features of Electromagnetic Radiation

All of the spectroscopic techniques in this workbook, except mass spectrometry, involve the interaction of electromagnetic radiation with matter. The responses of matter to electromagnetic radiation allow us to probe beyond our senses into the world of molecules and atoms. The following figure illustrates the usual spectroscopic divisions of the electromagnetic spectrum. Even though every designated region is a term in common everyday usage, you may be unfamiliar with these terms as methods to study the structure of molecules.

$$E = h\,\nu = h\,c\,(1/\lambda) = h\,c\,\bar{\nu}$$

High Energy $\longleftarrow\qquad\longrightarrow$ Low Energy

frequency ν (Hz = sec^{-1}) =	10^{18}	10^{16}	10^{15}	10^{14}	10^{13}	10^{12}	10^{11}	10^{10}	10^{9}	10^{8}	10^{7}
wave length λ (m) =	10^{-9}	10^{-8}	10^{-7}	10^{-6}	10^{-5}	10^{-4}	10^{-3}	10^{-2}	10^{-1}	1	10^{1}
wave number $\bar{\nu}$ (cm^{-1}) =	10^{7}	10^{6}	10^{5}	10^{4}	10^{3}	10^{2}	10^{1}	1	10^{-1}	10^{-2}	10^{-3}

x-rays ┊ UV ┊ Vis ┊ IR ┊ microwaves ┊ radiowaves

VIBGYOR
V = violet
I = indigo
B = blue
G = green
Y = yellow
O = ornage
R = red

higher energy
higher frequency
higher wave number
shorter wave length

lower energy
lower frequency
lower wave number
longer wave length

ν = frequency = # / sec = Hz (NMR)

λ − wave length − nm (UV/Vis)

$\bar{\nu}$ = (1/λ) = wave number
  = # / distance = cm^{-1} (IR)

Two constants used in the calculations of the energy in electromagnetic radiation.

The speed of light = c = 3.0 x 10^{8} m/s

Plank's constant = h = 6.62 x 10^{-34} j-s

Light is a form of energy that can produce changes in molecules, which can provide clues about how the atoms are connected together (their structure). Three common ways of viewing this energy are by frequency (ν, Hz, NMR), wave length (λ, nm, UV-Vis) and wave number ($\bar{\nu}$, cm^{-1}, IR).

Two constants used in the calculations of the energy in electromagnetic radiation.

The speed of light = $c = 3.0 \times 10^8$ m/s

Plank's constant = $h = 6.62 \times 10^{-34}$ j-s

$E = h \nu = h c (1/\lambda) = h c \bar{\nu}$ $c = (\nu)(\lambda)$

The units of hertz (Hz) are used in NMR.
units of frequency (#/second)

$$\nu = \frac{c}{\lambda}$$

$\nu_{red} = 3.8 \times 10^{14}$ Hz (lower energy)
$\nu_{violet} = 7.5 \times 10^{14}$ Hz (higher energy) } visible light

These units (nm) are used in UV-Vis.
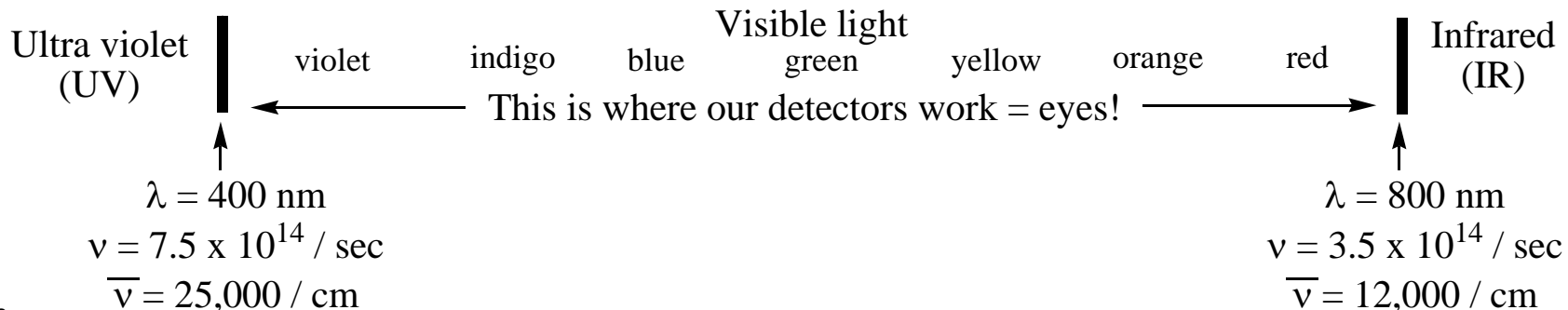units of wavelength (nm = 10^{-9} m)

$$\lambda = \frac{c}{\nu}$$

$\lambda_{red} = 800$ nm (lower energy)
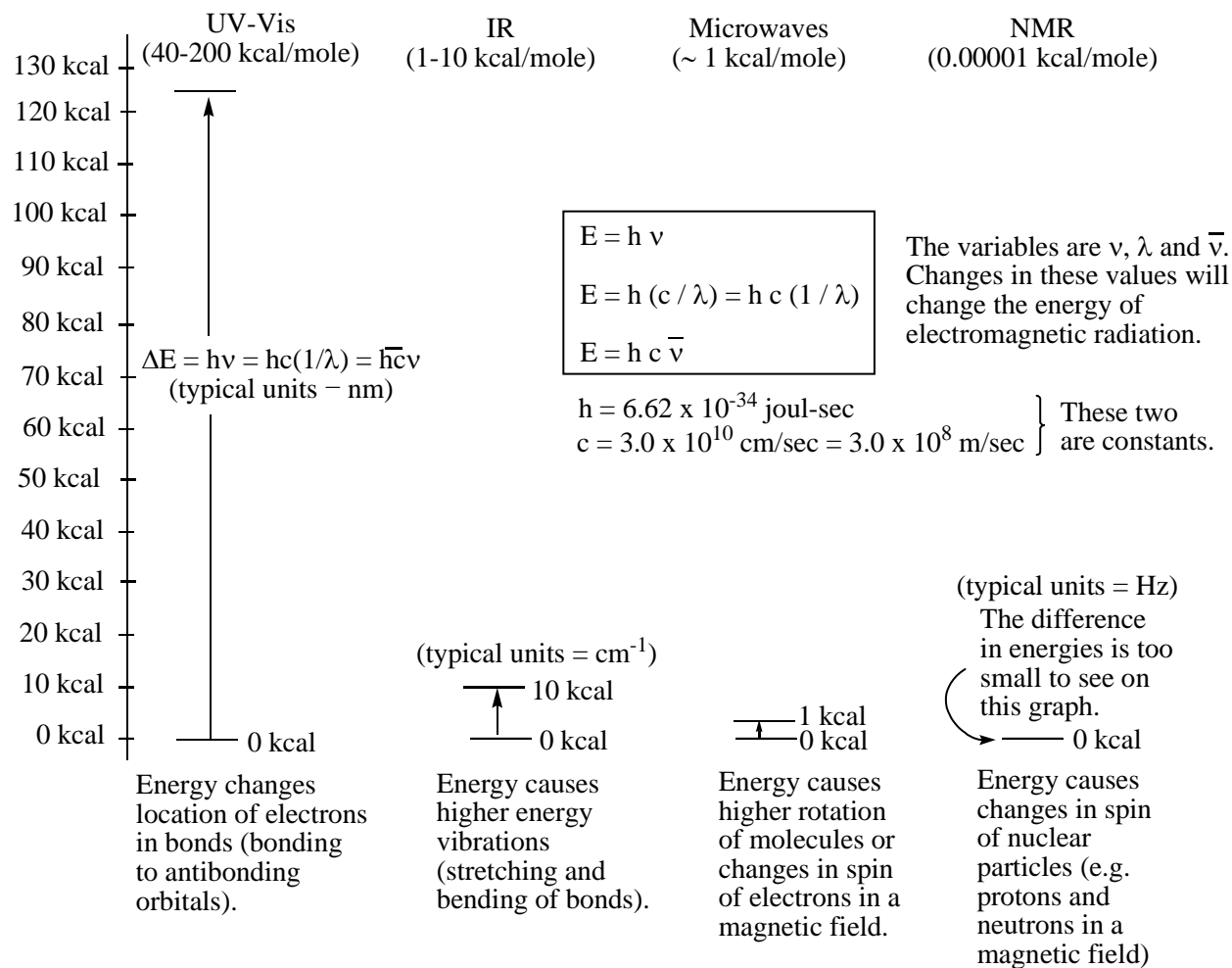$\lambda_{violet} = 400$ nm (higher energy) } visible light

These units (cm^{-1}) are used in IR.
units of wave number (#/cm)

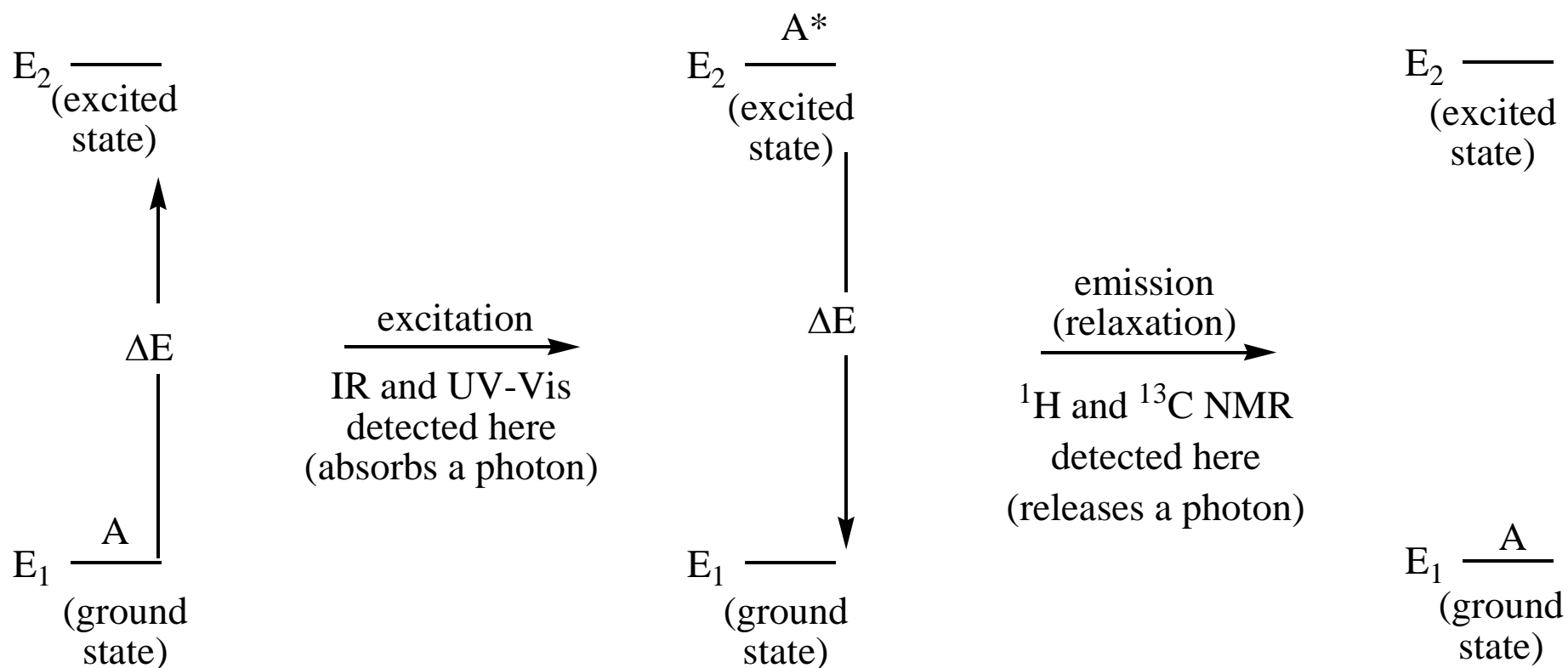$$\bar{\nu} = \frac{1}{\lambda} \qquad \bar{\nu} = \frac{\nu}{c}$$

$\bar{\nu}_{red} = 12,000$ cm^{-1} (lower energy)
$\bar{\nu}_{violet} = 25,000$ cm^{-1} (higher energy) } visible light

Ultra violet (UV)   violet   indigo   blue   Visible light   green   yellow   orange   red   Infrared (IR)

← This is where our detectors work = eyes! →

$\lambda = 400$ nm
$\nu = 7.5 \times 10^{14}$ / sec
$\bar{\nu} = 25,000$ / cm

$\lambda = 800$ nm
$\nu = 3.5 \times 10^{14}$ / sec
$\bar{\nu} = 12,000$ / cm

UV-Vis
(40-200 kcal/mole)

IR
(1-10 kcal/mole)

Microwaves
(~ 1 kcal/mole)

NMR
(0.00001 kcal/mole)

130 kcal
120 kcal
110 kcal
100 kcal
90 kcal
80 kcal
70 kcal
60 kcal
50 kcal
40 kcal
30 kcal
20 kcal
10 kcal
0 kcal

$\Delta E = h\nu = hc(1/\lambda) = \overline{hc\nu}$
(typical units − nm)

$$E = h\nu$$
$$E = h(c/\lambda) = hc(1/\lambda)$$
$$E = hc\overline{\nu}$$

The variables are ν, λ and $\overline{\nu}$.
Changes in these values will
change the energy of
electromagnetic radiation.

$h = 6.62 \times 10^{-34}$ joul-sec
$c = 3.0 \times 10^{10}$ cm/sec $= 3.0 \times 10^{8}$ m/sec } These two are constants.

(typical units = Hz)
The difference
in energies is too
small to see on
this graph.

(typical units = cm^{-1})
10 kcal
0 kcal

1 kcal
0 kcal

0 kcal

0 kcal

0 kcal

Energy changes
location of electrons
in bonds (bonding
to antibonding
orbitals).

Energy causes
higher energy
vibrations
(stretching and
bending of bonds).

Energy causes
higher rotation
of molecules or
changes in spin
of electrons in a
magnetic field.

Energy causes
changes in spin
of nuclear
particles (e.g.
protons and
neutrons in a
magnetic field)

Other Ways of Looking at Energy (ν = frequency, $\overline{\nu}$ = wave number, λ = wavelength)

Parameter	X-rays	UV	Vis	IR	Microwave	Radiowaves
E (kcal/mole)	24,000	200	50	10	3×10^{-3}	6×10^{-6}
E (kj/mole)	100,000	800	200	40	1.2×10^{-2}	2×10^{-5}
E (eV/photon)	1,200	8	2	0.4	1×10^{-4}	3×10^{-7}
ν (Hz)	3×10^{17}	2×10^{15}	5×10^{14}	1×10^{14}	3×10^{10}	3×10^{8}
$\overline{\nu}$ (cm^{-1})	1×10^{7}	50,000	17,000	3,000	1	0.01
λ (nm)	1	200	600	3,000	1×10^{7}	1×10^{9}

E_2 ─── (excited state)

ΔE

E_1 ─── A (ground state)

excitation
IR and UV-Vis detected here (absorbs a photon)

A*
E_2 ─── (excited state)

ΔE

E_1 ─── (ground state)

emission (relaxation)
^{1}H and ^{13}C NMR detected here (releases a photon)

E_2 ─── (excited state)

E_1 ─── A (ground state)

A = molecule of interest in ground state

A* = molecule of interest in excited state

$E_2 > E_1$ = energy states of the molecule

$\Delta E = (E_2 - E_1)$

5

Infrared Spectroscopy

Vibrational changes between atoms in molecules are excited when IR light is passed through a sample. When the electrical component of the oscillating frequency of electromagnetic radiation matches the electrical dipole oscillation of the vibrating atoms, efficient transfer of energy occurs from the photon to the vibrating bond. In effect, the bond receives a synchronous push from the light wave (think of you and a swing). The two frequencies are said to be coupled. Bonds without an electrical dipole moment cannot efficiently couple to the electrical vector of the oscillating photon. Symmetrically substituted bonds are said to be IR inactive and are either very weak or do not show an absorption band at all. Common inactive patterns include symmetrically substituted alkene and alkyne bonds.

vibrating dipole of a bond
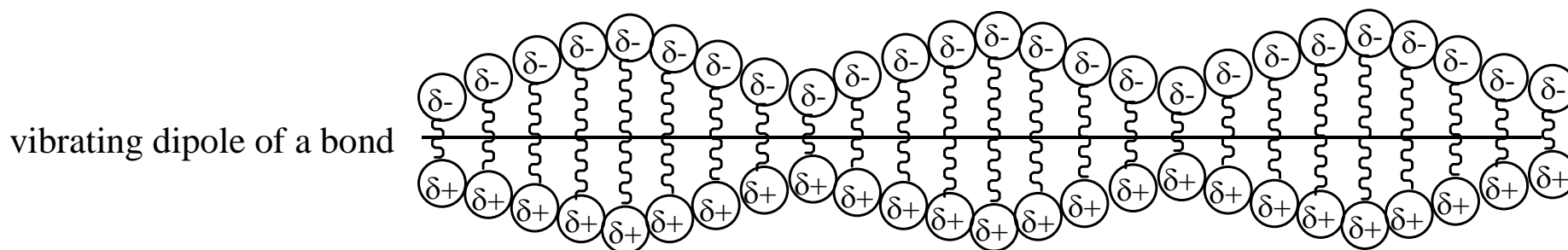
matching frequency from the electrical component of electromagnetic radiation causes absorption and excitation

$$E = h\nu \longrightarrow$$
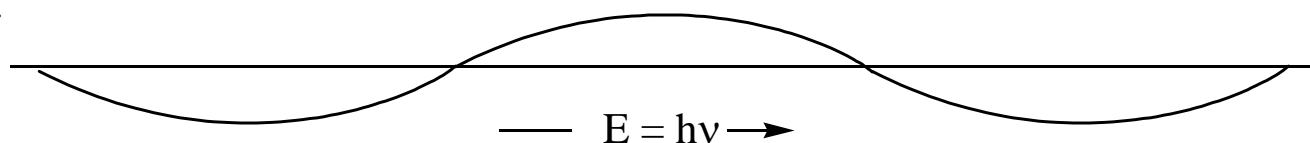
electromagnetic radiation (UV, Vis, IR, microwaves, radiowaves)

magnetic component

electrical component

source

detector
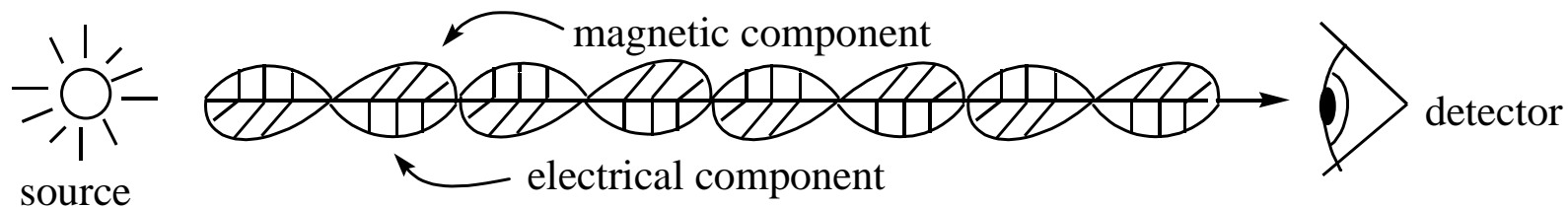
A Ball and Spring Model of a Bond

Atoms in molecules can be approximated as balls of various relative masses attached through bonds, roughly considered to be springs with relative force constants (Hook's Law).
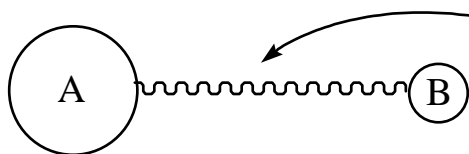
A bond is viewed as a spring and the atoms are viewed as balls. The vibrations between the two atoms can be estimated using Hook's law (depends on the masses and the force constant).

Hook's Law

$$\nu = (1/2\pi)\sqrt{k/\mu_{reduced}}$$

$$\mu = \frac{m_1 \times m_2}{m_1 + m_2} = \frac{reduced}{mass}$$

k = force constant

This means that different vibrations will occur depending on what atoms are connected together and how strong the bonds are connecting them. For example, organic atoms can be attached in single bonds in a variety of ways. Each bond has characteristic vibrational frequencies dependent on reduced masses and force constants present in the IR spectrum.

