IR absorption spectroscopy

► IR spectroscopy - an analytical technique which helps determine molecules structure

►When a molecule absorbs IR radiation, the vibrational energy of the molecule increase!

► The amount of light absorbed by the sample depend on the incident radiation wavelength (wavenumber).

► IR spectroscopy measures the *bond vibration frequencies* in a molecule and is used to determine the *functional groups* *from the molecule.*

► **The frequency of the absorbed radiation matches the vibration frequency of the bond or group.** (M*olecules absorb only those frequencies* that are characteristic to their structure).

► A vibrational mode in a molecule is "**IR active**," only it is associated with *changes of the dipole moment*.
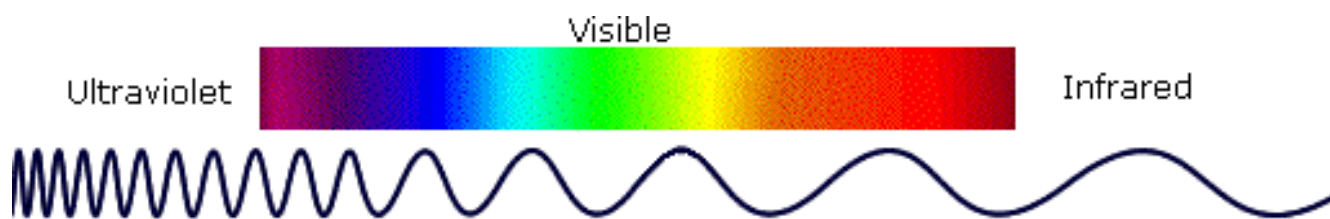
The IR domain

► Just above red in the visible region (wavelength > 800 nm).

► Near IR: 0.8 - 2.5 µm   Medium IR: 2.5 - 25 µm   Far IR: 25 - 300 µm

► More common units are cm^{-1} (wavenumbers): the reciprocal of the wavelength in centimeters.

► Near IR: 12.500 - 4000 cm^{-1} Medium IR: 4000 - 400 cm^{-1} Far IR: 400 - 33 cm^{-1}

► Wavenumbers are proportional to frequency and energy!

For analysis of organic compounds radiation from medium IR range is used:
Wavelemgth: 2.500 nm - 16.000 nm;
Wavenumbers: 4000 cm^{-1} - 625 cm^{-1};
Frequencies: $1.9 \cdot 10^{13}$ Hz - $1.2 \cdot 10^{14}$

IR absorption

► *Only certain value for the molecule energie levels are allowed (the energy are quantified).*
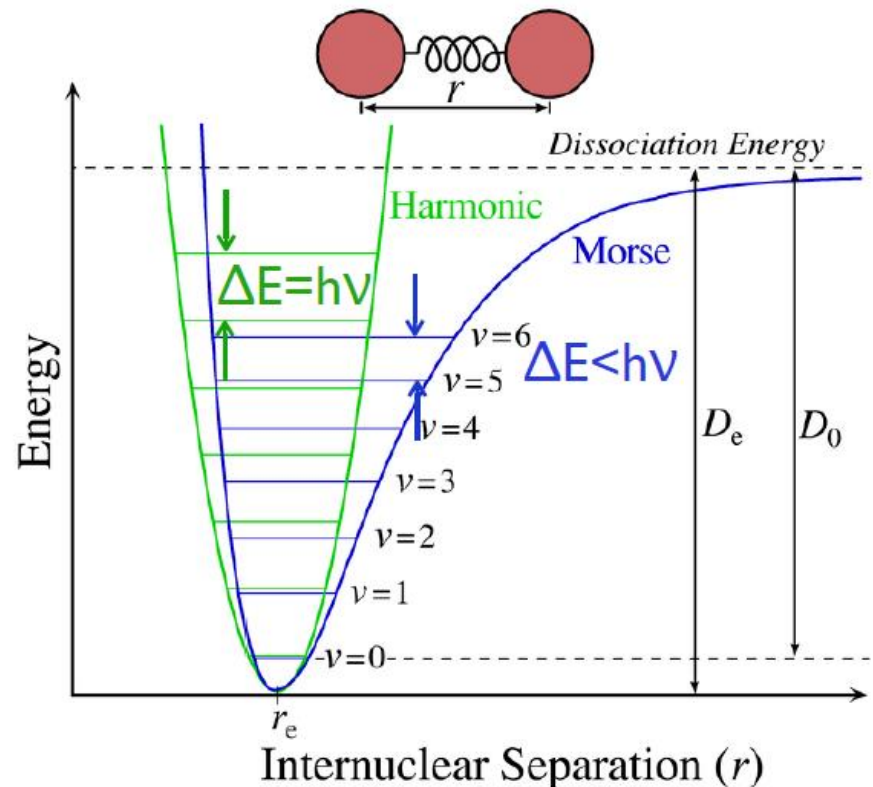
Energy of vibrational levels:
$$E_v = (v + \frac{1}{2})hc\overline{v}_0 - x_e(v + \frac{1}{2})^2 hc\overline{v}_0$$