(sp, sp^2, sp^3)
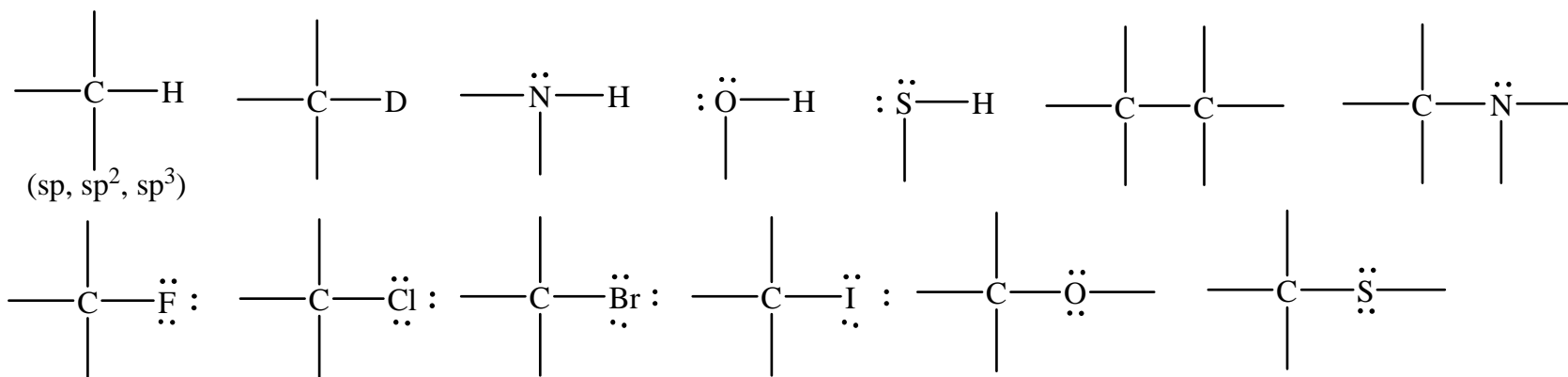
Additionally, even when the same type of atom is bonded to carbon, there can be variable strength bonds, i.e. single, double and triple bonds (changes the force constant).

triple	double	single
C≡C	C=C	C—C
C≡N	C=N	C—N
⊖C≡O⊕	C=O	C—O

bond strengths

triple > double > single

$$E = h\,\nu = h\,c\,(1/\lambda) = h\,c\,\bar{\nu}$$

Two Types of Vibrations are Common in IR Spectroscopy - Stretching and Bending of Bonds

Two atoms present a very simple picture of vibration and bending. In a stretching vibration the two atoms stretch away from one another or contract towards one another.

average bond length   stretched   contracted
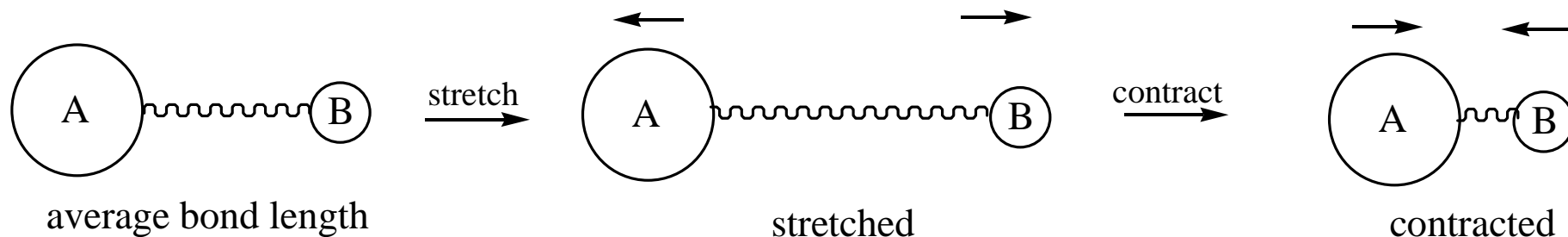
Additionally, a two atom bond can also bend. If we arbitrarily fix a carbon atom, then the hydrogen atom can move up and down or front and back (relative to the rest of the molecule).

$E_{vibrations}$ tend to be larger than $E_{bendings}$

8
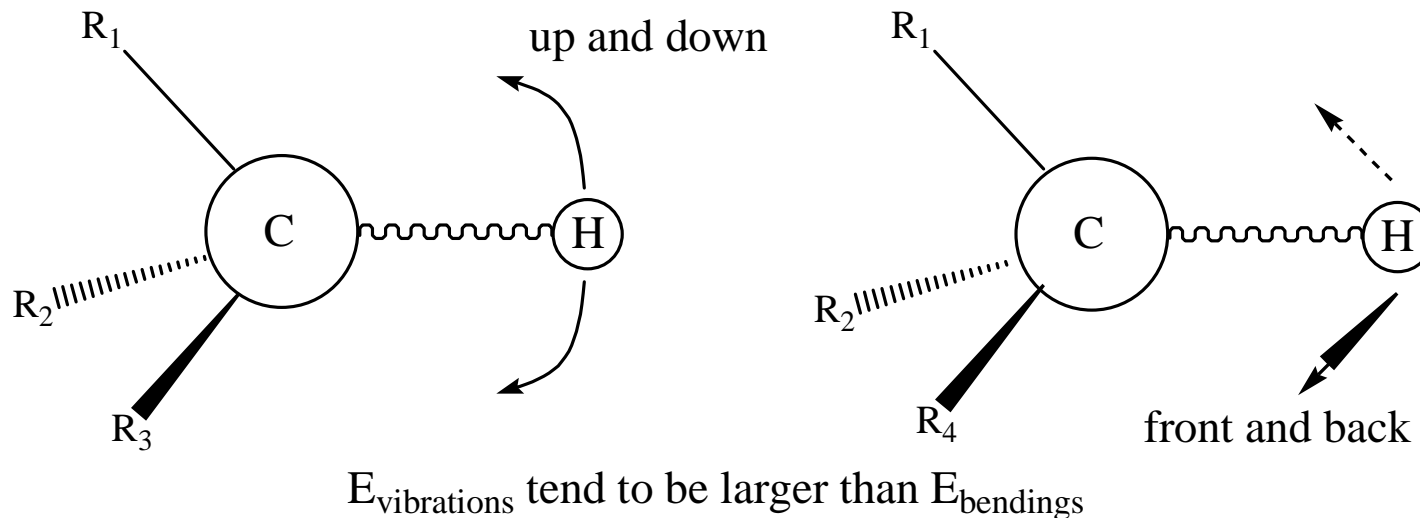
Nearby atoms and bonds tend to act as subgroups in concert with one another. By increasing our atom pattern from two vibrating atoms to three, we can gain an appreciation of the increased complexity. A simple methylene, CH_2 subgroup illustrates some of the possibilities. Simultaneous stretching of the two hydrogen atoms away from and towards the carbon is a symmetric stretching vibration, which has a characteristic range of wave numbers. When one hydrogen stretches away and the other hydrogen moves toward the carbon an asymmetric stretch occurs. For each particular three atom system the asymmetric stretch is usually the higher energy vibration.
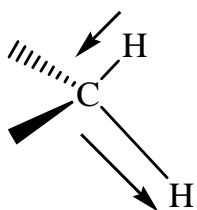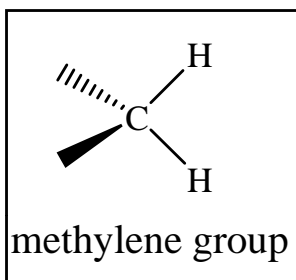
methylene group CH_2 asymmetrical stretch ≈ 2930 cm^{-1} CH_2 symmetrical stretch ≈ 2850 cm^{-1}
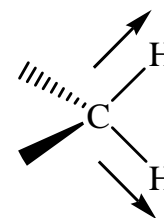
Usually the wave number of asymmetric stretch > symmetric stretch

Several bending vibrations are also IR active in a methylene subunit. These bending modes are shown below along with their approximate resonant wavenumber. If you use your hands as the hydrogen atoms, your torso as the carbon atom and your arms as the bonds, you can mimic these same vibrations and bending modes, and you'll remember them a lot easier! The IR cheers!
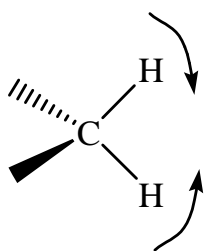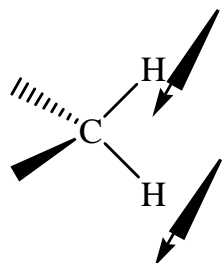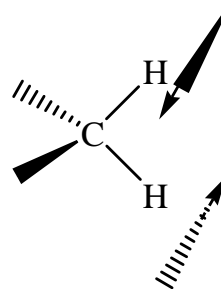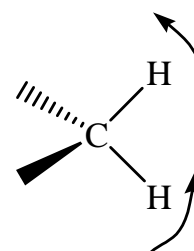
CH_2 scissoring	CH_2 wagging	CH_2 twisting	CH_2 rocking
~1450 cm^{-1}	~1250 cm^{-1}	~1250 cm^{-1}	~720 cm^{-1}
in the plane	out of the plane	out of the plane	in the plane

9

Other functional groups having asymmetric and symmetric vibrational bands
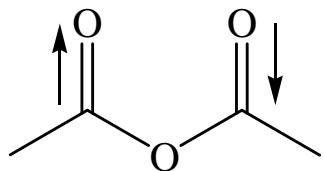
asymmetrical stretching	symmetrical stretching
anhydride asymmetrical stretching ≈ 1800 cm^{-1}	anhydride symmetrical stretching ≈ 1760 cm^{-1}
nitro asymmetrical stretching ≈ 1550 cm^{-1}	nitro symmetrical stretching ≈ 1350 cm^{-1}
primary amine and amide (NH$_2$) asymmetrical stretching ≈ 3400 cm^{-1}	primary amine and amide (NH$_2$) symmetrical stretching ≈ 3300 cm^{-1}
methyl asymmetrical stretching ≈ 2960 cm^{-1}	methyl symmetrical stretching ≈ 2870 cm^{-1}
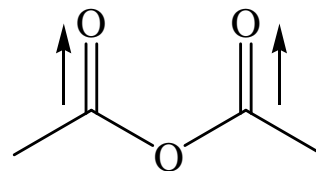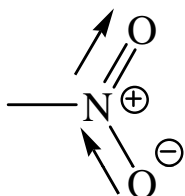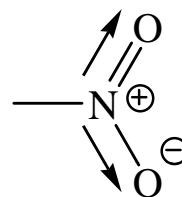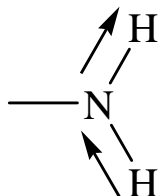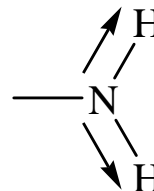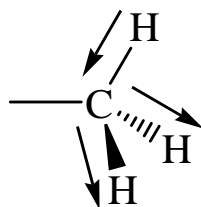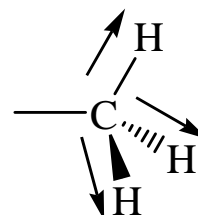
Real organic molecules are much more complicated than simple 2 or 3 atom groups. Many atoms are present and numerous bonds can approximate a whole collection of vibrating springs. Commonly encountered arrangements of atoms in organic and biochemistry are called functional groups, and produce reasonably predictable IR wavenumbers. These IR bands can be used to identify the presence of a functional group when detected in the IR spectrum. Functional group patterns are sometimes referred to as 'fundamental bands'.

alkane C-H and C-C bonds

alcohol O-H

alkoxy C-O bond

carbonyl
C=O bond

acyl C-O bond

...and other groups

carboxylic acid O-H
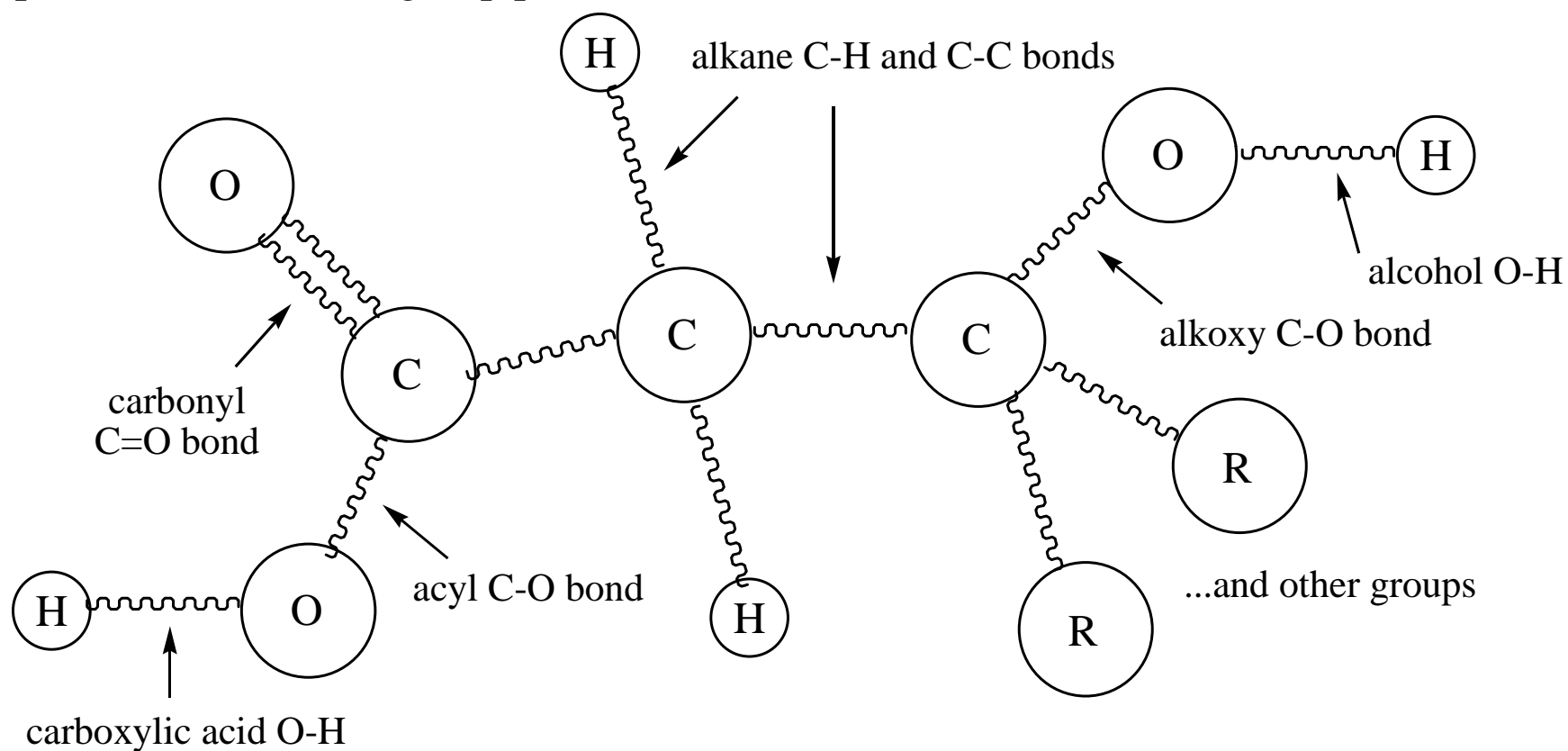
Overtones, combination bands and difference bands can make an IR spectrum much more complicated than a simple consideration of the fundamental bands would lead us to believe. They can hide or confuse an otherwise straight forward analysis. On the other hand, the complicated patterns generated tend to be unique for each arrangement of atoms. The patterns of absorption bands generated can be used in much the same way as our fingerprints are for exact identification. The lower wavenumber region of an IR spectrum (1500-400 cm^{-1}) is often called the finger print region for this reason. Many of the fundamental bands of functional groups appear above 1500 cm^{-1} and are useful in identifying the functional groups present. Accordingly, this region is often called the functional group region (1500-4000 cm^{-1}).

Additional Bands include overtones and
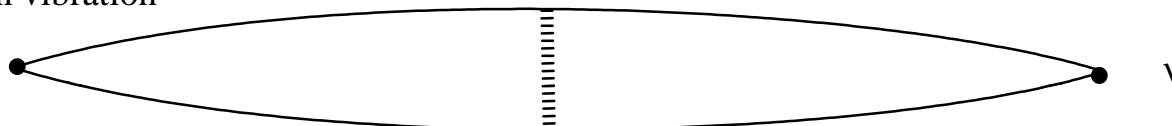
combination bands
$(\nu_1 + \nu_2)$

main vibration

ν

and

first overtone

2ν
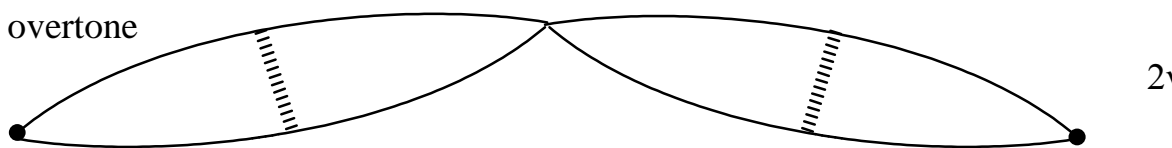
difference bands
$(\nu_1 - \nu_2)$

The
modern
way

4000 cm^{-1} $\bar{\nu}$ = wavenumber = cm^{-1} 1500 cm^{-1} 400 cm^{-1} ←

$E = h\,c\,\bar{\nu}$
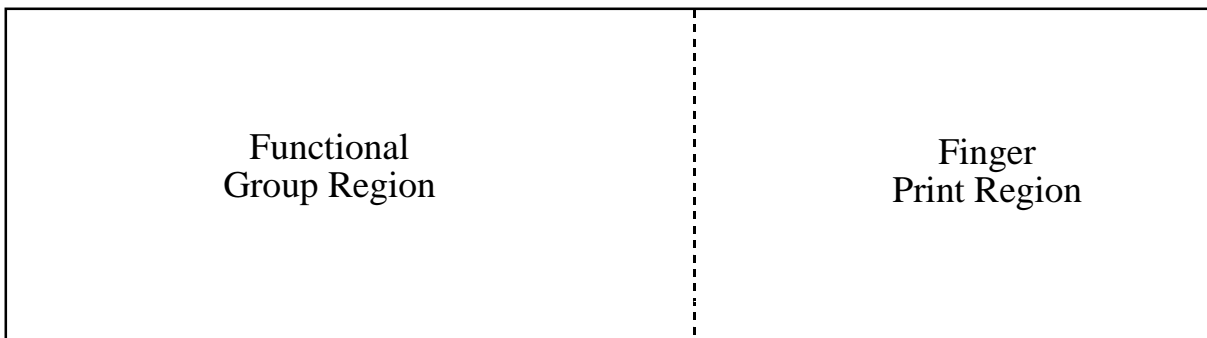
Functional
Group Region

Finger
Print Region

$E = h\,c\,(1/\lambda)$
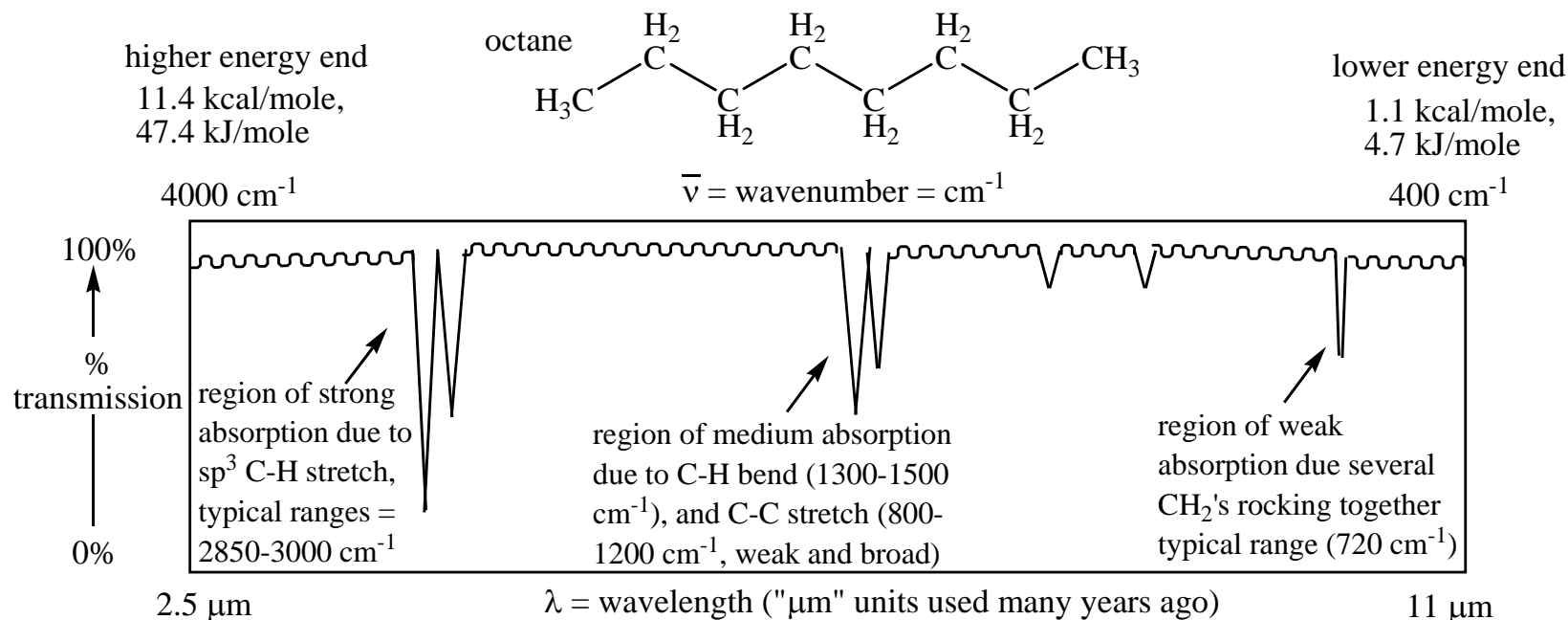The

2.5 μm λ = wavelength = μm
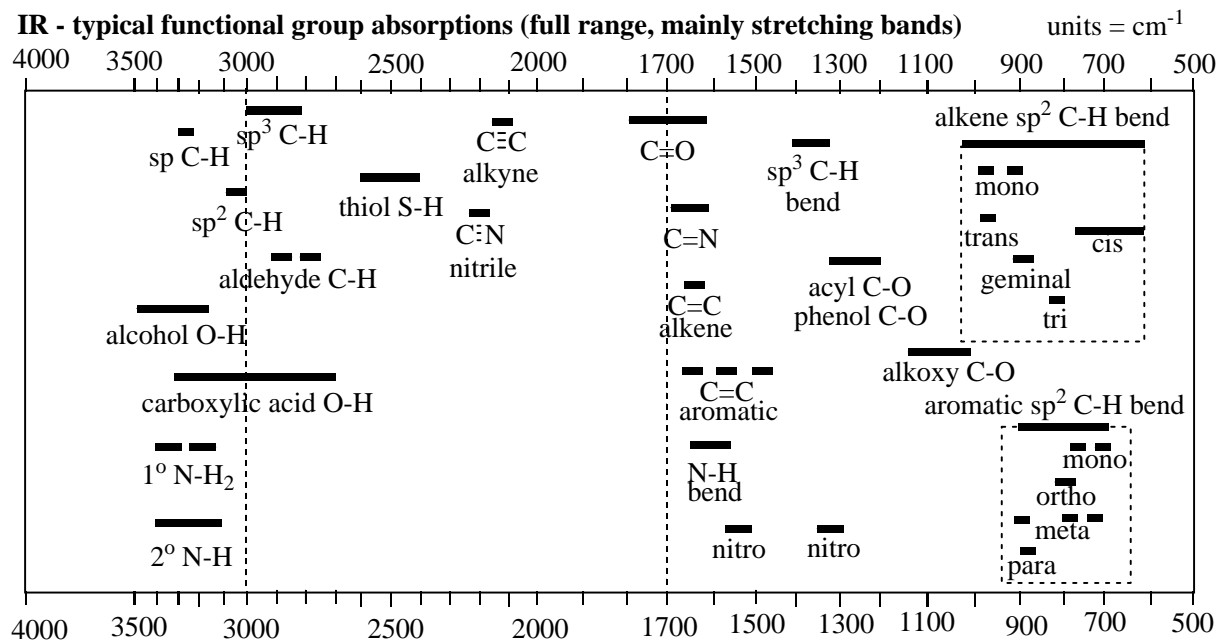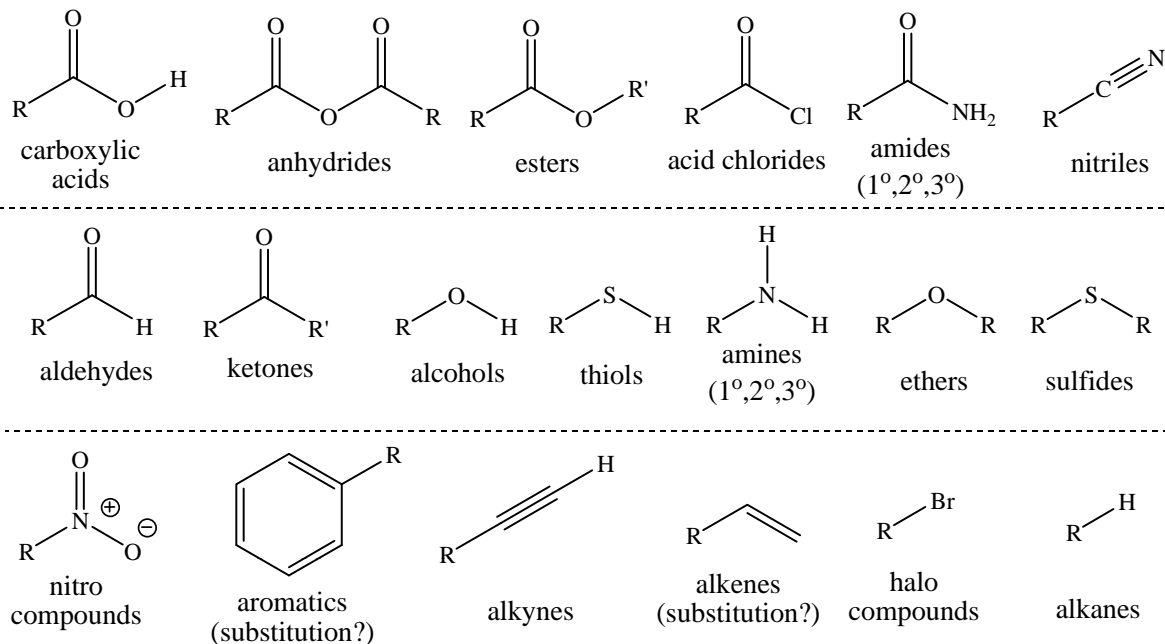(units used many years ago)