At room temperature, most molecules are in the lower vibrational level (ground state vibrational level) characterized by a vibrational quantum number v = 0:

$$E_0 = \frac{1}{2}hc\overline{v}_0 - x_e \frac{1}{4}hc\overline{v}_0$$

A molecule that absorbs IR radiation chage its vibrational state, therefore *a change in the vibrational energy* appears.

► *Only radiation with certain energies will excite molecular vibrations* (the energy radiation must match the difference between levels).


Dissociation Energy

Harmonic

Morse

$\Delta E = h\nu$

$\Delta E < h\nu$

$v=6$
$v=5$
$v=4$
$v=3$
$v=2$
$v=1$
$v=0$

D_e D_0

Energy

r_e

Internuclear Separation (r)

► Vibrational frequencies for stretching bonds in molecules are related to the strength of the chemical bonds and the masses of the atoms.

$$\overline{v}_0 = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}}$$

μ - reduce mass

*The interaction between molecule and electric field of IR radiation appear only then the induce vibration of molecule involve **the oscillation** of **the dipole moment** (μ)!*

+q ←—— r ——→ −q

$$\mu = q\boldsymbol{r}$$
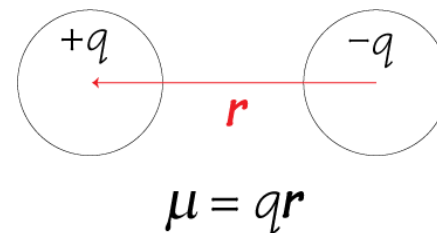
► The amount of IR radiation absorbed is proportional to the square of the rate of change of the dipole during the vibration.

► There must be a **change in the dipole moment** of the molecule as a result of a molecular vibration.

► The symmetry of the molecule will also determine whether the IR radiation can be absorbed.

► Symmetric vibrations (from symmetric molecules) do not absorb IR radiation since there is **no change in dipole moment**.

IR absorption = change in dipol moment!

$$\mu = \sum_i q_i \cdot r_i$$

μ - dipole moment, q_i – electric charge, r_i -coordinate

Taylor series:
$$\vec{\mu} = \vec{\mu}_0 + \sum_{k=1}^{3N-6} \left[\frac{\partial \vec{\mu}}{\partial Q_k} \right]_0 Q_k + \dots$$

μ → *total* dipole moment of vibrating molecule
μ_0 → equilibrum dipole moment, Q_k → normal coordinate

$$W = \vec{\mu}\vec{E}_0 \neq 0 \implies \left[\frac{\partial \vec{\mu}}{\partial Q_k} \right]_0 \neq 0$$

W - interaction energy,
E_0 - electric field of incident radiation

The interaction energy is **non zero** when **at least for one vibration** there is a variation of the molecular dipol moment.

The molecule will absorb electromagnetic radiation with ν_k frequency **only if there is a change of dipole moment during vibration** (with ν_k frequency).

Quantum mechanic: $\langle \mu_t \rangle = \int \Psi^*_{final} \cdot \vec{\mu} \cdot \Psi_{init} \cdot d\tau \neq 0$ in order to have interaction!

Ψ_{final}, Ψ_{init} - initial and final wave functions

Selection rule:

harmonic oscilator: $\boxed{\Delta v = v_{final} - v_{init} = 1}$ v - vibrational quantum number
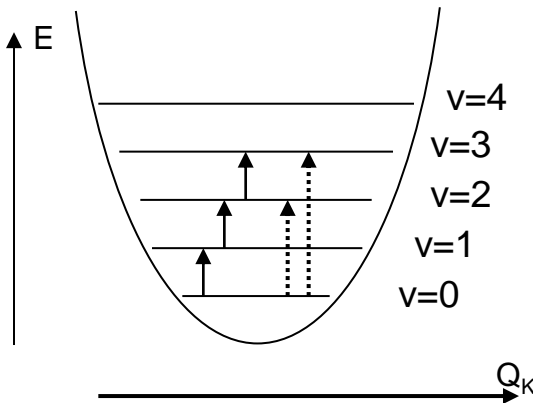
anharmonic oscilator: $\boxed{\Delta v = v_{final} - v_{init} = 1, 2, ...}$

For a real molecule there are two types of transitions:

Fundamental transitions: caused by the selection rule of $\Delta v = 1$ (strictly valid only for harmonic potentials)

Overtones transitions: caused by the selection rule $\Delta v = 2, 3, ..$ (because of the anharmonicity)

IR spectrum:

► *fundamental* bands $\Delta v = 1$

► *overtone* bands $\Delta v = 2, 3,...$

► *combination* bands: more vibrational quantum number *change simultaneous* with one or more units

only for polyatomic molecules
$\Delta v_k \geq 1$ $k = 2,3, \dots$

The intensity of the overtone bands are typically only 1 - 5 % of the fundamental!

The intensity of the combination band are usually very small (< 1%).
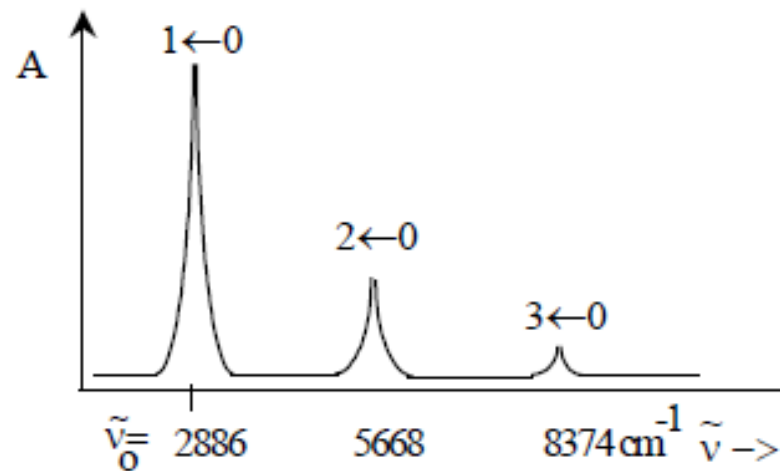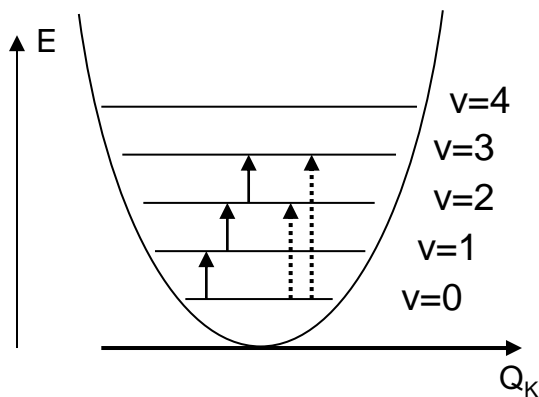
Vibrational energy level of a polyatomic molecule with **k different normal modes** are characterized by **k quantum numbers**.