11 μm ← old
way

Data Presentation

A typical IR spectrum is shown below. Current practice stresses the divisions of energy in wavenumbers ($\bar{\nu} = cm^{-1}$). Older usage utilized wavelength in micrometers (abbreviated as microns $= \mu m = 10^{-6}$ m = λ). Older spectrometers used chart paper with both scales plotted along the horizontal axis, one scale on the top and the other scale on the bottom. Recall that these two parameters are inversely related. Energy is directly proportional to wavenumber, $\bar{\nu}$ (cm^{-1}), and inversely proportional to wavelength, λ (μm).

A typical spectrum shows the high energy end on the left side (4000 cm^{-1}, 2.5 μm, 11.4 kcal/mole, 47.4 kJ/mole) and the low energy end on the right side (400 cm^{-1}, 11 μm, 1.1 kcal/mole, 4.7 kJ/mole). The vertical axis generally shows percent transmission, (but can show absorbance). At wavenumbers where the sample absorbs IR radiation, the plot will deflect downward producing inverted peaks. Strong absorptions produce large deflections and weaker absorptions only minor deflections. The wavenumbers where the deflections occur often provide useful clues concerning the functional groups in the substance being scanned. The following is a simulated IR spectrum of a typical alkane.
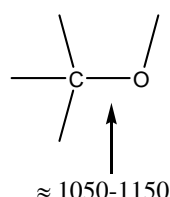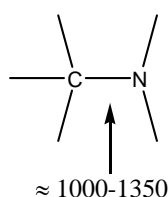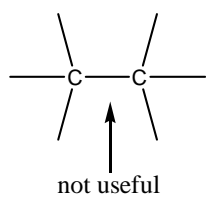

higher energy end
11.4 kcal/mole,
47.4 kJ/mole

octane

lower energy end
1.1 kcal/mole,
4.7 kJ/mole

4000 cm^{-1}

$\bar{\nu}$ = wavenumber = cm^{-1}

400 cm^{-1}

100%

%
transmission

0%

region of strong absorption due to sp^3 C-H stretch, typical ranges = 2850-3000 cm^{-1}

region of medium absorption due to C-H bend (1300-1500 cm^{-1}), and C-C stretch (800-1200 cm^{-1}, weak and broad)

region of weak absorption due several CH$_2$'s rocking together typical range (720 cm^{-1})

2.5 μm

λ = wavelength ("μm" units used many years ago)

11 μm

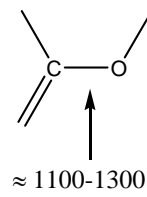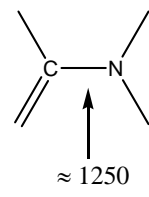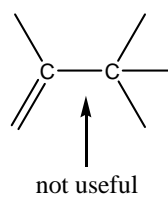**IR Information - These are the typical functional groups we might see.**

carboxylic acids   anhydrides   esters   acid chlorides   amides (1º,2º,3º)   nitriles

aldehydes   ketones   alcohols   thiols   amines (1º,2º,3º)   ethers   sulfides

nitro compounds   aromatics (substitution?)   alkynes   alkenes (substitution?)   halo compounds   alkanes

IR - typical functional group absorptions (full range, mainly stretching bands)   units = cm^{-1}

4000   3500   3000   2500   2000   1700   1500   1300   1100   900   700   500

sp C-H, sp^3 C-H, sp^2 C-H, thiol S-H, aldehyde C-H, alcohol O-H, carboxylic acid O-H, 1º N-H$_2$, 2º N-H

C≡C alkyne, C≡N nitrile, C≡O, C=N, sp^3 C-H bend, acyl C-O phenol C-O, alkoxy C-O, C=C alkene, C=C aromatic, N-H bend, nitro, nitro

alkene sp^2 C-H bend: mono, trans, cis, geminal, tri

aromatic sp^2 C-H bend: mono, ortho, meta, para

4000   3500   3000   2500   2000   1700   1500   1300   1100   900   700   500

14

Slide 14

Infrared Tables (short summary of common absorption frequencies)

Bonds to Carbon (stretching bands)

<u>sp^3 C-X single bonds</u>

not useful   ≈ 1000-1350   ≈ 1050-1150

<u>sp^2 C-X single bonds</u>

not useful   ≈ 1250   ≈ 1100-1300

<u>sp^2 C-X double bonds</u>

≈ 1600-1680   ≈ 1640-1690   ≈ 1640-1810 expanded table below

<u>sp C-X triple bonds</u>

≈ 2100-2250   ≈ 2230-2260
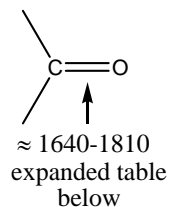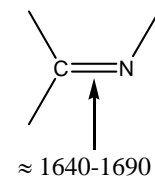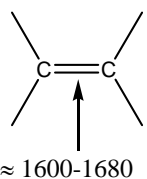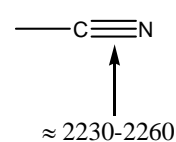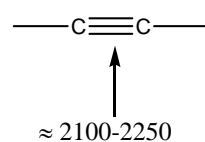
Stronger dipoles produce more intense IR bands and weaker dipoles produce less intense IR bands. When a dipole completely disappears, the IR band may also disappear.

Bonds to Hydrogen (stretching and bending bands)

sp C-H
stretch ≈ 3300
bend ≈ 600-650

sp^2 C-H
stretch ≈ 3000-3100
bend ≈ 600-1000
expanded table on next page
(alkenes and aromatics)

sp^3 C-H
stretch ≈ 2850-3000
bend ≈ 1370-1460

aldehyde C-H
(two bands, weak)
2700-2760
2800-2860

stretch ≈ 3300-3500
primary NH$_2$ secondary N-H
(two bands)   (one band)
amides = strong, amines = weak
bend ≈ 1640-1500 & 800 (varies)

alcohol O-H
stretch ≈ 3200-3400
bend ≈ not as useful

acid O-H
stretch ≈ 2500-3300
bend ≈ 930 (varies)

thiol S-H
stretch ≈ 2560 (weak)
bend ≈ not used

15

Slide 15

Carbonyl Highlights (stretching bands, approximate values in cm^{-1}, usually very strong)

Aldehydes

saturated = 1725
conjugated = 1690
aromatic = 1700

Ketones

saturated = 1715
conjugated = 1680
aromatic = 1690
6 atom ring = 1715
5 atom ring = 1745
4 atom ring = 1780
3 atom ring = 1850

Esters

saturated = 1735
conjugated = 1720
aromatic = 1720
6 atom ring = 1735
5 atom ring = 1775
4 atom ring = 1840

Acids

saturated = 1715
conjugated = 1690
aromatic = 1690

Amides

saturated = 1650
conjugated = 1660
aromatic = 1660
6 atom ring = 1670
5 atom ring = 1700
4 atom ring = 1745
3 atom ring = 1850

Anhydrides

saturated = 1760, 1820
conjugated = 1725, 1785
aromatic = 1725, 1785
6 atom ring = 1750, 1800
5 atom ring = 1785, 1865

2 bands
(symmetric and asymmetric)

Acid Chlorides

saturated = 1800
conjugated = 1770
aromatic = 1770

Alkene Substitution Patterns (C-H bending frequencies)

monosubstituted
985-1000
900-920

cis disubstituted
675-730
(broad)

geminal disubstituted
880-900

trans disubstituted
960-990

trisubstituted
790-840

tetrasubstituted
none

Aromatic Substitution Patterns (C-H bending frequencies)

monosubstituted
690-710
730-770

ortho disubstituted
735-770

meta disubstituted
680-725
750-810
880-900 (sometimes)

para disubstituted
790-840

(Characteristic weak overtone patterns often show between 1650-2000, not used in this book)
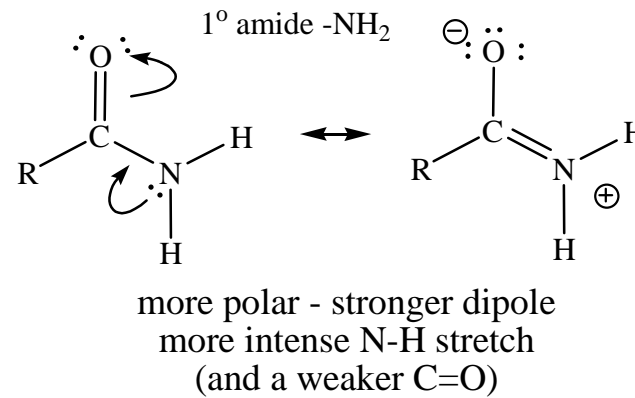
16

Slide 16

Special differences to note.

3340

alcohol OH

variable "H" bond

3300-2500

2970   2860

carboxylic acid OH

variable "H" bond

1300   1200   1100   1000

1240
acyl C-O

1070
alkoxy C-O

alkoxy C-O (weaker)

acyl C-O (stronger)

3400   3300   3200

3360   3290

1° amine
-NH₂

3400   3300   3200

3360   3200

1° amide -NH₂

more polar - stronger dipole
more intense N-H stretch
(and a weaker C=O)

17

Slide 17

stronger C=O
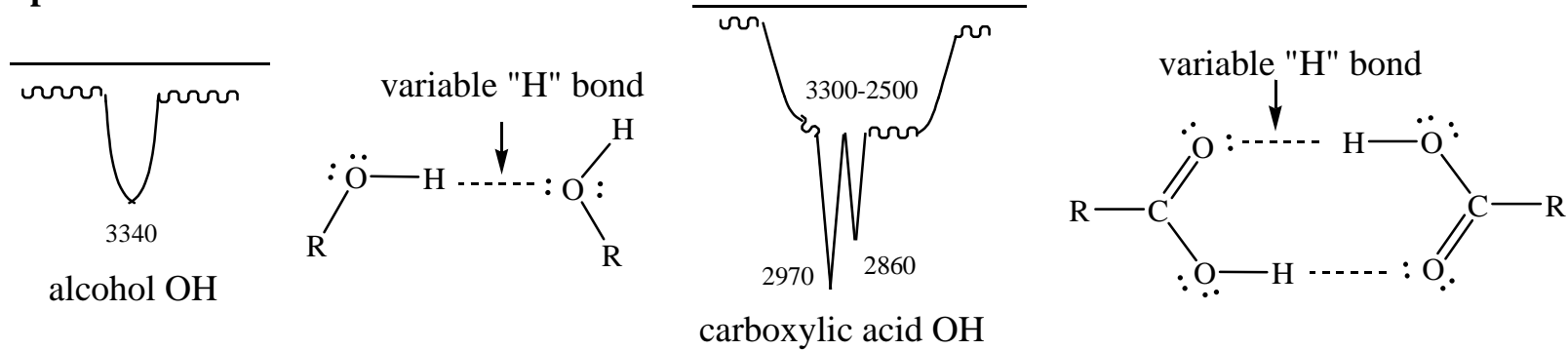
simple ester

simple ketone
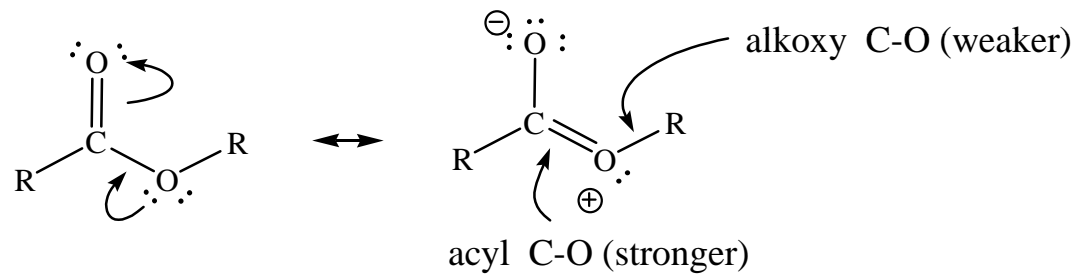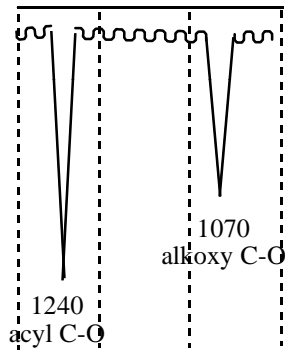
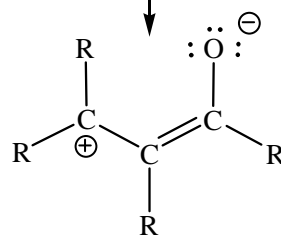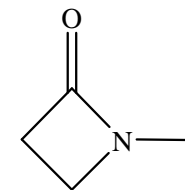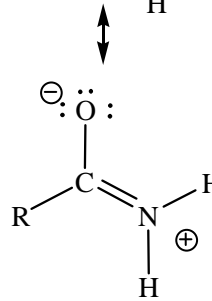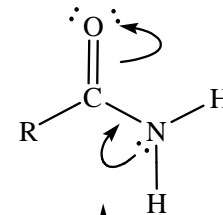conjugated ketone, weaker C=O
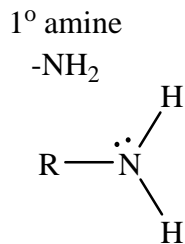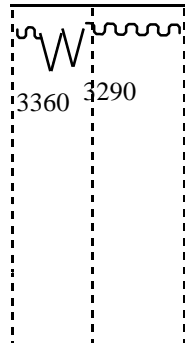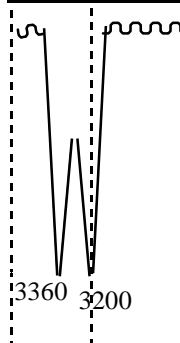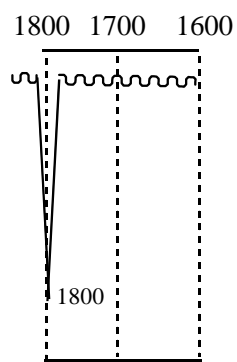
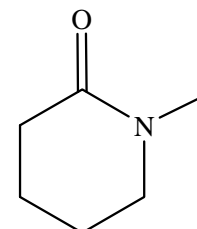amide C−O, even weaker
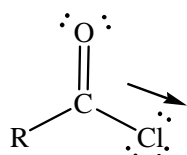
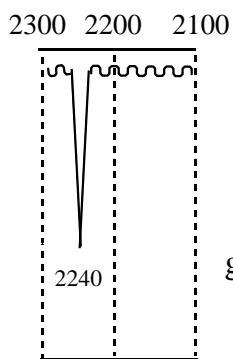poor resonance, strong inductive withdrawal
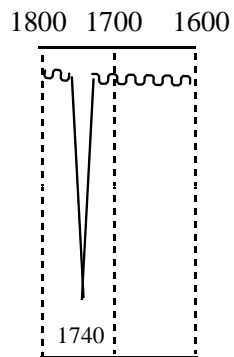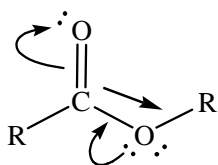
has resonance, and inductive withdrawal
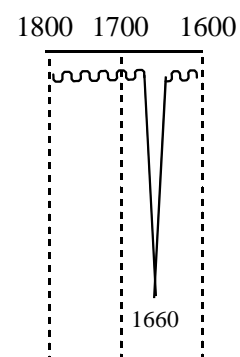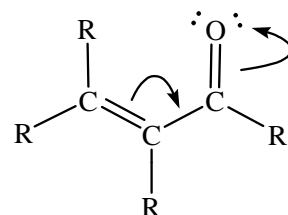
$\nu_{C=O} = 1780$
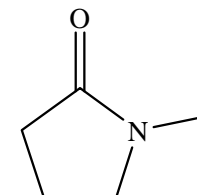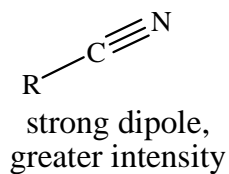
$\nu_{C=O} = 1690$

$\nu_{C=O} = 1660$

simple nitrile

strong dipole, greater intensity

terminal alkyne

medium dipole, medium intensity
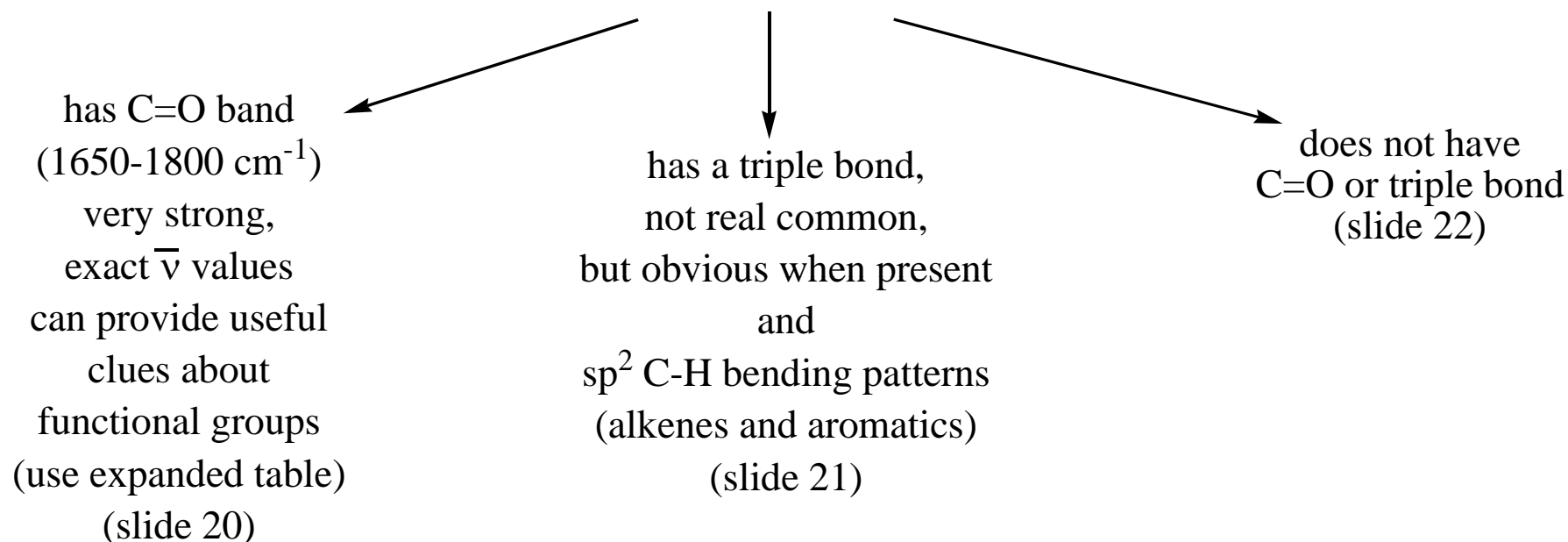
internal alkyne

weak dipole, weak intensity

Slide 19

18
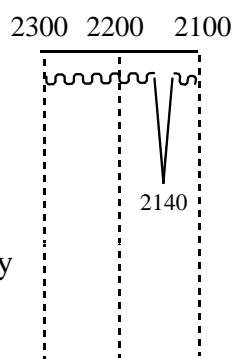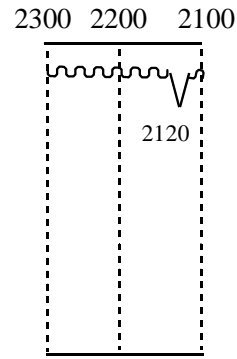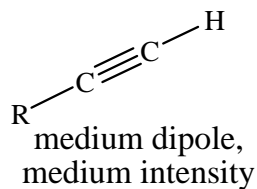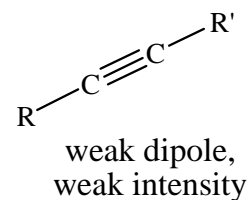
IR Flowchart to Determine Functional Groups in a Compound (all values in cm^{-1})

IR Spectrum (all values are approximate, ±)

has C=O band
(1650-1800 cm^{-1})
very strong,
exact $\bar{\nu}$ values
can provide useful
clues about
functional groups
(use expanded table)
(slide 20)

has a triple bond,
not real common,
but obvious when present
and
sp^2 C-H bending patterns
(alkenes and aromatics)
(slide 21)

does not have
C=O or triple bond
(slide 22)

All IR values are approximate and have a range of possibilities depending on the molecular environment in which the functional group resides. Resonance often modifies a peak's position because of electron delocalization (conjugated C=O have lower $\bar{\nu}$, and acyl C-O > alkoxy C-O, etc.). IR peaks are not 100% reliable. Peaks tend to be stronger (more intense) when there is a large dipole associated with a vibration in the functional group and weaker in less polar bonds (to the point of disappearing in some completely symmetrical bonds). Also, IR shows generic functional group information, not specfic connectivities of the atoms. We need NMR for that.