H—C≡C—H 3372.8 cm^{-1}

H—C≡C—H 1974.3 cm^{-1}

H—C≡C—H 3294.8 cm^{-1}

H—C≡C—H 612.9 cm^{-1}

H—C≡C—H 730.3 cm^{-1}
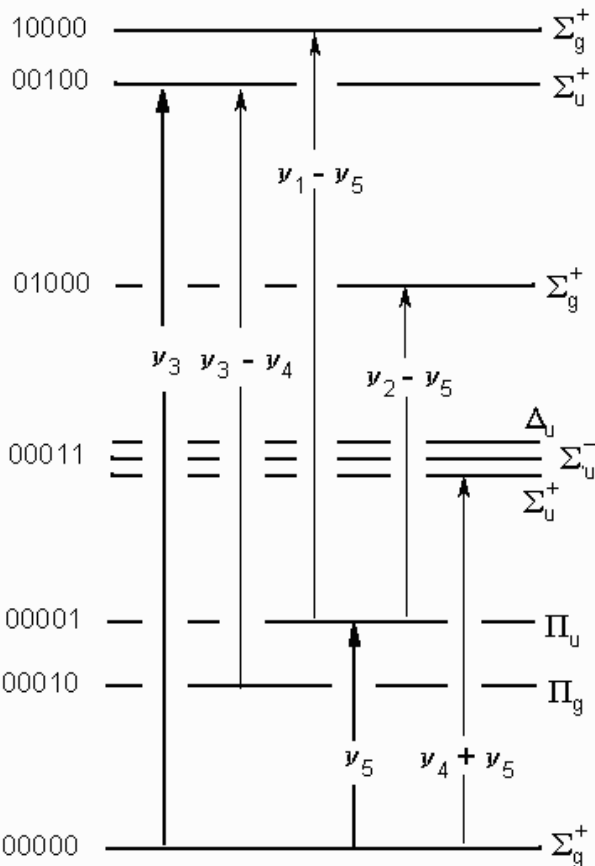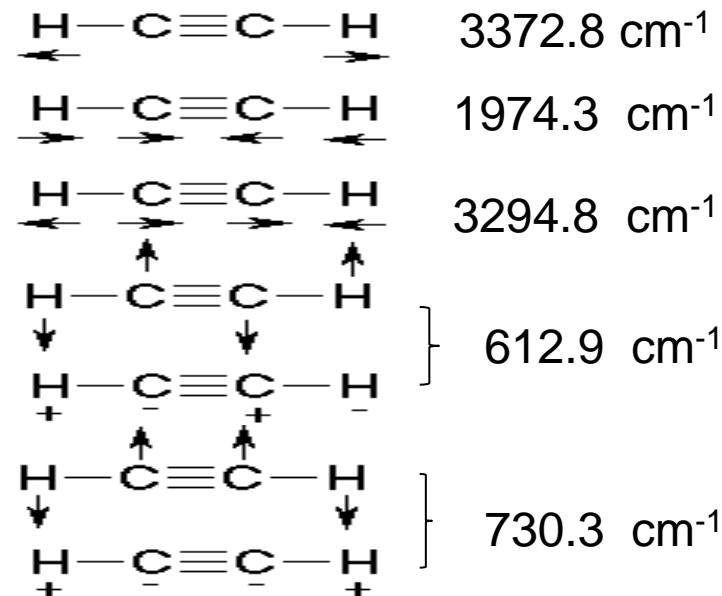
Ex.: H_2C_2 (linear) (3N-5 = 7 normal modes)

Vibrational energy level of H_2C_2 (5 different normal modes) are characterized by 5 quantum numbers (one for each normal mode):

Vibrational ground state (zero point vibrational energy):
   (00000) (all $v_i = 0$) (i = 1,2,3,4,5)

Vibrational excited levels: (10000,01000,00100, 00010, 00001) (one $v_i = 1$)
Vibrational overtones levels : (20000, 03000, 00020,...) (one $v_i > 1$)
Vibrational combination levels: (00011, 10100, …) (more than one $v_i \neq 0$)

https://web.nmsu.edu/~snsm/classes/chem435/Lab9/

The figure shows an IR transmittance spectrum with a chemical structure (polystyrene repeat unit) and combination band labels:

- $980 + 965 = 1945 \text{ cm}^{-1}$
- $980 + 905 = 1885 \text{ cm}^{-1}$
- $965 + 842 = 1807 \text{ cm}^{-1}$
- $905 + 842 = 1748 \text{ cm}^{-1}$
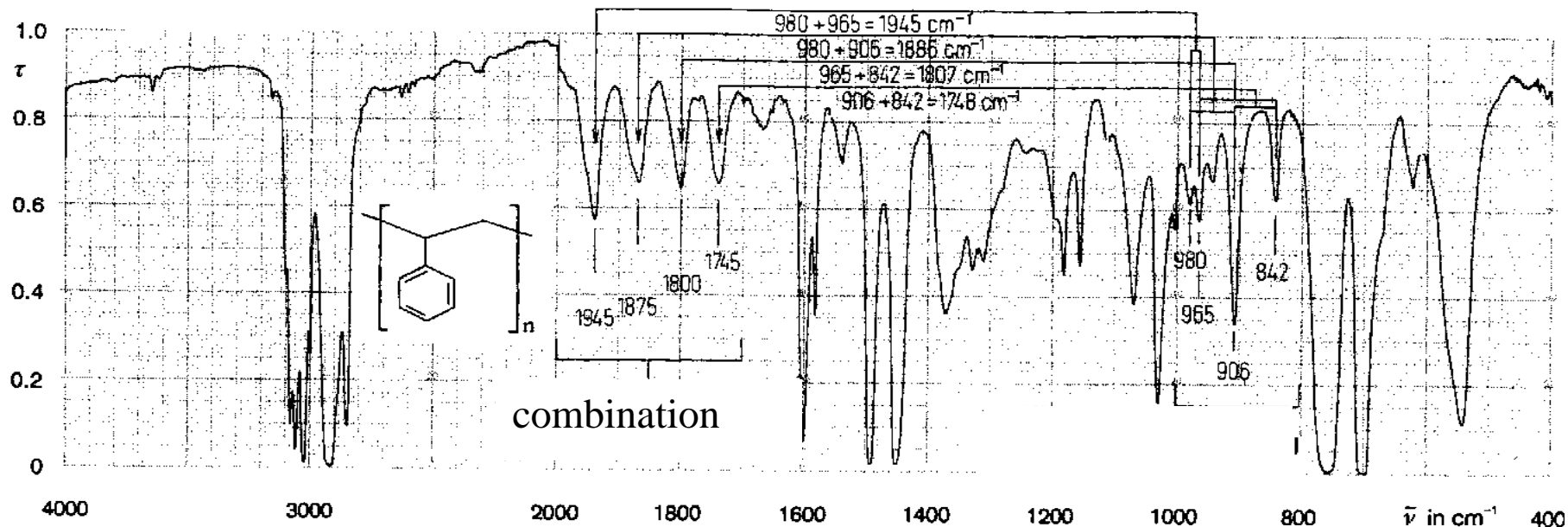
combination

Combination bands involve changes in vibrational quantum numbers of more than one normal mode.

Theoretically these transitions are forbidden by harmonic oscillator selection rules, but are observed in vibrational spectra of real molecules due to anharmonic couplings of normal modes.