C=O bonds (1650-1800 cm^{-1}), have very strong IR absorptions

Factors to consider for each functional group having a C=O.

aldehydes

C-H stretch (two weak bands)

2860-2800
2760-2700

C=O stretch
~1740-1720, saturated
~1700-1660, conjugated

esters - rule of 3

stretch
1750-1730, saturated
1740-1680, conjugated
1820-1720, in rings

acyl C-O
1350-1150

alkoxy C-O
1200-1050

acid chlorides

stretch (very high)
1810-1770, when saturated
1780-1760, when conjugated

C-Cl   730-550 not real useful
when many peaks are present

ketones

stretch

~1720-1710, when saturated
~1700-1660, when conjugated
~1810-1720, when in rings

acids

stretch
1730-1700, saturated
1700-1680, conjugated

acyl C-O
1320-1150

acid O-H
3400-2500
very broad

amides

1680-1630, always conjugated with nitrogen lone pair, higher in small rings (4 atom = 1745)

1° ~3350 & ~3180, 2 bands for 1° amides, 3300, one band for 2° amides, stronger than in amines, sometimes an extra overtone ≈3200, no bands for 3° amides

2°

~1640-1550, N-H bend, strong in amides with polar resonance form

anhydrides

1830-1800
1770-1740,

acyl C-O   1300-900
strong

Triple bond IR absorptions come where nothing else does.

Nitriles are polar and strong.
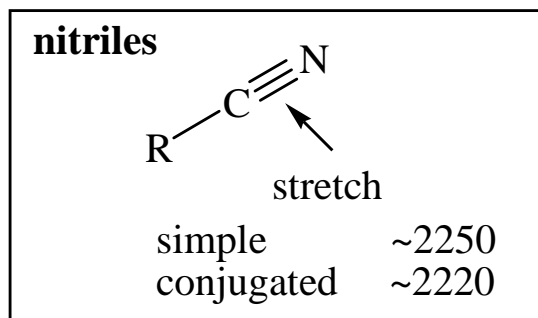
Alkynes are less polar and
weaker or even missing.

nitriles

$$R-C\equiv N$$
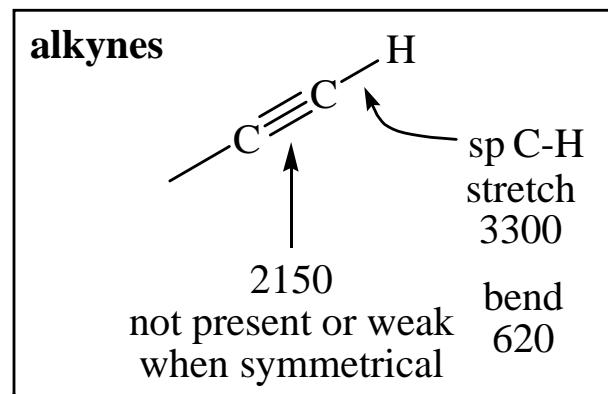
stretch

simple   ~2250
conjugated   ~2220

alkynes

$$C\equiv C-H$$

sp C-H
stretch
3300

2150
not present or weak
when symmetrical

bend
620

IR has characteristic alkene and aromatic sp^2 C-H bending vibration substitution patterns.
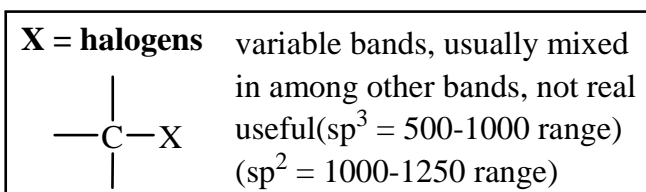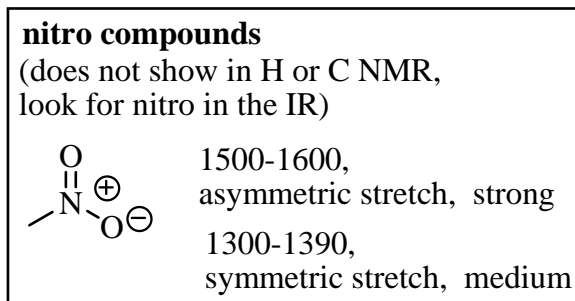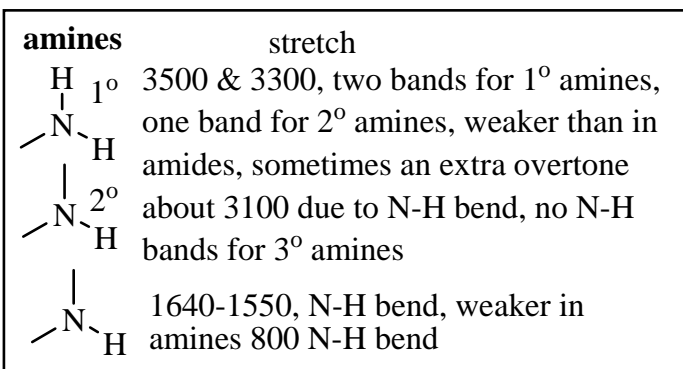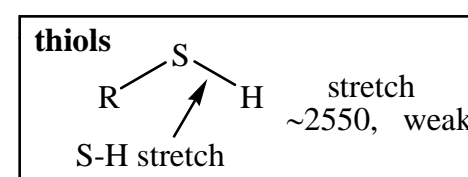
Alkene sp^2 C-H bending patterns (cm^{-1})

monosubstituted alkene (985-1000, 900-920)
trans disubstituted (960-990)
cis disubstituted (670-730)
gem disubstituted (880-900)
trisubstituted (790-840)
tetrasubstituted (none, no sp^2 C-H)

Aromatic sp^2 C-H bending patterns (cm^{-1})

monosubstituted (730-770,690-710)
ortho disubstituted (730-770)
meta disubstituted (880-900, sometimes
                750-810, 680-730)
para disubstituted (790-840)

There are also weak overtone bands between
1660 and 2000, but are not shown here. You
can consult pictures of typical patterns in
other reference books. If there is a strong
C=O band, they may be partially covered up.

21

IR functional groups that do not have C=O bonds or triple bonds

alkanes

sp^3 C-H
stretch
3000-2840

bend
CH$_2$ ~1450
CH$_3$ ~1370

not useful

alkenes

sp^2 C-H
stretch
3100-3000

bend
1000-650
(see table)

1660-1600
not present or weak
when symmetrical

aromatics

sp^2 C-H
stretch
3100-3000

bend
900-680
(see table)

1600-1450
variable number
(2-4 bands)

alcohols

R — O — H

alkoxy C-O stretch
1200-1050
phenyl > 3º > 2º > 1º

O-H stretch
≈ 3600-3650,
sharp when no H bonding

≈ 3400-3300,
broad with H bonding
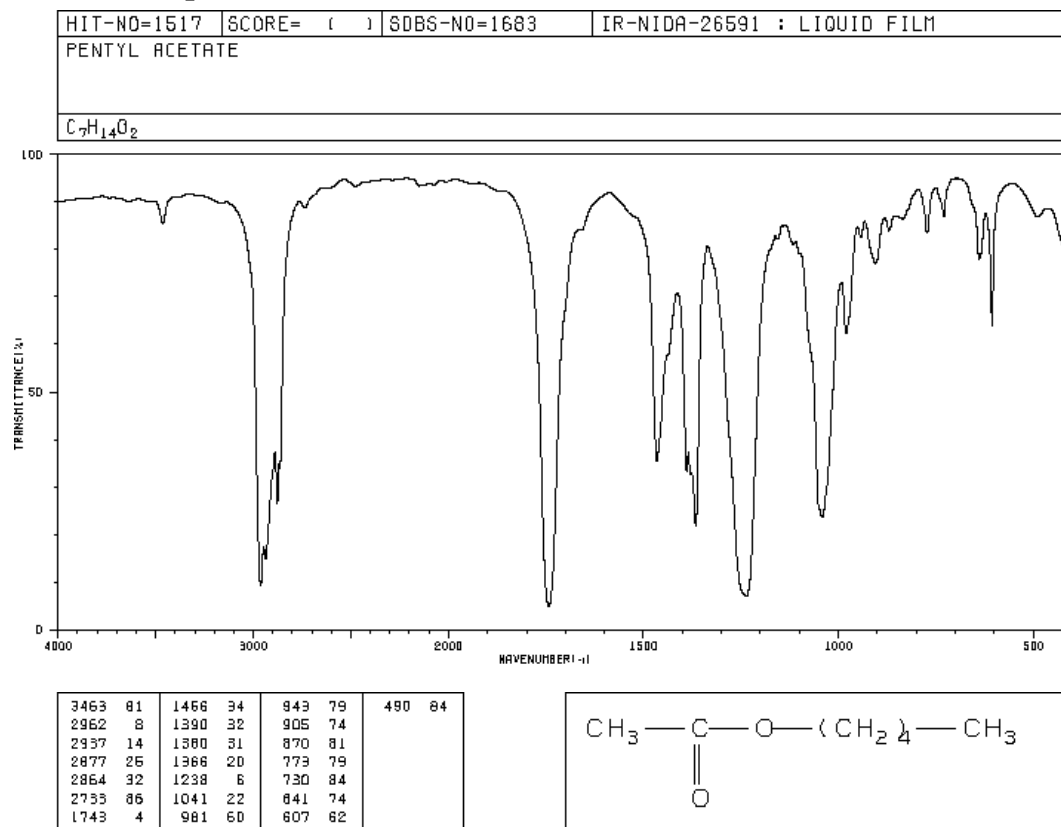
ethers

R — O — R

alkoxy C-O stretch
aliphatic ≈1120 (variable)
aromatic ≈1250

thiols

R — S — H

S-H stretch

stretch
~2550, weak

nitro compounds
(does not show in H or C NMR,
look for nitro in the IR)

O
||
—N⊕
O⊖

1500-1600,
asymmetric stretch, strong

1300-1390,
symmetric stretch, medium

amines

H 1º
N
H

N 2º
H

N
H

stretch
3500 & 3300, two bands for 1º amines,
one band for 2º amines, weaker than in
amides, sometimes an extra overtone
about 3100 due to N-H bend, no N-H
bands for 3º amines

1640-1550, N-H bend, weaker in
amines 800 N-H bend

X = halogens

—C—X

variable bands, usually mixed
in among other bands, not real
useful(sp^3 = 500-1000 range)
(sp^2 = 1000-1250 range)

Real IR Spectrum

| HIT-NO=1517 | SCORE= ( ) | SDBS-NO=1683 | IR-NIDA-26591 : LIQUID FILM |

PENTYL ACETATE

$C_7H_{14}O_2$

3463	81	1466	34	943	79	490	84
2962	8	1390	32	905	74		
2937	14	1380	31	870	81		
2877	25	1366	20	773	79		
2864	32	1238	8	730	84		
2735	86	1041	22	641	74		
1743	4	981	60	607	62		

$$CH_3 - C - O - (CH_2)_4 - CH_3$$
with C=O below the C

Simulated IR Spectrum

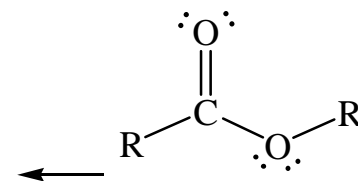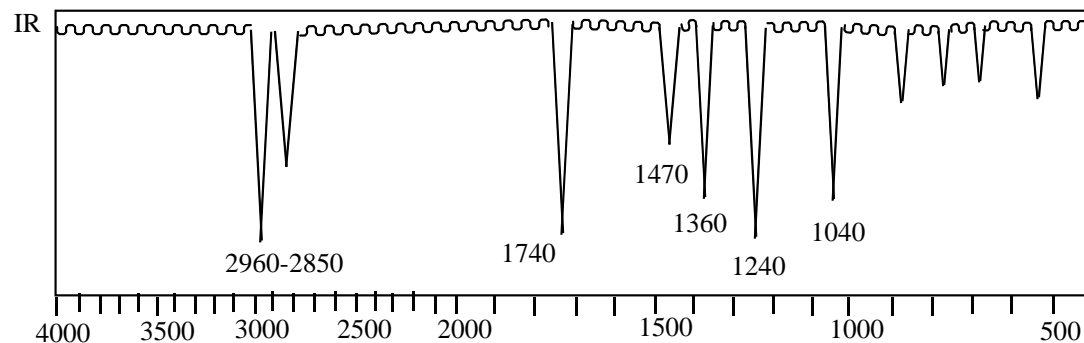IR peaks labeled: 2960-2850, 1740, 1470, 1360, 1240, 1040

Spectral Database for Organic Compounds, SDBS.

This is a free site organized by National Institute of Advanced Industrial Science and Technology (AIST), Japan.

Excellent web site for information on specific compounds or generic patterns. MS, CNMR, HNMR, IR, Ramen, ESR are possibilities.
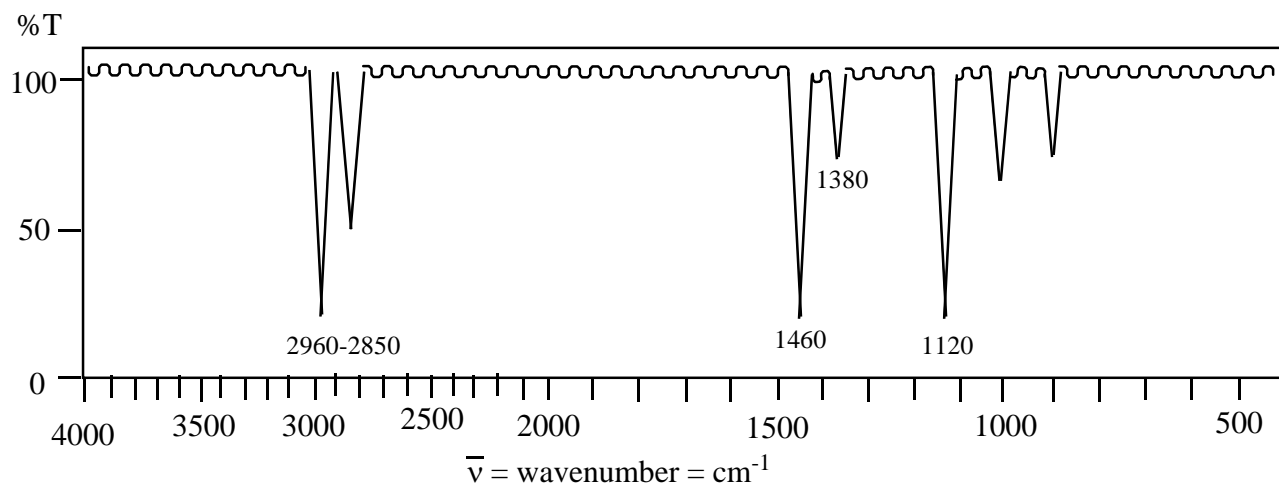
What does the IR tell us about this structure? It has C=O, acyl C-O, alkoxy C-O. It does not have...?

23

Let's say we have an unknown compound with a molecular weight of 116 amu. If we divide 116 by 13 we get 8 with a remainder of 12. That would give us a formula of C_8H_{20}, which is not possible since we have more Hs than there are bonding locations (maximum saturation is 2x8+2 = 18). However, we could have one oxygen with a formula of $C_7H_{16}O$, which is completely saturated (has zero degrees of unsaturation). Two oxygen atoms would give us a formula of $C_6H_{12}O_2$, having one degree of unsaturation (1 pi bond or 1 ring). If we also had an IR spectrum we might be able to propose reasonable possible structures, but we cannot completely solve the structure. Propose possible structures using the given IR spectra below ($C_7H_{16}O$) and on the next slide ($C_6H_{12}O_2$).
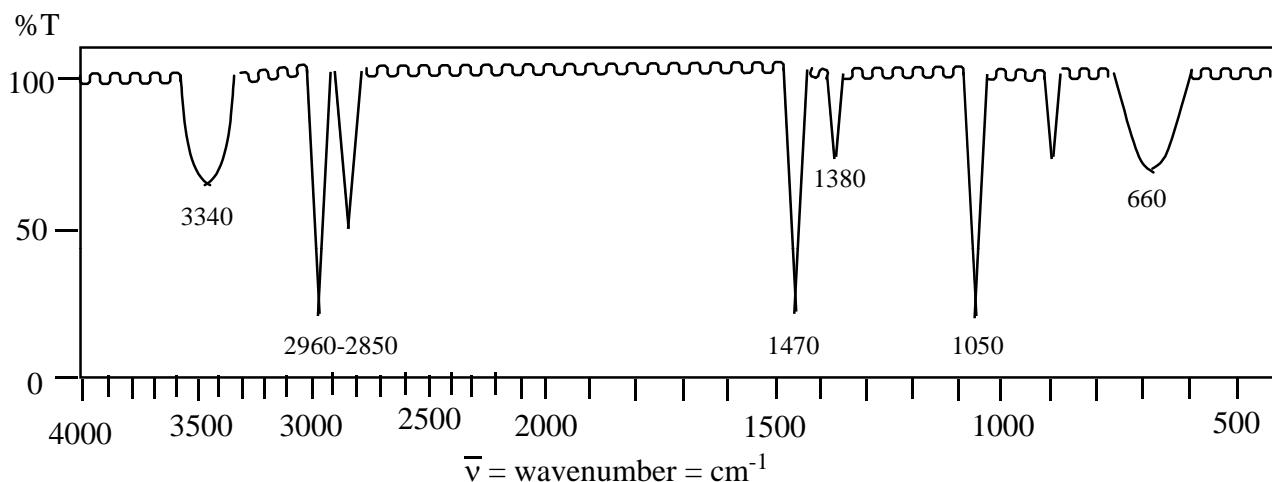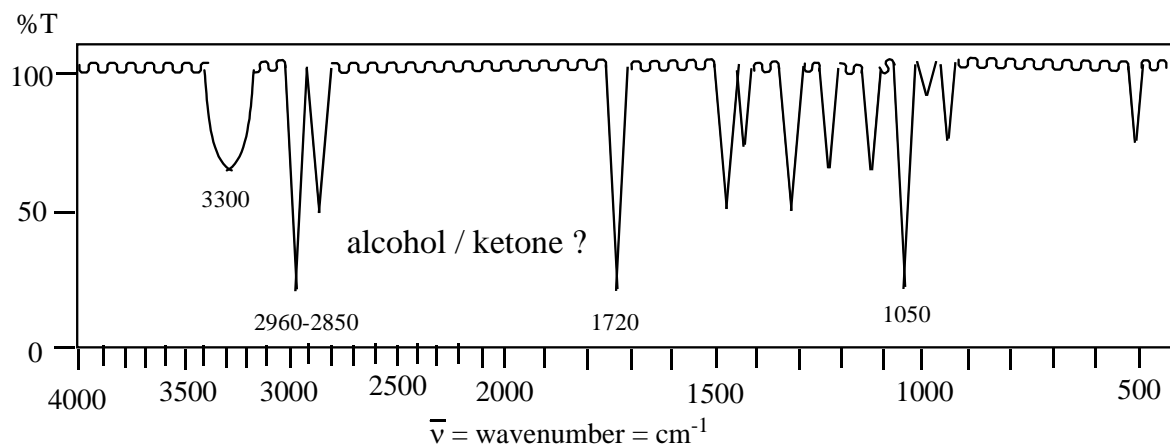

IR shows typical alkane bands mentioned earlier, plus alcohol O-H stretch at 3200-3300; alkoxy C-O stretch at 1050-1200; alcohol O-H bend at 650

$C_7H_{16}O$ could be a saturated alcohol or ether. There are many possibilities.
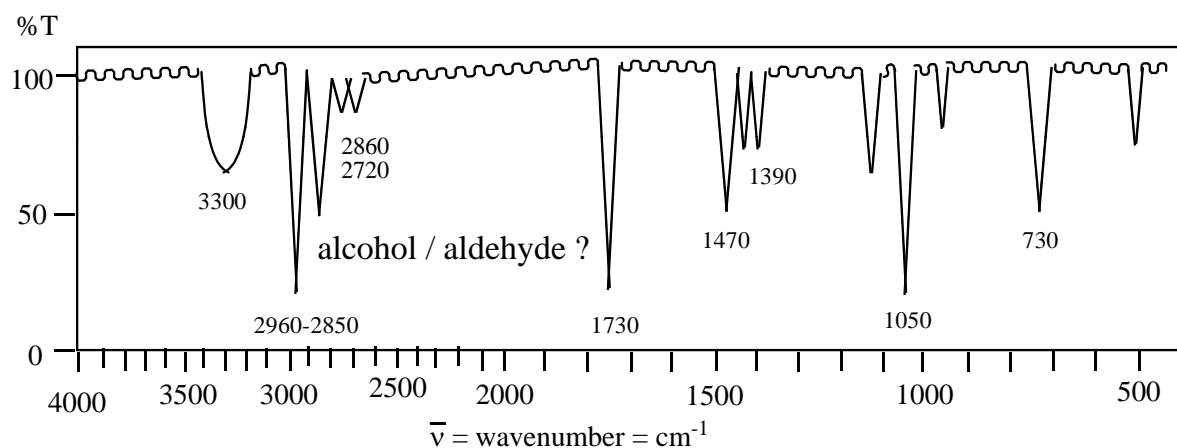
IR shows typical alkane bands mentioned earlier, plus C-O stretch at ~1100

%T

3300

alcohol / ketone ?