Combination bands typically have weak spectral intensities, but can become quite intense in cases where the anharmonicity of the vibrational potential is large.

There are *two types of combination bands*, due to: difference bands and
sum bands

► Difference bands

A difference band, occurs when both initial and final states are excited vibrational states. (two frequencies couple such that $v_3 = v_1 - v_2$)

Example : $010 \rightarrow 100 \qquad \sim (v_1 - v_2)$

In this case (one quantum transfer), the frequency of the difference band is approximately equal to the difference between the fundamental frequencies.

The difference is not exact because there is anharmonicity in both vibrations.

The term "difference band" also applies to cases where more than one quantum is transferred, such as $020 \rightarrow 100 \qquad \sim (v_1 - 2v_2)$

Difference bands are seldom observed in conventional vibrational spectra, because they are forbidden transitions according to harmonic selection rules, and because populations of vibrationally excited states tend to be quite low.

► Sum bands

A band, occurs when two or more vibrational excited states are excited simultaneously. (two vibrational frequencies may couple to produce a new frequency $v_3 = v_1 - v_2$)

Example: 000 → 101   ~$(v_1 + v_3)$;
        001 → 012   ~ $(v_2 + v_3)$

The frequency of a sum band is slightly less than the sum of the frequencies of the fundamentals, again due to anharmonic shifts in both vibrations.

Sum bands are harmonic-forbidden, and thus typically have low intensities relative to fundamental bands.

Sum bands are more commonly observed than difference bands in vibrational spectra
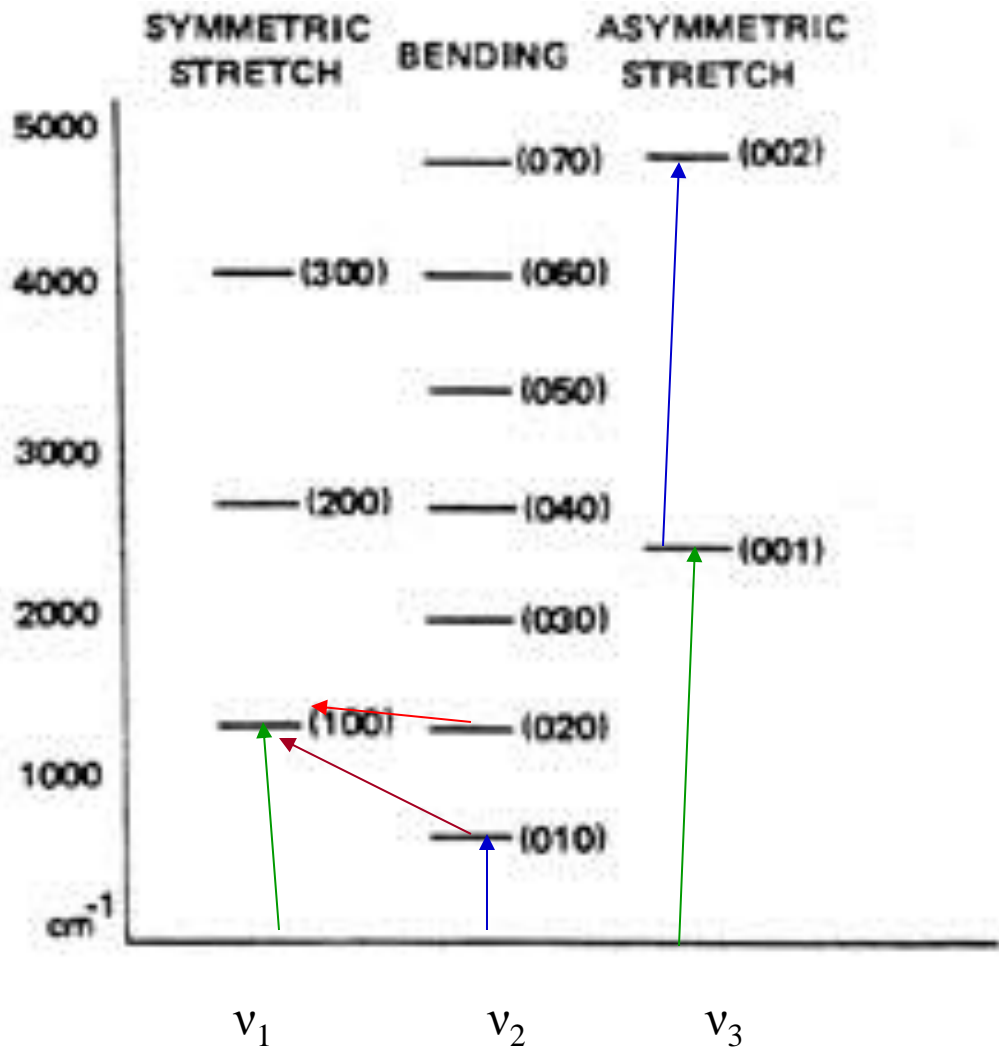
Difference transitions:

$010 \rightarrow 100$ ~ $(\nu_1 - \nu_2)$

$020 \rightarrow 100$ ~ $(\nu_1 - 2\nu_2)$

Sum transition:

$000 \rightarrow 101$ ~ $(\nu_1 + \nu_3)$

$001 \rightarrow 012$ ~ $(\nu_2 + \nu_3)$

Vibrational coupling
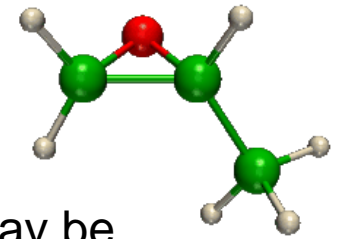
The energy of a vibration, (the position of its absorption peak) may be influenced by (or coupled with) other vibrators in the molecule.

A number of factors influence the extent of such coupling.

1. Coupling between two stretching vibrations occurs only when there is an atom common to the vibrating groups. (Coupling is strong!)

2. Coupling between two bending vibrations requires a common bond between the vibrating groups.

3. Coupling between a stretching and a bending vibrations can occur if the stretching bond form one side of the angle that varies in the bending vibration.

4. Interaction is greatest when the coupled groups have individual energies that are approximately equal.

5. Little or no interaction is observed between groups separated by two or more bonds.

6. Coupling requires that the vibrations be of the same symmetry species.

Rules of vibrational coupling:

Coupling of different vibrations shifts frequencies
 Energy of a vibration is influenced by coupling

Coupling likely when
– common atom in stretching modes
– common bond in bending modes
– similar vibrational frequencies
– common bond in bending+stretching modes

Coupling not likely when
– atoms separated by two or more bonds
– symmetry inappropriate

Ex:
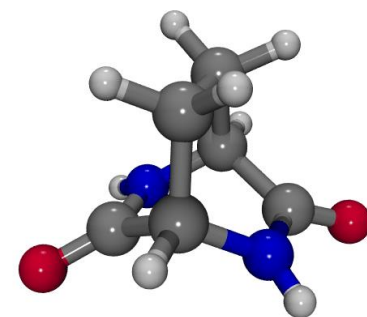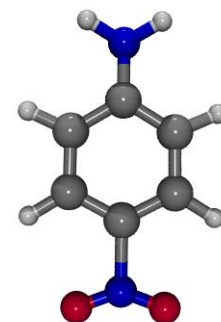
The C=O=C assimetrical stretching vibration due to coupling is at $\nu' = 2330$ cm^{-1}

The C=O stretching vibration (no coupling occurs) is at $\nu' = 1700$ cm^{-1}

Interaction is greatest when the coupled groups have individual energies that are approximately equal