2960-2850   1720   1050

$\overline{\nu}$ = wavenumber = cm^{-1}
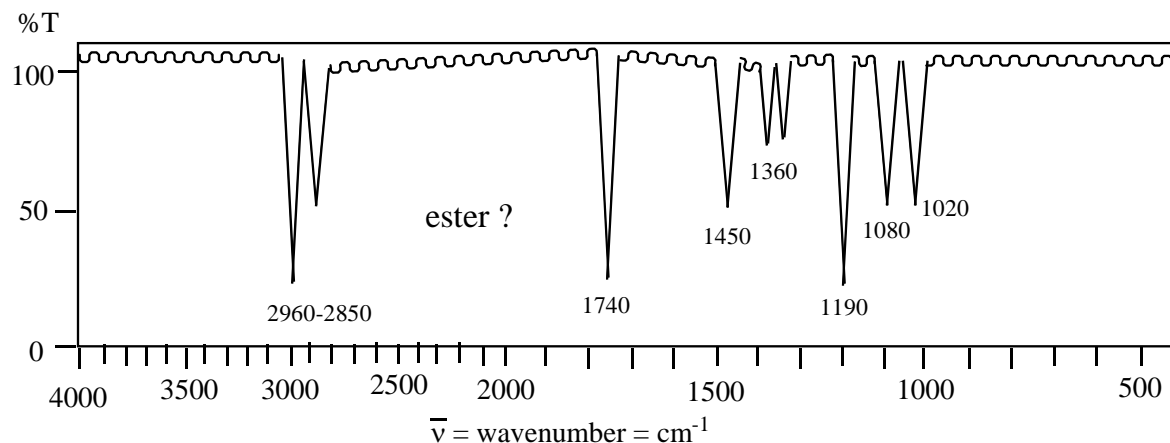
4000 3500 3000 2500 2000 1500 1000 500

IR shows typical alkane bands mentioned earlier, plus alcohol O-H stretch at 3200-3300; alkoxy C-O stretch at 1050-1200; and carbonyl stretch (C=O) at 1720.

$C_6H_{12}O_2$ There are many possibilities having one degree of unsaturation.

%T

2860
2720

3300

alcohol / aldehyde ?

2960-2850   1730   1470   1390   1050   730

$\overline{\nu}$ = wavenumber = cm^{-1}

4000 3500 3000 2500 2000 1500 1000 500

IR shows typical alkane bands mentioned earlier, plus alcohol O-H stretch at 3200-3300; alkoxy C-O stretch at 1050-1200; and carbonyl stretch (C=O) at 1720 and the aldehyde C-H doublet at 2860 and 2720.

$C_6H_{12}O_2$ There are many possibilities having one degree of unsaturation.

%T

ester ?

2960-2850   1740   1450   1360   1190   1080   1020

$\overline{\nu}$ = wavenumber = cm^{-1}
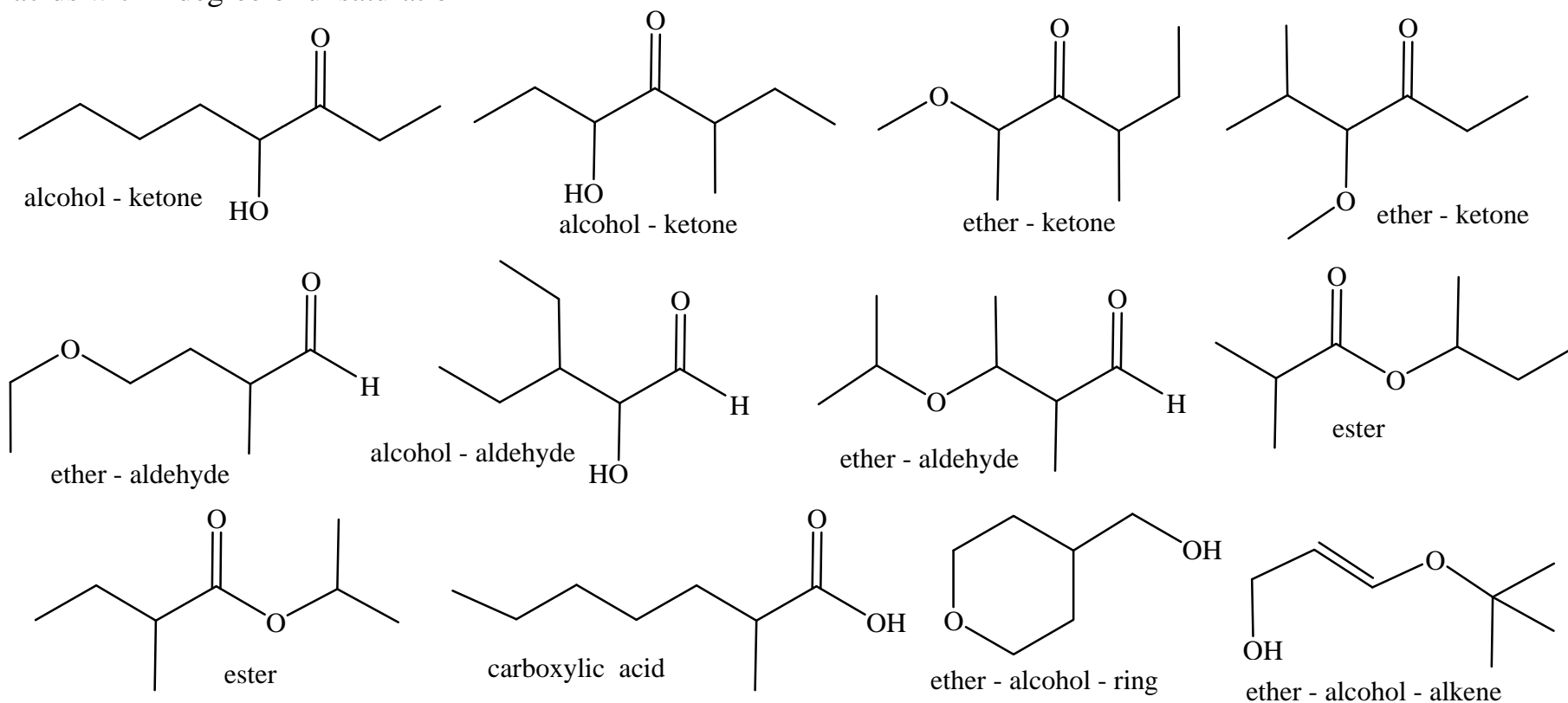
4000 3500 3000 2500 2000 1500 1000 500

Typical alkane bands, plus C=O at ~1740; acyl C-O at ~1190; alkoxy C-O at ~1080. (Ester rule of 3.) Looks like a simple ester.

None of these possibilities actually solve the structure. We need more information.

25

$C_8H_{18}O$: examples of alcohols and ethers with 0 degrees of unsaturation

alcohol   alcohol   ether   ether
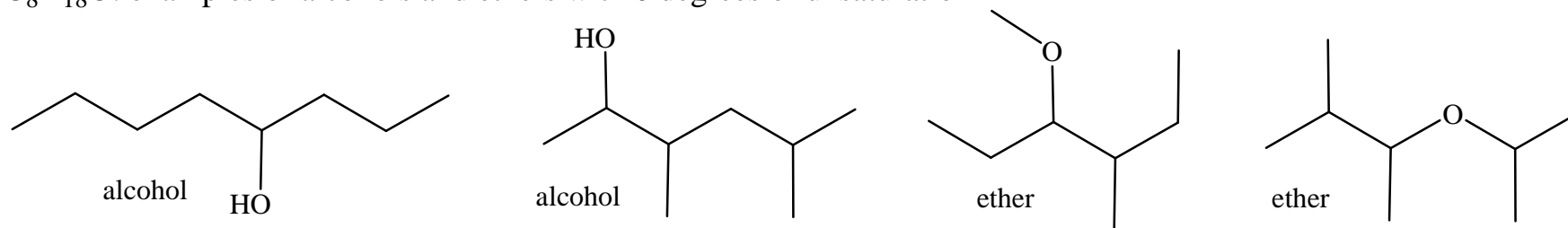
$C_7H_{14}O_2$: examples of hydroxyketones, hydroxyaldehydes, alkoxyketones, alkoxyaldehydes, esters and carboxylic acids with 1 degree of unsaturation

alcohol - ketone   alcohol - ketone   ether - ketone   ether - ketone

ether - aldehyde   alcohol - aldehyde   ether - aldehyde   ester

ester   carboxylic acid   ether - alcohol - ring   ether - alcohol - alkene

NMR can solve all of these structures!

26

IR Functional Group Examples (Single functional groups are easier to interpret than multiple functional groups.)
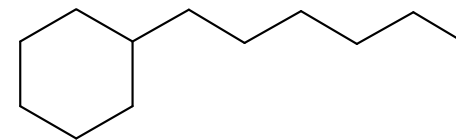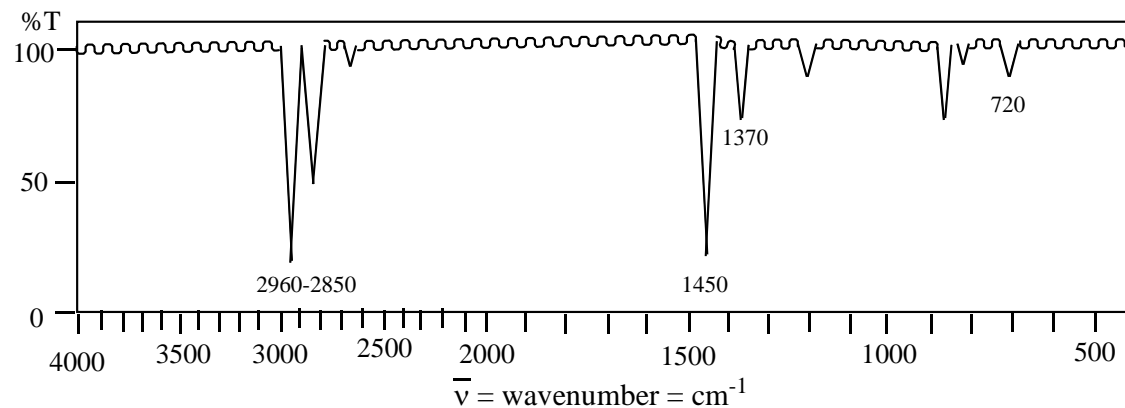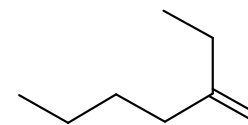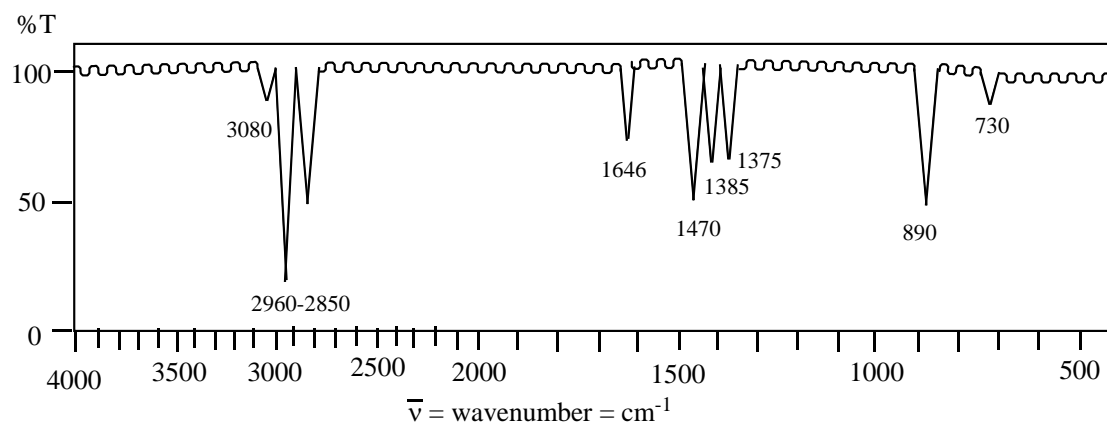

hexylcyclohexane

sp^3 CH stretch at ~2850-3000;
sp^3 CH bend at ~1380, 1470;
sp^3 CH$_2$ rock at ~720;
sp^3 branching ~900-1250;

Chart labels: 2960-2850, 1450, 1370, 720

$\overline{\nu}$ = wavenumber = cm^{-1}
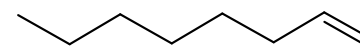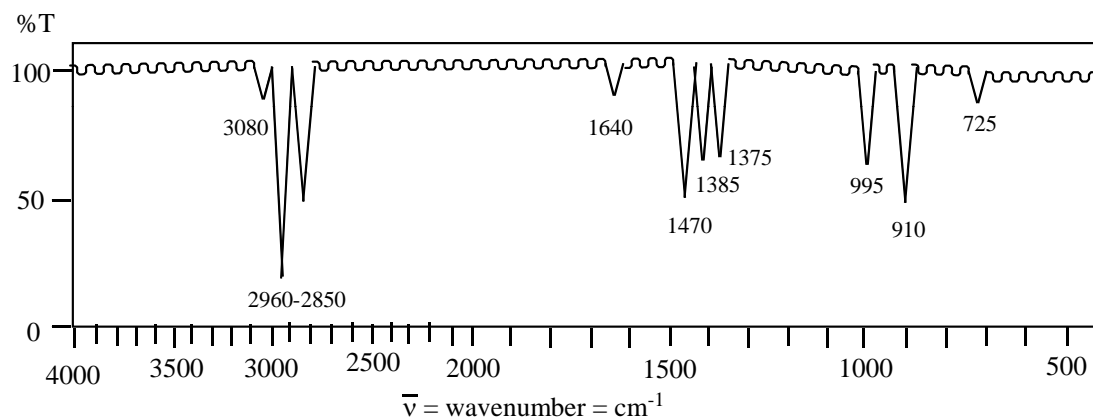
oct-1-ene
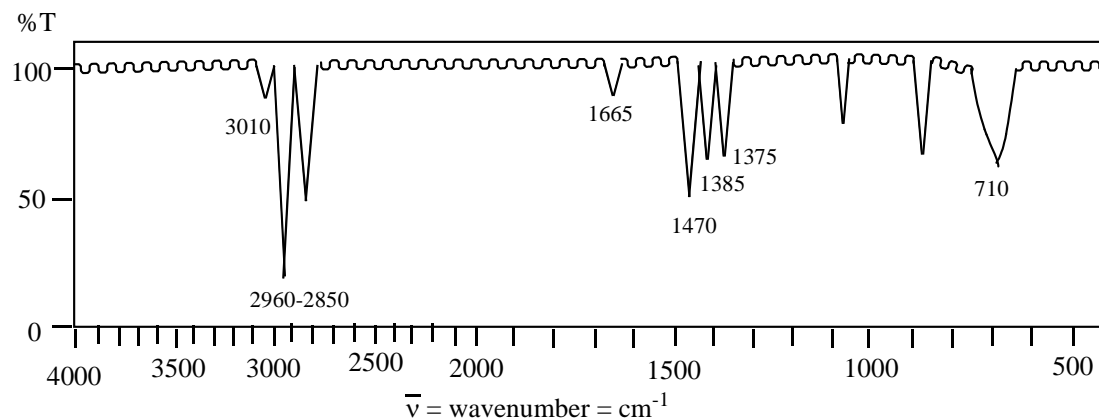
IR shows typical alkane bands mentioned earlier, plus sp^2 CH stretch at ~3000-3100; C=C stretch at ~1600-1670; monosubstituted sp^2 CH bend at ~910 and ~990 cm^{-1}

Chart labels: 3080, 2960-2850, 1640, 1470, 1385, 1375, 995, 910, 725

$\overline{\nu}$ = wavenumber = cm^{-1}

2-ethyl-1-hexene

IR shows typical alkane bands mentioned earlier, plus sp^2 C-H stretch at ~3000-3100; C=C stretch at ~1600-1670; germinal disubstituted alkene, sp^2 C-H bend at ~890
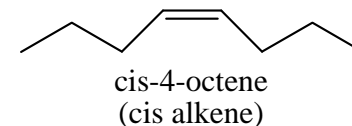
Chart labels: 3080, 2960-2850, 1646, 1470, 1385, 1375, 890, 730

$\overline{\nu}$ = wavenumber = cm^{-1}

27

IR Functional Group Examples

%T

3010
1665
1375
1385
1470
710
2960-2850

$\overline{\nu}$ = wavenumber = cm^{-1}

cis-4-octene
(cis alkene)

IR shows typical alkane bands mentioned earlier, plus sp^2 C-H stretch at ~3000-3100; C=C stretch at ~1600-1670; cis disubstituted alkene, sp^2 C-H bend at ~670-730 (often wide)
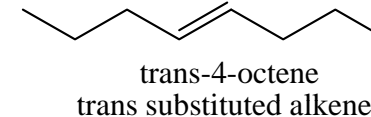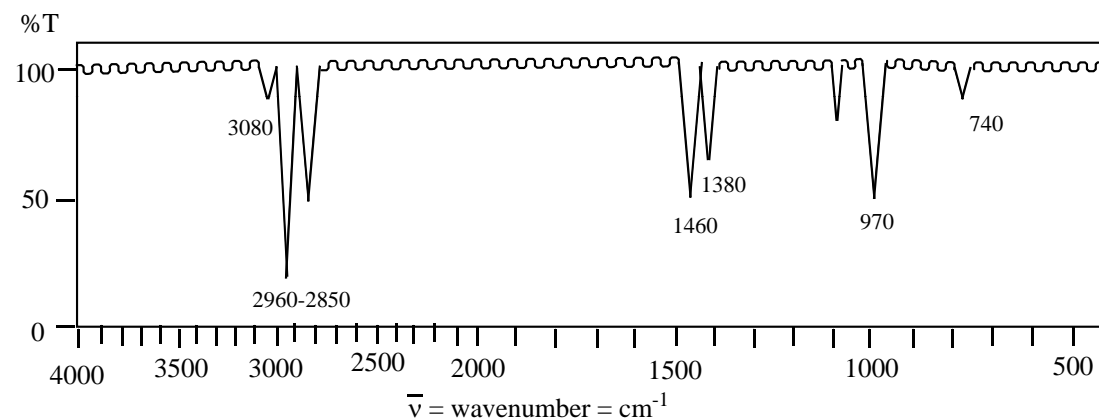
%T

3080
1380
1460
970
740
2960-2850

$\overline{\nu}$ = wavenumber = cm^{-1}

trans-4-octene
trans substituted alkene)

IR shows typical alkane bands mentioned earlier, plus sp^2 C-H stretch at ~3000-3100; C=C stretch at ~1600-1670 is missing,probably due to its symmetry; trans disubstituted alkene, sp^2 C-H bend ~960
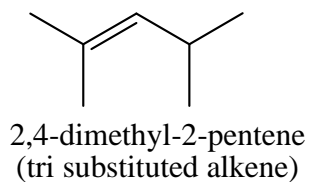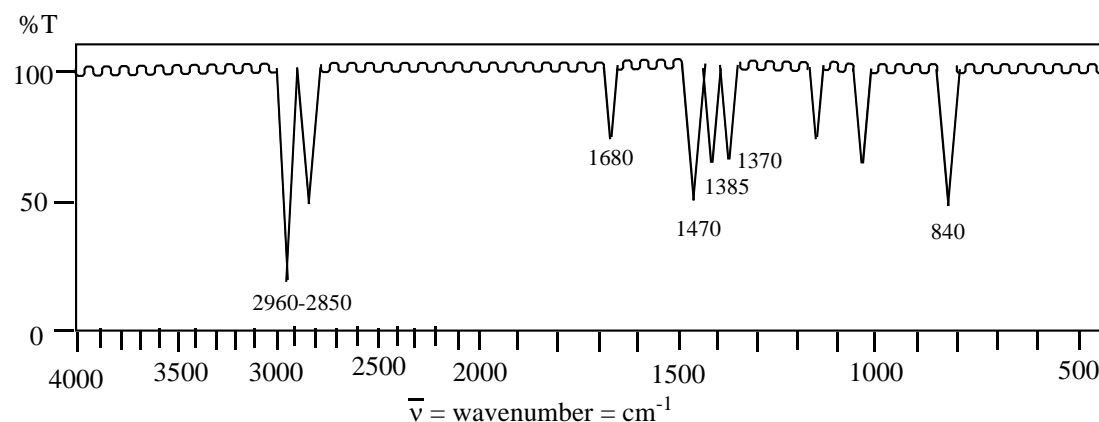
%T

1680
1370
1385
1470
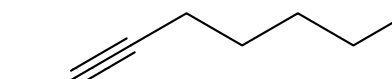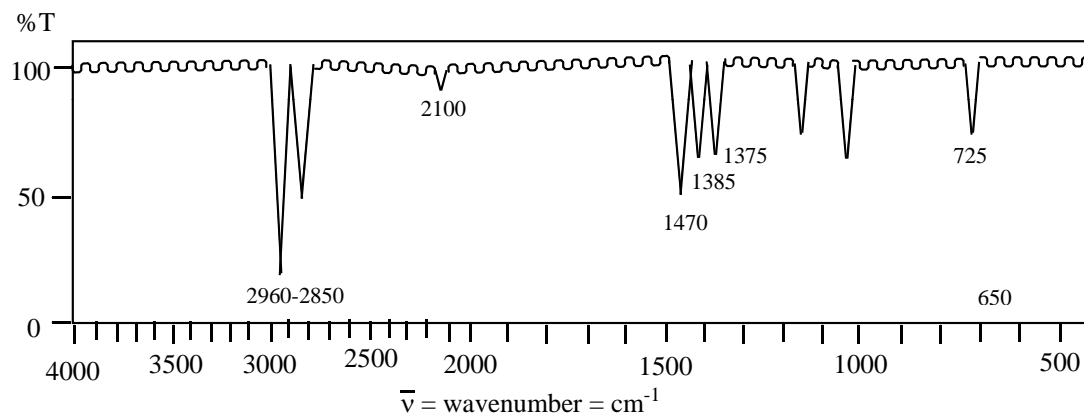840
2960-2850

$\overline{\nu}$ = wavenumber = cm^{-1}

2,4-dimethyl-2-pentene
(tri substituted alkene)

IR shows typical alkane bands mentioned earlier, plus sp^2 C-H stretch at ~3000-3100; C=C stretch at ~1600-1670; tri- substituted alkene, sp^2 C-H bend ~800-840

28

IR Functional Group Examples

%T

100

50

0

3310

2960-2850

2120

1375
1385

1470

725

650

4000   3500   3000   2500   2000   1500   1000   500

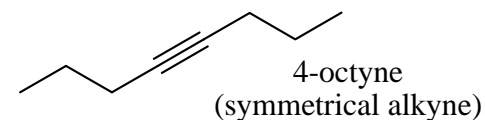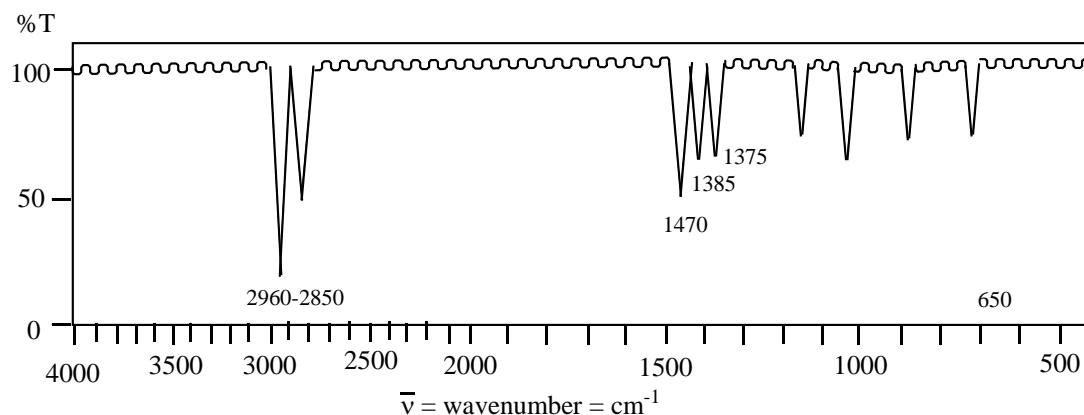$\overline{\nu}$ = wavenumber = cm^{-1}
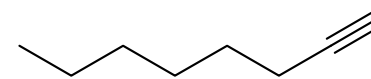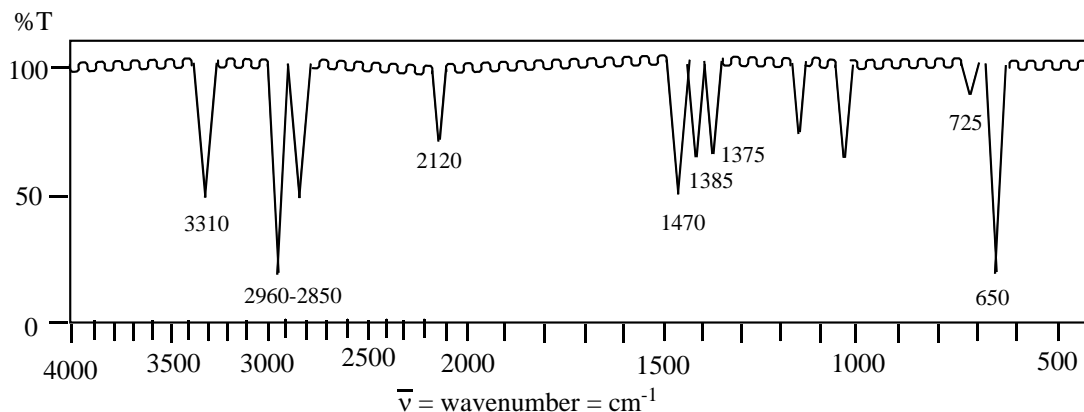
1-octyne
(terminal alkyne)

IR shows typical alkane bands mentioned earlier, plus; sp C-H stretch ~3300; sp CC stretch ~2100-2250 (highly variable strength); sp C-H bend ~600-700

%T

100

50

0

2100

2960-2850

1375
1385

1470

725

650

4000   3500   3000   2500   2000   1500   1000   500

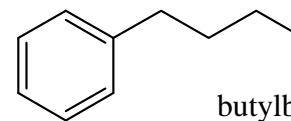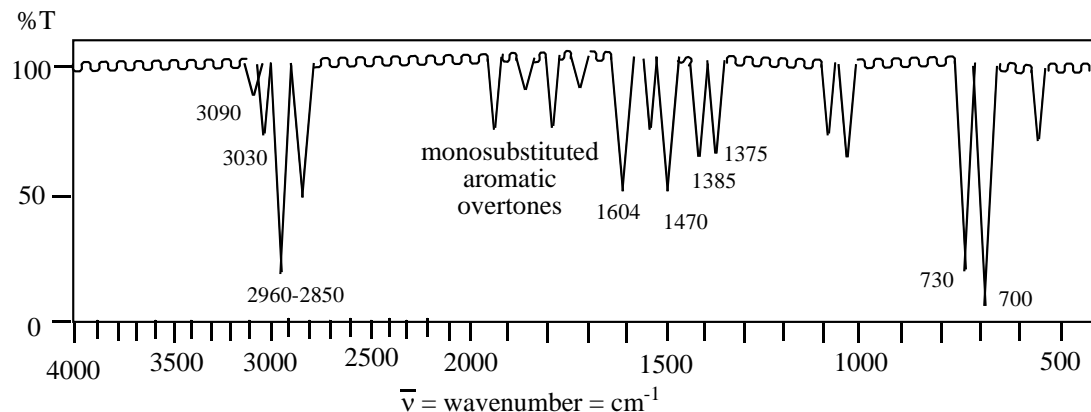$\overline{\nu}$ = wavenumber = cm^{-1}

2-octyne
(unsymmetrical alkyne)

IR shows typical alkane bands mentioned earlier, no sp C-H stretch present; sp CC stretch 2100-2250 (often quite weak, unless very unsymmetrical);

%T

100

50

0

2960-2850

1375
1385

1470

650

4000   3500   3000   2500   2000   1500   1000   500

$\overline{\nu}$ = wavenumber = cm^{-1}
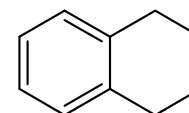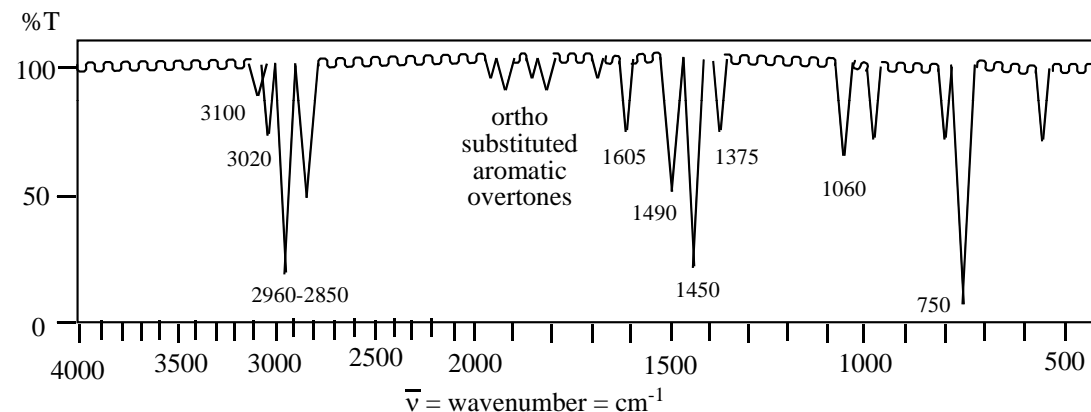
4-octyne
(symmetrical alkyne)

IR shows typical alkane bands mentioned earlier, no sp C-H stretch, sp CC stretch disappears when symmetrical. There would be 2 degrees of unsaturation in the formula. Also, the ^{13}C NMR would show 1-2 peaks in the region of 70-90 ppm.

29

IR Functional Group Examples

%T

100

50

0

3090
3030
2960-2850
monosubstituted
aromatic
overtones
1604
1470
1375
1385
730
700

4000   3500   3000   2500   2000   1500   1000   500

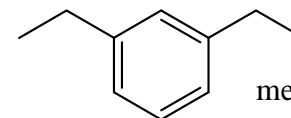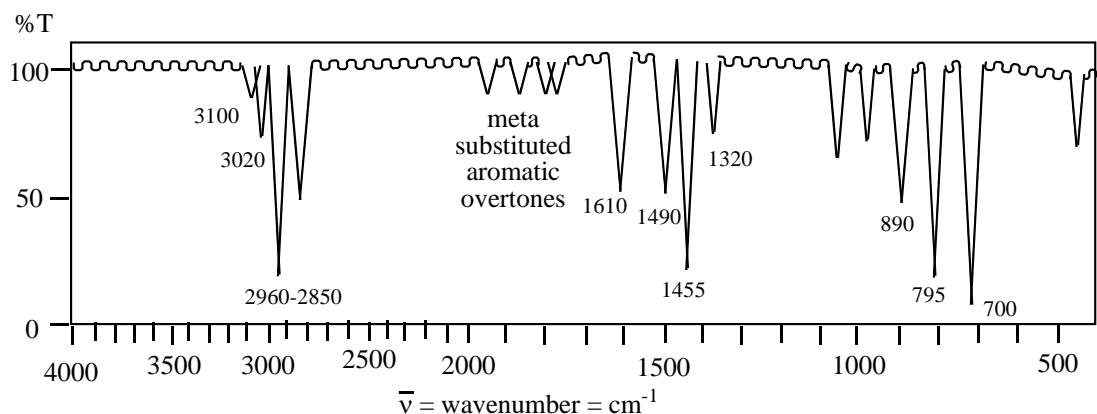$\overline{\nu}$ = wavenumber = cm^{-1}

butylbenzene

Typical alkane bands, plus sp^2 C-H stretch at 3030-3100 (usually weak); aromatic overtones of sp^2 CH bending at 1660-2000 (patterns useful, when present); aromatic C=C stretch at 1480-1600 (highly variable, not real useful); monosubstituted aromatic sp^2 at C-H bend at 690-710 and 730-770 often useful, but can change with some substituents

%T

100

50

0

3100
3020
2960-2850
ortho
substituted
aromatic
overtones
1605
1490
1450
1375
1060
750

4000   3500   3000   2500   2000   1500   1000   500

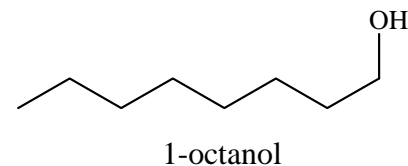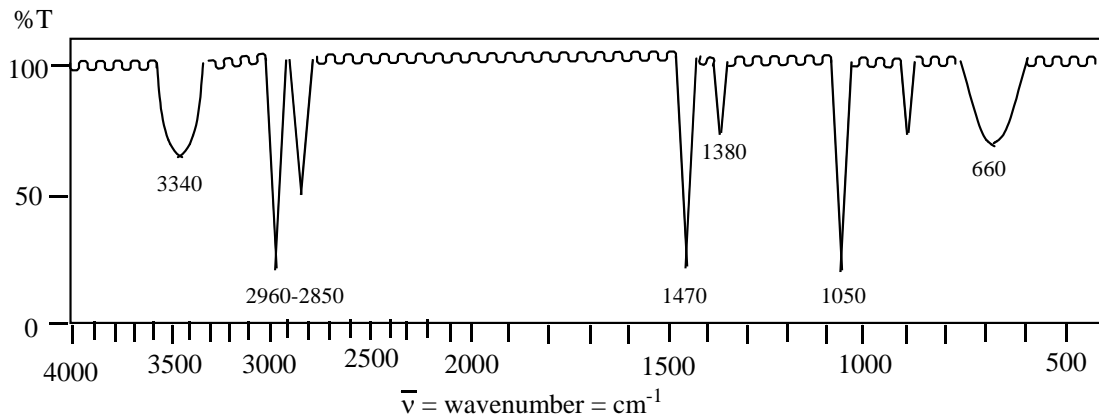$\overline{\nu}$ = wavenumber = cm^{-1}

ortho diethylbenzene

Typical alkane bands, plus sp^2 C-H stretch at ~3030-3100; aromatic overtones of sp^2 CH bending at ~1660-2000 (patterns useful, when present); aromatic C=C stretch at ~1480-1600 (highly variable, not real useful); ortho substituted aromatic sp^2 C-H bend at ~730-770 often useful, but can change with some substituents
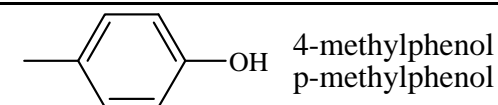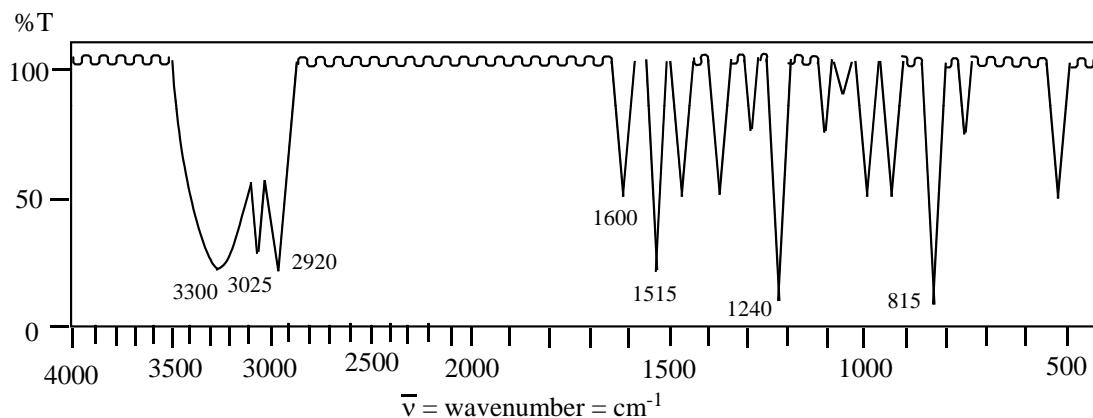
%T

100

50

0

3100
3020
2960-2850
meta
substituted
aromatic
overtones
1610
1490
1455
1320
890
795
700

4000   3500   3000   2500   2000   1500   1000   500

$\overline{\nu}$ = wavenumber = cm^{-1}

meta diethylbenzene

Typical alkane bands, plus sp^2 C-H stretch at 3030-3100; aromatic overtones of sp^2 CH bending at 1660-2000 (patterns useful, when present); aromatic C=C stretch at 1480-1600 (highly variable, not real useful); meta substituted aromatic sp^2 C-H bend at 690-710, 750-810, 850 (sometimes) often useful, but can change with some substituents
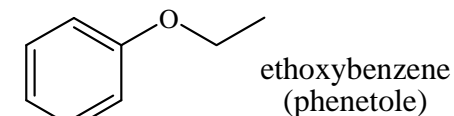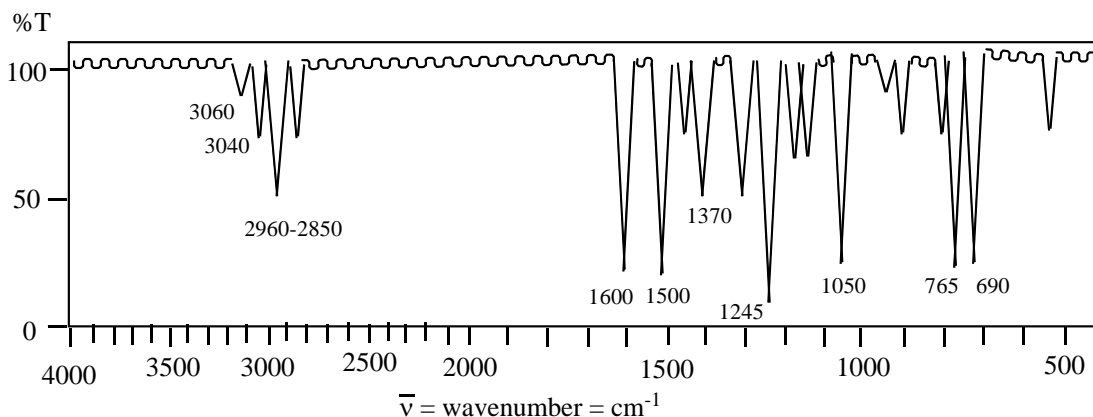
30

IR Functional Group Examples

%T

3340

2960-2850

1380

1470

1050

660

$\overline{\nu}$ = wavenumber = cm^{-1}

1-octanol

IR shows typical alkane bands mentioned earlier, plus alcohol O-H stretch at 3200-3300; alkoxy C-O stretch at 1050-1200; alcohol O-H bend at 650


%T

3300 3025 2920

1600

1515

1240

815

$\overline{\nu}$ = wavenumber = cm^{-1}

4-methylphenol
p-methylphenol

Phenol O-H stretch at ~3200-3300; might see sharp OH if ortho substituted sp^2 C-H stretch ~3000-3120 (usually weak); aromatic overtones of sp^2 CH bending at ~1660-2000 (patterns useful, when present); aromatic C=C stretch at ~1480-1600 (highly variable, not real useful); phenolic C-O stretch at ~1200; para substituted aromatic sp^2 C-H bend at ~800-860 often useful, but can change with some substituents


%T

3060

3040

2960-2850

1600 1500

1370

1245

1050

765 690

$\overline{\nu}$ = wavenumber = cm^{-1}

ethoxybenzene
(phenetole)

Typical alkane bands, plus sp^2 C-H stretch at ~3030-3100 (usually weak); aromatic overtones of sp^2 CH bending at ~1660-2000 (patterns useful, when present); aromatic C=C stretch at ~1480-1600 (highly variable, not real useful); aromatic C-O stretch at ~1200; alkoxy C-O stretch at ~1050; monosubstituted aromatic sp^2 C-H bend at ~690-710 and 730-770; often useful, but can change with some substituents
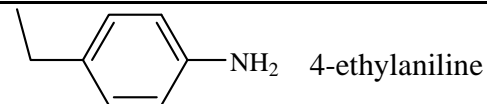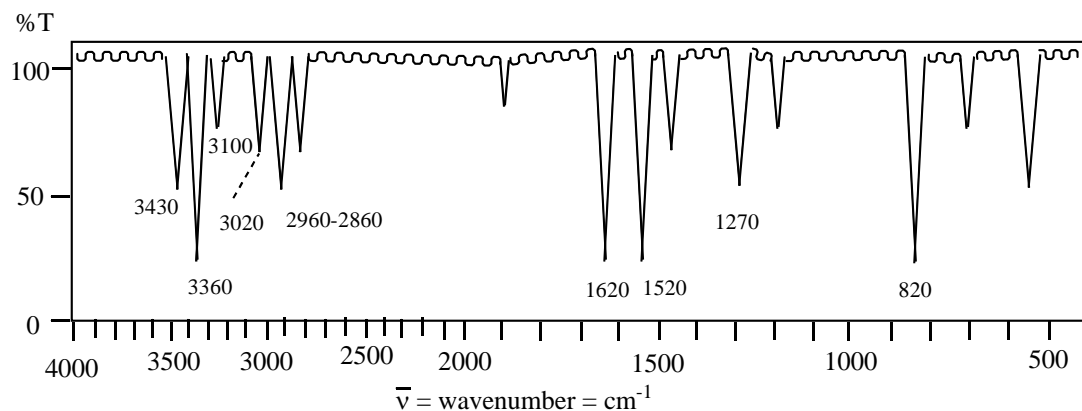
31

IR Functional Group Examples

nonylamine (1° amine)
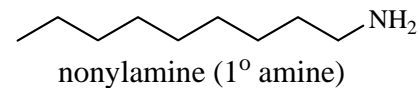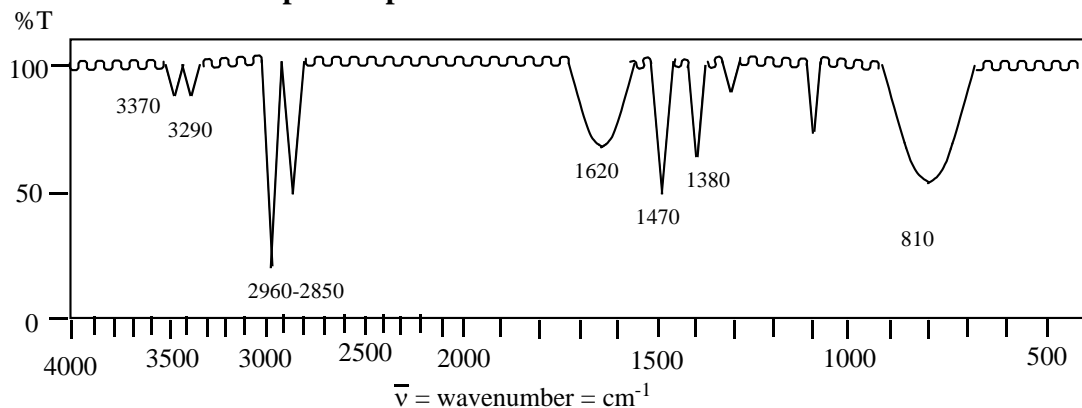
Typical alkane bands, plus two peaks at ~3370 and ~3290 due to NH_2 asymmetric and symmetric N-H stretch. Because of a weaker dipole moment the intensity of these peaks is much less than would show in a primary amide. N-H bending peaks are at ~1620 and ~810, In an uncrowded spectrum these might be helpful.


N-methyloctylamine (2° amine)
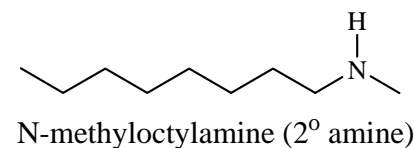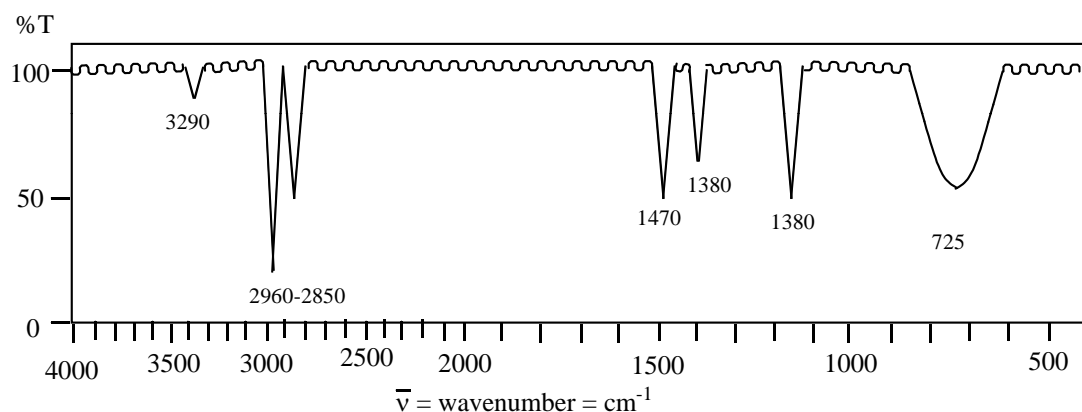
Typical alkane bands, plus a single peak at 3290 is due to N-H stretch (weak). Sometimes it is so weak it can't be seen. Look for it in the proton NMR. In this spectrum the N-H bending peak shows at 725, but doesn't show at 1500.


4-ethylaniline

Typical alkane bands, plus two peaks at 3430 and 3360 are due to NH_2 asymmetric and symmetric N-H stretch (stronger due to resonance with the aromatic ring, more polar). An overtone appears at 3100, probably from the N-H bend peak at 1620. sp^2 C-H stretch is present at 3000-3120, aromatic C=C stretch at 1500-1600; para substituted aromatic sp^2 C-H bend 820, often useful, but can change with some substituents

32

IR Functional Group Examples

%T

3410

2960-2850

1720

1120

$\overline{v}$ = wavenumber = cm^{-1}
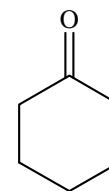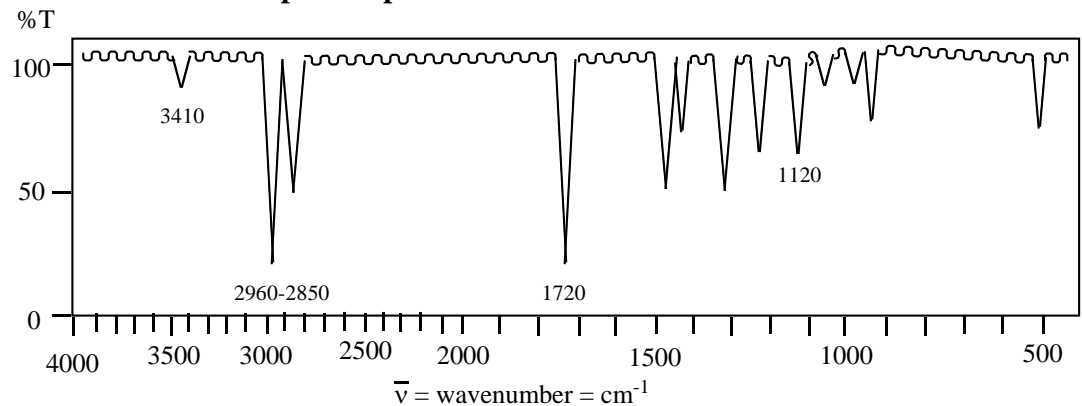
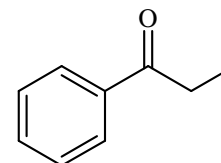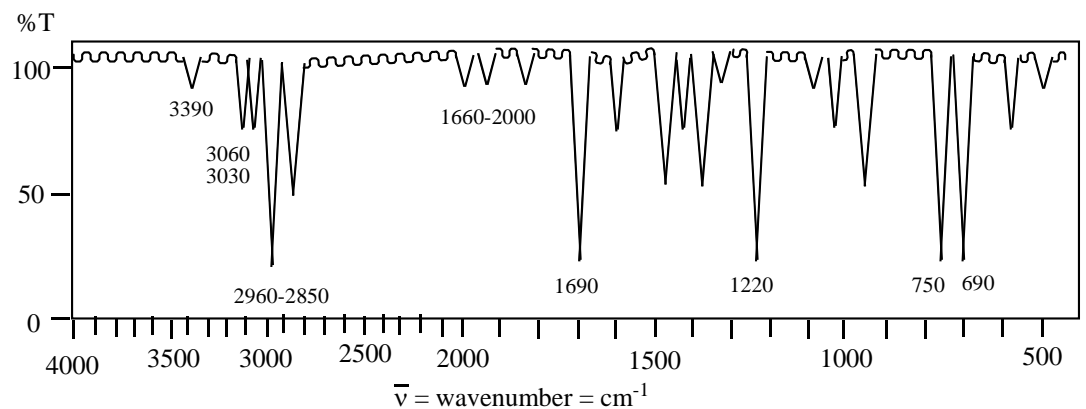cyclohexanone

Typical alkane bands, plus C=O stretch at ~1720; probably a C=O bend around ~1100, but too many peaks to know which it might be. The overtone band near ~3400 can be confused for a weak OH band.

%T

3500

3030

2960-2850

1685

1620
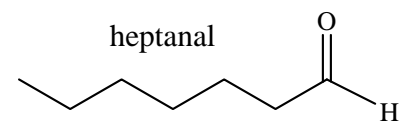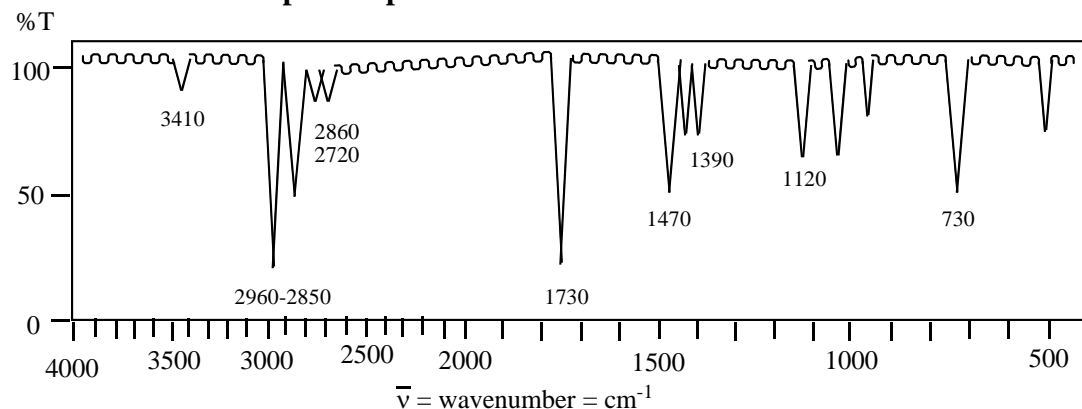
$\overline{v}$ = wavenumber = cm^{-1}
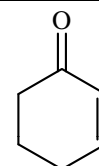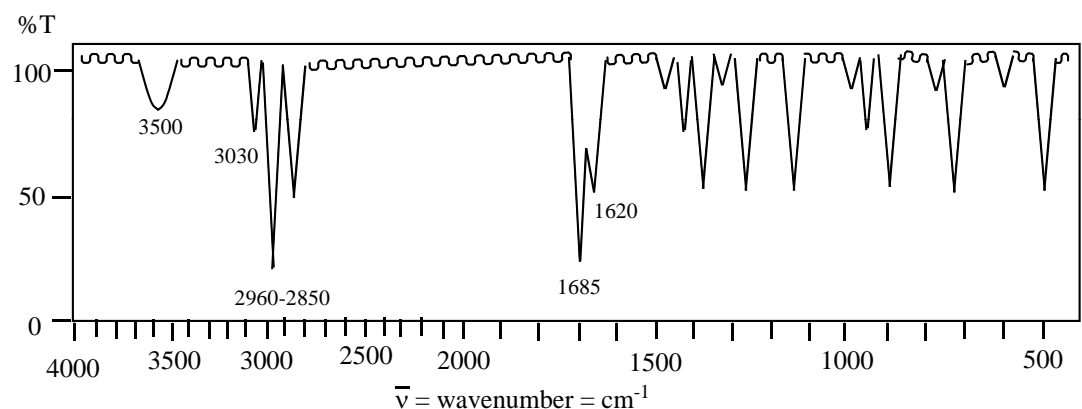
cyclohex-2-enone

Typical alkane bands, plus the band ~3400 possibly some water in the sample, or perhaps C=O overtone, sp^2 C-H stretch is at ~3000-3100; C=O stretch (lower than simple ketones due to conjugation) at ~1685; C=C stretch bond at ~1617, more intense from conjugation with C=O
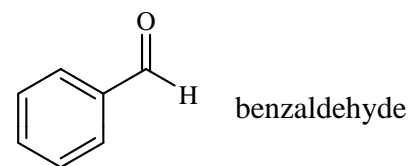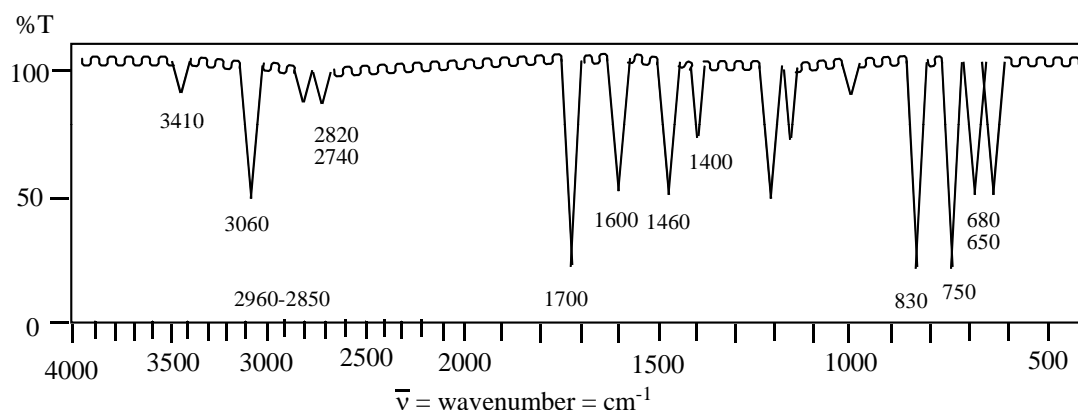

%T

3390

3060
3030

2960-2850

1660-2000

1690

1220

750 690

$\overline{v}$ = wavenumber = cm^{-1}

1-phenylpropan-1-one
(propiophenone)
(aromatic ketone)

C=O overtone at ~3390, sp^2 C-H stretch ~3000-3100, aromatic overtones of sp^2 CH bending ~1660-2000 (useful, when present); C=O stretch (lower than simple ketones due to conjugation) at ~1685 aromatic C=C stretch ~1480-1600 (not real useful); monosubstituted aromatic sp^2 C-H bend at ~690-710 and ~730-770
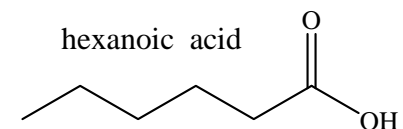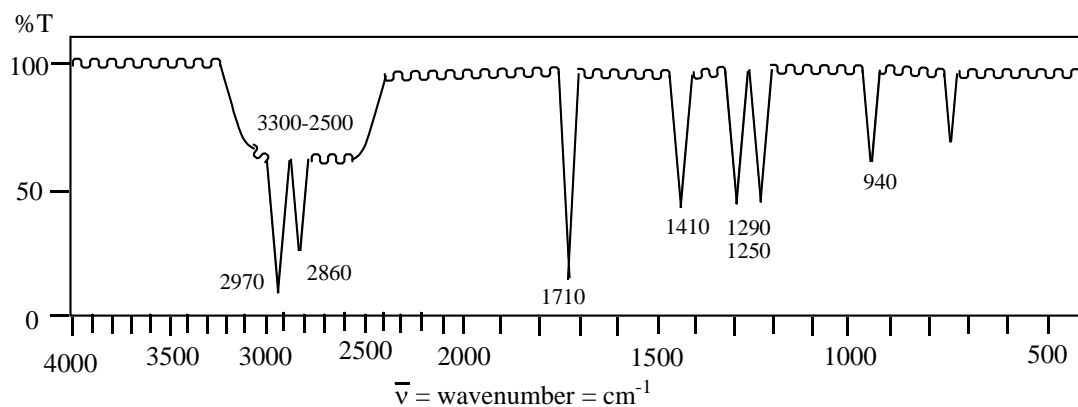
33

Slide 34

IR Functional Group Examples

%T (top graph, heptanal)

3410
2860
2720
1390
1120
1470
730
2960-2850
1730

4000 3500 3000 2500 2000 1500 1000 500
$\overline{\nu}$ = wavenumber = cm^{-1}

heptanal

Typical alkane bands, plus the overtone band near ~3400 can be confused for a weak OH band; C=O stretch at ~1730; probably a C=O bend around ~1120, but not confidently diagnostic.

%T (middle graph, benzaldehyde)

3410
2820
2740
3060
1400
1600 1460
680
650
2960-2850
1700
830 750

4000 3500 3000 2500 2000 1500 1000 500
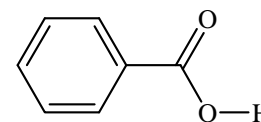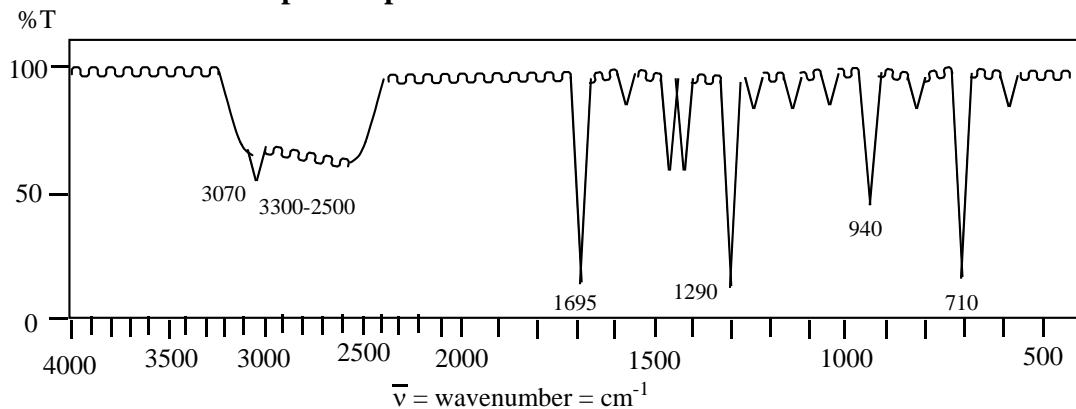$\overline{\nu}$ = wavenumber = cm^{-1}

benzaldehyde

Typical aromatic bands, does not show any alkane bands, plus C=O band at ~1700 and probably a C=O bend around ~1100, but too many peaks to know which it might be. The overtone band near ~3400 can be confused for a weak OH band.

%T (bottom graph, hexanoic acid)

3300-2500
940
1410 1290
1250
2970 2860
1710

4000 3500 3000 2500 2000 1500 1000 500
$\overline{\nu}$ = wavenumber = cm^{-1}
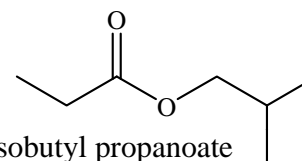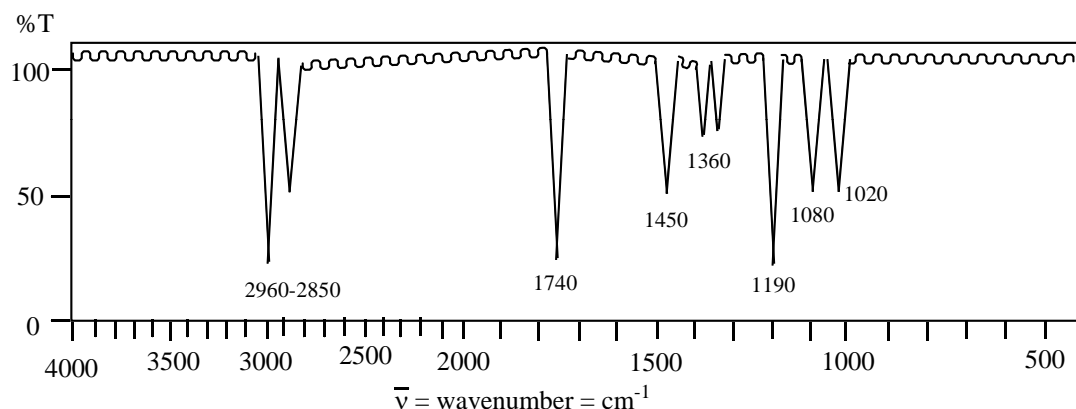
hexanoic acid

Typical alkane bands, plus broad acid OH at ~2500-3350; C=O stretch at ~1710; probably a C=O bend maybe around ~1250, but not confidently diagnostic.
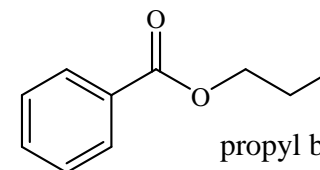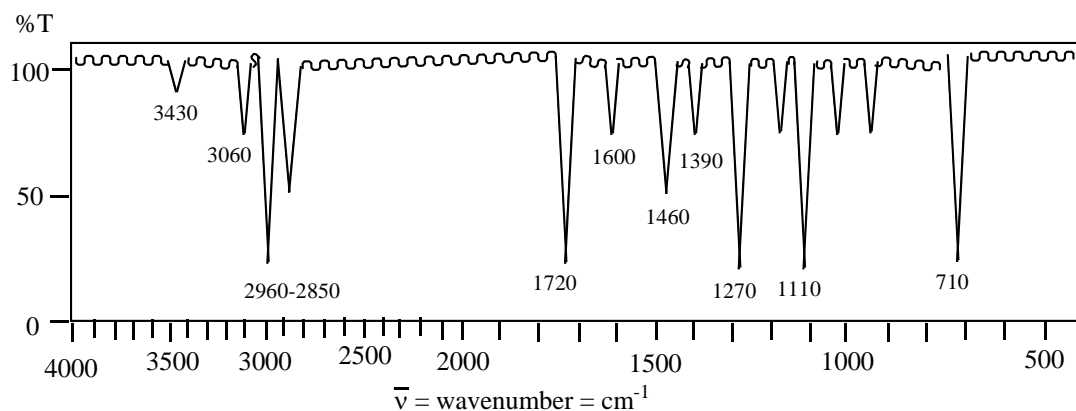
34

IR Functional Group Examples

%T

100

50

0

3070

3300-2500

1695

1290

940

710

4000   3500   3000   2500   2000   1500   1000   500

$\overline{\nu}$ = wavenumber = cm^{-1}

benzoic acid
(KBr pellet)

Broad acid OH at ~2500-3400; sp^2 C-H ~3000-3100 (pokes through just a little bit); conjugated C=O at ~1700; acyl C-O at ~1290 monosubstituted aromatic. sp^2 C-H bend at 710, (atypical, normally = ~700 & ~750)

%T

100

50

0

2960-2850

1740

1450

1360

1190

1080

1020

4000   3500   3000   2500   2000   1500   1000   500
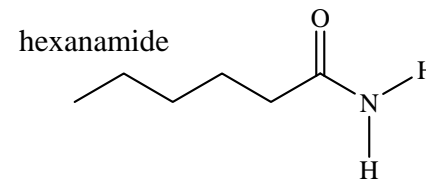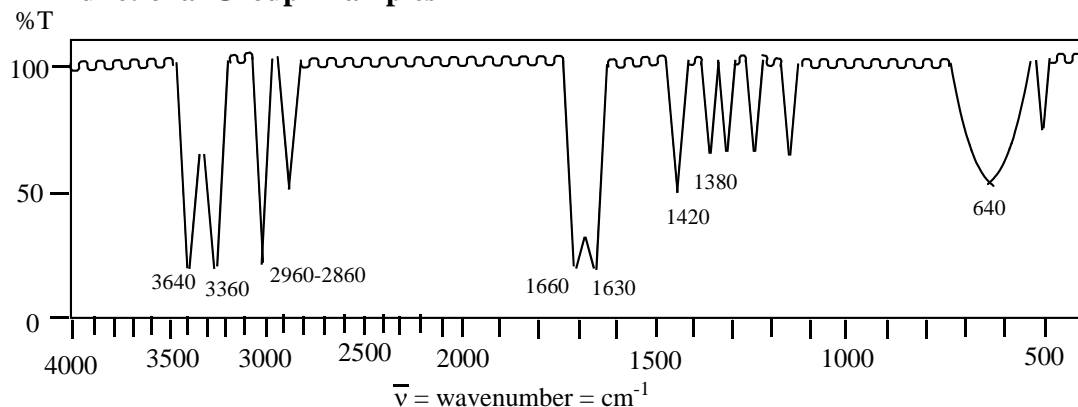
$\overline{\nu}$ = wavenumber = cm^{-1}

isobutyl propanoate

Typical alkane bands, plus C=O at ~1740; acyl C-O at ~1190; alkoxy C-O at ~1080. (Ester rule of 3.) Overtone does not show.

%T
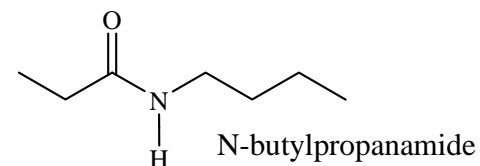
100

50

0

3430

3060

2960-2850

1720

1600

1460

1390

1270   1110

710

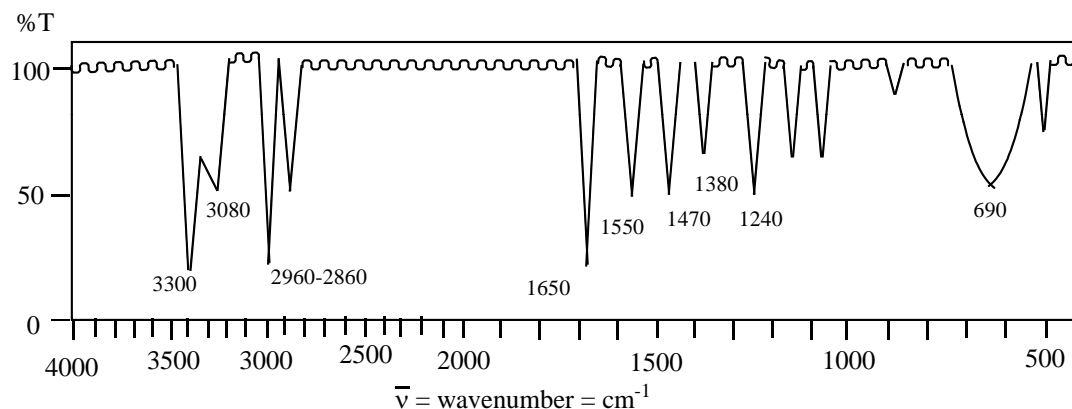4000   3500   3000   2500   2000   1500   1000   500

$\overline{\nu}$ = wavenumber = cm^{-1}

propyl benzoate

Typical alkane bands, C=O overtone at ~3430; sp^2 C-H at ~3030-3100; conjugated C=O at ~1720; acyl C-O at ~1270; alkoxy C-O at ~1110; monosubst. arom. sp^2 C-H at 710 (atypical here, normally ~700 & ~ 750)
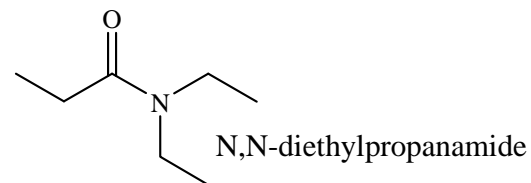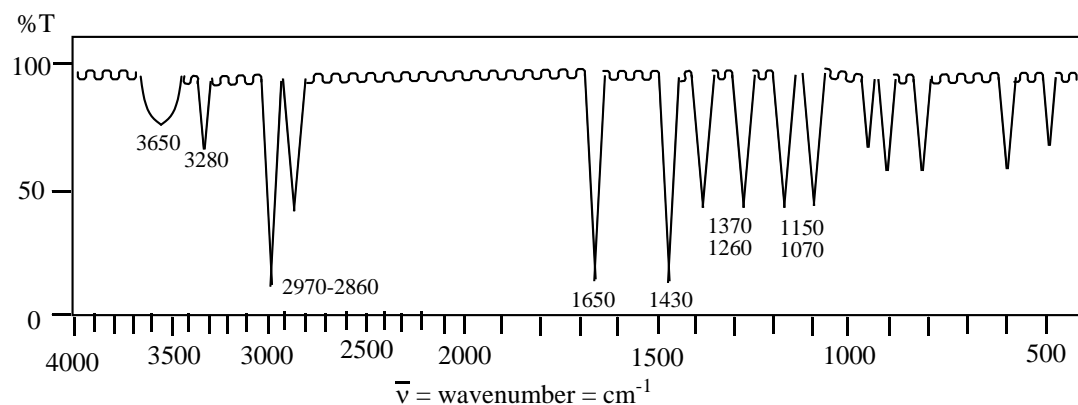
35

IR Functional Group Examples

%T

100

50

0

3640 3360   2960-2860   1660 1630

1380
1420

640

4000   3500   3000   2500   2000   1500   1000   500

$\overline{\nu}$ = wavenumber = cm^{-1}

hexanamide

Typical alkane bands, plus 1° NH$_2$ at ~3640 and ~3360 (stronger); conjugated C=O at ~1660; N-H bend at ~1630, ~640 (sometimes a confusing overtone band appears around 3100)


%T

100

50

0

3080

3300   2960-2860

1550   1470   1240

1380

690

1650

4000   3500   3000   2500   2000   1500   1000   500

$\overline{\nu}$ = wavenumber = cm^{-1}

N-butylpropanamide

Typical alkane bands, plus 2° NH at ~3360 (stronger); N-H bending overtone at ~3080; conjugated C=O at ~1650; 2° N-H bend at ~1550, 690

%T

100

50

0

3650   3280

2970-2860

1650   1430

1370   1150
1260   1070

4000   3500   3000   2500   2000   1500   1000   500

$\overline{\nu}$ = wavenumber = cm^{-1}

N,N-diethylpropanamide

Typical alkane bands, plus maybe wet OH peak? at ~3640 (ideally should be nothing); probably C=O overtone at ~3280; conjugated C=O at ~1650; no N-H bend, various other bands

36

Slide 37

IR Functional Group Examples
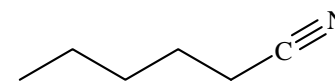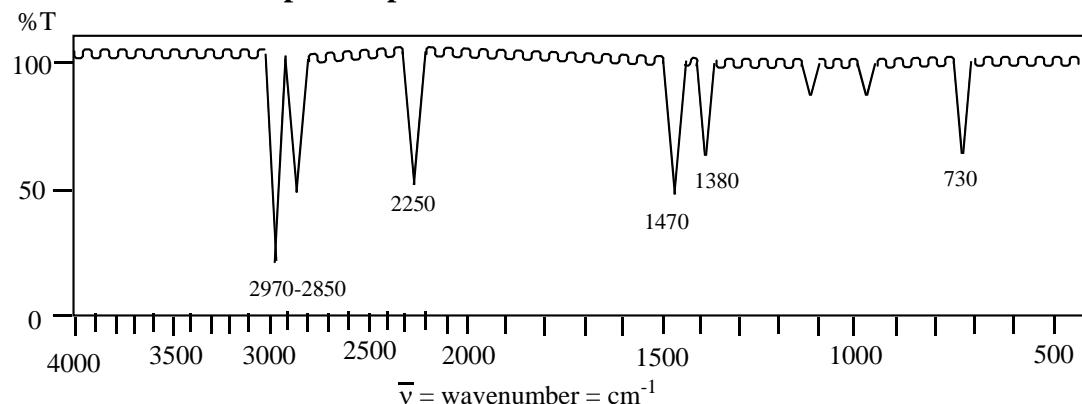
hexanenitrile

The CN triple bond at 2250 is much more intense than most alkyne stretches because of the strong dipole moment. Typical alkane bands, plus CN triple bond at ~2250;
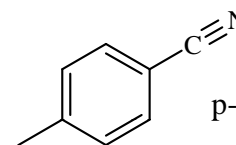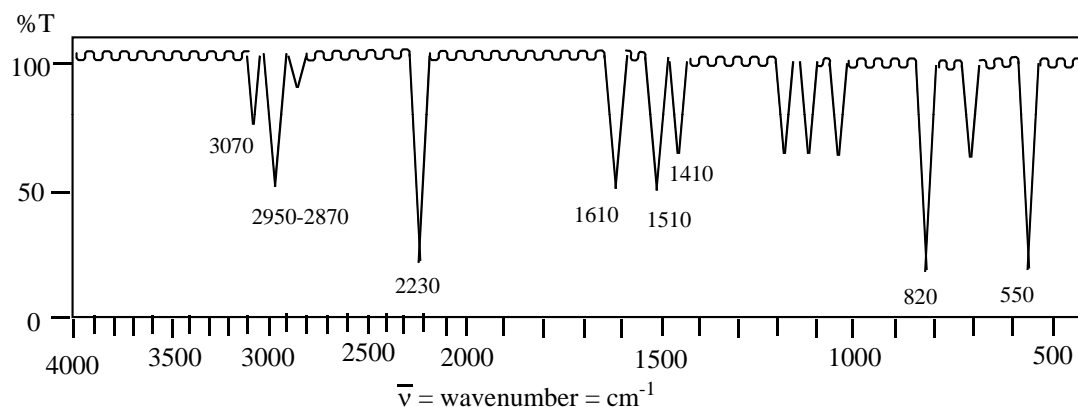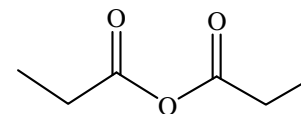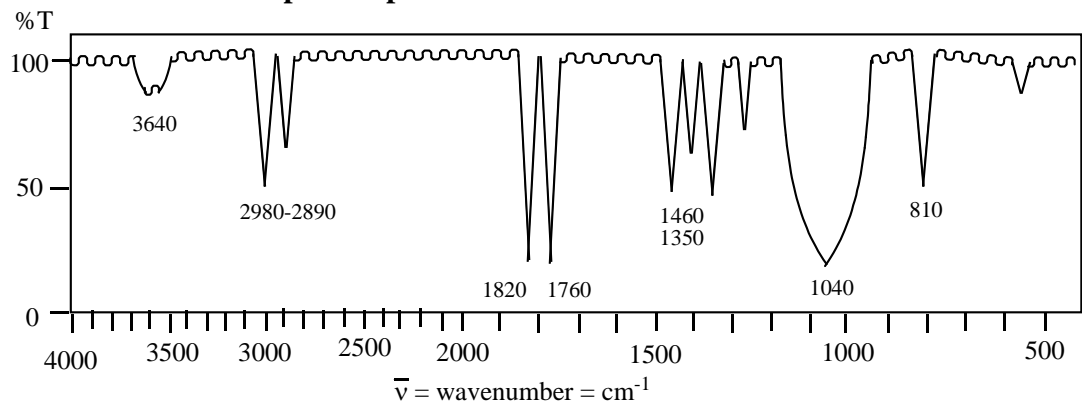

p-methylbenzonitrile

The CN triple bond at 2230 is a tiny bit lower than the saturated nitrile. It is very intense (resonance) and shows para aromatic at 820, also shows typical sp^2 and sp^3 C-H bands.
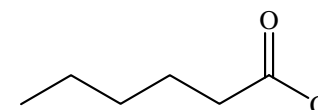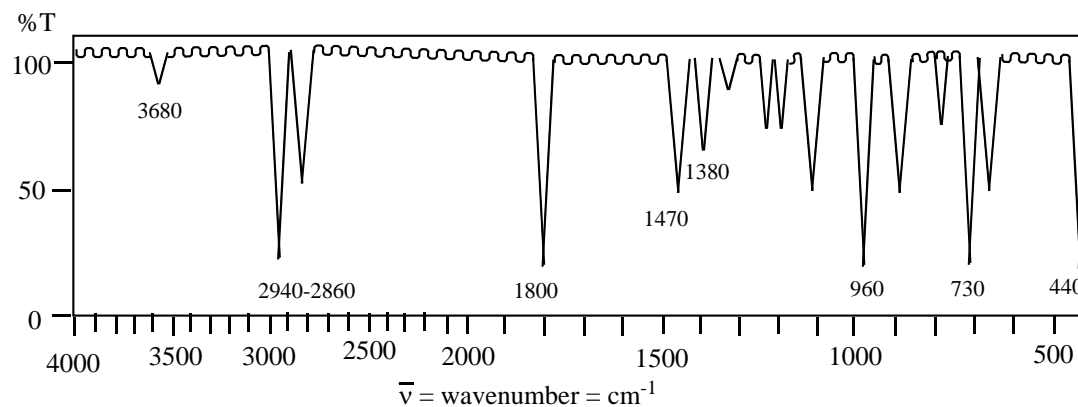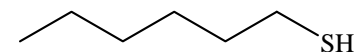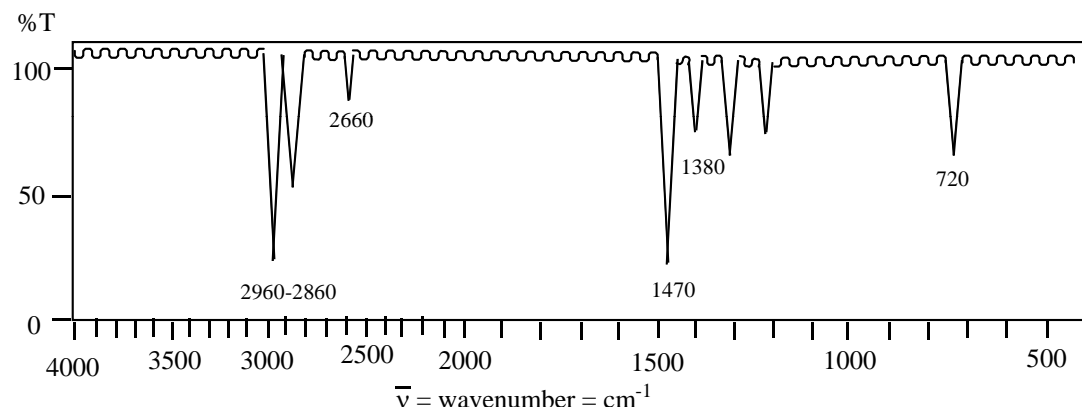

hexanoyl chloride

Typical alkane bands, plus C=O overtone band at ~3680; very high C=O stretch at ~1800; C-Cl stretch at ~730 (maybe)

37

IR Functional Group Examples

%T

3640

2980-2890

1820 1760

1460
1350

1040

810

50

0

4000   3500   3000   2500   2000   1500   1000   500
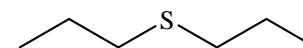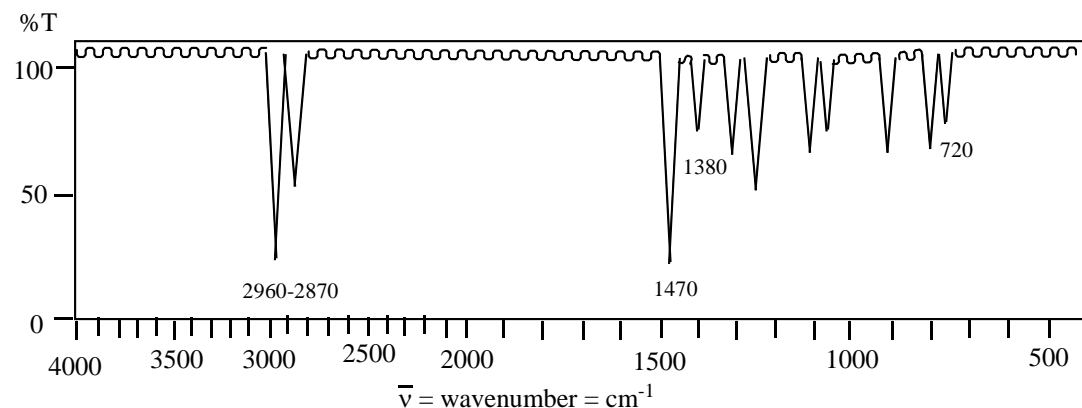
$\overline{\nu}$ = wavenumber = cm^{-1}

propanoic anhydride

Typical alkane and aromatic bands, plus
C=O overtone band at ~3640; two very
high C=O stretching bands at ~1820
and ~1770; very strong acyl C-O band
at ~1040

%T

2660

2960-2860

1380

1470

720

50

0

4000   3500   3000   2500   2000   1500   1000   500
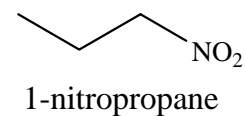
$\overline{\nu}$ = wavenumber = cm^{-1}

1-hexanethiol

Typical alkane bands, plus the thiol
S-H band at 2660 (very small). This
one would be very stinky.
(Remember M+2 peak in the mass
spec $\approx$ 5% of M+ peak)

%T

2960-2870

1380

1470

720

50

0

4000   3500   3000   2500   2000   1500   1000   500

$\overline{\nu}$ = wavenumber = cm^{-1}

dipropyl sulfide

Typical alkane bands, and not much else
(maybe a few more bands than a simple
alkane). This one would be stinky. You
wouldn't have many friends in the lab.
(Remember M+2 peak in the mass spec
$\approx$ 5% of M+ peak)

38

Slide 39

IR Functional Group Examples

%T

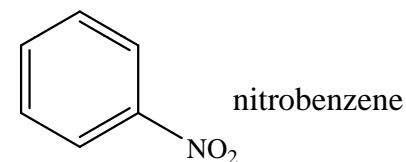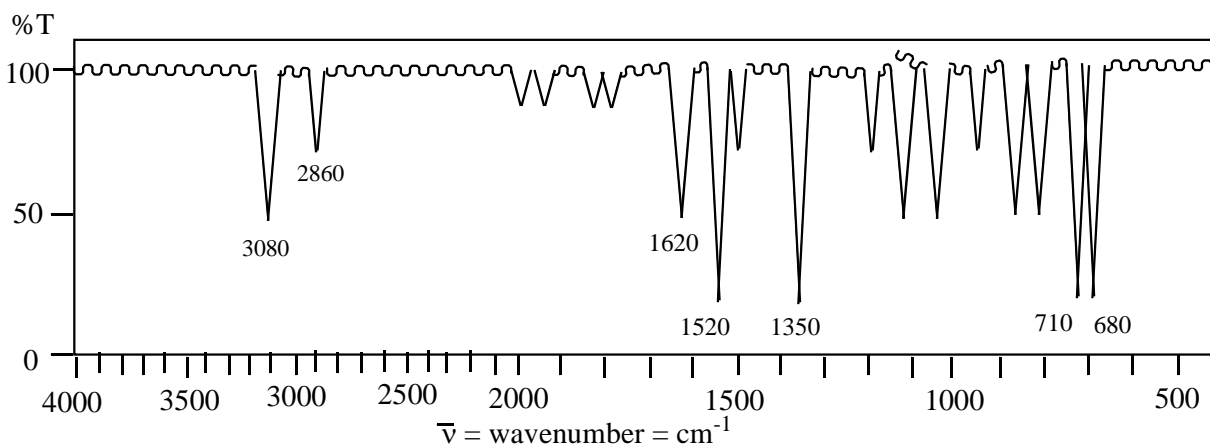Spectrum 1 (1-nitropropane): labeled bands 2940-2980, 1560, 1380; x-axis 4000, 3500, 3000, 2500, 2000, 1500, 1000, 500; $\overline{\nu}$ = wavenumber = cm^{-1}

1-nitropropane
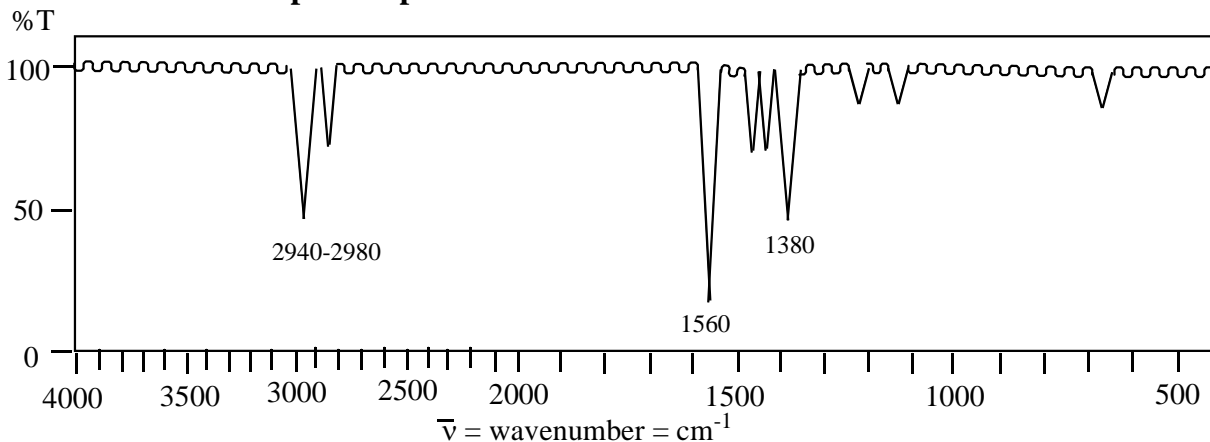
Typical alkane bands, plus R-NO$_2$ asymmetric at ~1540 (stronger); R-NO$_2$ symmetric at ~1380 (weaker). This may be your best indication of the nitro group because N=O pi bonds do not show in the proton or carbon NMR.

Spectrum 2 (nitrobenzene): labeled bands 3080, 2860, 1620, 1520, 1350, 710, 680; x-axis 4000, 3500, 3000, 2500, 2000, 1500, 1000, 500; $\overline{\nu}$ = wavenumber = cm^{-1}

nitrobenzene

Typical alkane bands, plus R-NO$_2$ asymmetric at ~1520 (strong); R-NO$_2$ symmetric at ~1350 (strong). Not sure what the band at 2860 is due to. Also shows onosubstituted aromatic C-H bend at 710 and 680 and C=C stretch at 1620.

These examples all have only 1 functional group. IR spectra of molecules with multiple functional groups become more difficult to interpret. IR bands can overlap and hide one another, or even disappear. Functional groups can interact in unexpected ways having unexpected bands (overtones, combination and difference bands). IR won't solve our structures by itself, but can provide important functional group clues.

Our next lectures will cover NMR (H, C and 2D). This is a much larger and more useful topic for solving organic structures. We will need more than one lecture to get through all of that material.