- The position of an absorption peak corresponding to a given organic functional group varies due to coupling:
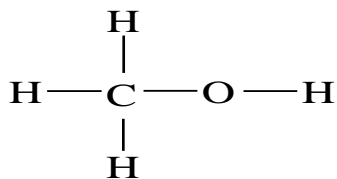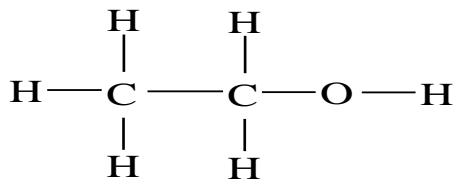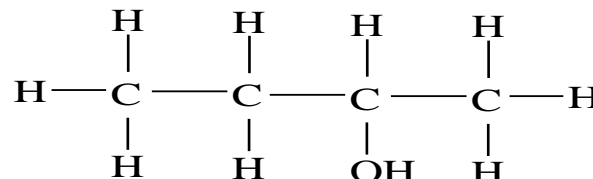
1034 cm^{-1} 1053 cm^{-1} 1105 cm^{-1}

These variations result from a coupling of the C - O stretching with adjacent C - C stretching or C - H vibrations.

Diatomic molecule (linear!) **:** N = 2 → 3N - 5 = 1 → one normal mode (1 stretching)

Symmetric molecules are IR *inactive* → the dipole moment does not change during vibration

$$k = 4 \cdot \pi^2 \cdot c^2 \cdot \mu \cdot \bar{v}^2$$

$$\bar{v} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}}$$

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

Molecule	Wavenumber [cm^{-1}]	Force constant [N/cm]	Active
H$_2$	4159.2	5.2	Raman
D$_2$	2990.3	4.3	Raman
HF	3958.4	8.8	IR
HCl	2885.6	4.8	IR
HI	2230.0	2.9	IR
CO	2143.3	18.7	IR
NO	1876.0	15.5	IR
F$_2$	892.0	4.5	Raman
Cl$_2$	556.0	3.2	Raman
Br$_2$	321.0	2.4	Raman
I$_2$	213.4	1.7	Raman
O$_2$	1556.3	11.4	Raman
N$_2$	2330.7	22.6	Raman
Li$_2$	246.3	1.3	Raman
Na$_2$	157.8	1.7	Raman
NaCl	378.0	1.2	IR
KCl	278.0	0.8	IR

Each peak (*fundamental* band) in a vibrational spectrum corresponds to a normal mode.

Linear molecules with N atoms:

$3N-5$ normal modes: $N-1$ stretching modes

$2N-4$ bending modes

Nonlinear molecules with N atoms (non-cyclic):

$3N-6$ normal modes: $N-1$ stretching modes

$2N-5$ bending modes

Diatomic molecules (linear)   - 1 normal mode (1 stretching; no bending)

$N = 2 \rightarrow 3N - 5 = 1$

Linear tri-atomic molecules   - 4 normal modes (2 stretching and 2 bending)

   (CO_2, COS) $N = 3 \rightarrow 3N - 5 = 4$

Nonlinear tri-atomic molecules - 3 normal modes (2 stretching and 1 bending)

   (H_2O) $N = 3 \rightarrow 3N - 6 = 3$

CO$_2$ molecule:

    linear and symmetric: N = 3 → 3N - 5 = 4 normal modes (2 stretchings)

► Symmetric stretching is not IR active (because **there *isn't a dipole moment variation*)**.

► Asymmetric stretching is IR active (**determine the change of the dipol moment**)

► Bending vibration is IR active (**determine the change of the dipol moment**)
   Bending vibration is double degenerate (same energy is necessary to oscilate in the two perpendicular planes to the molecular axis)

O   C   O
ν_3 - asymmetric
stretching (2349 cm^{-1})

O   C   O
ν_1 - symmetric
Stretching (1330 cm^{-1})

O   C   O
ν_2-symmetric
bending (667,3 cm^{-1})

O   C   O

3000   2500   2000   1500   1000   500

cm -1
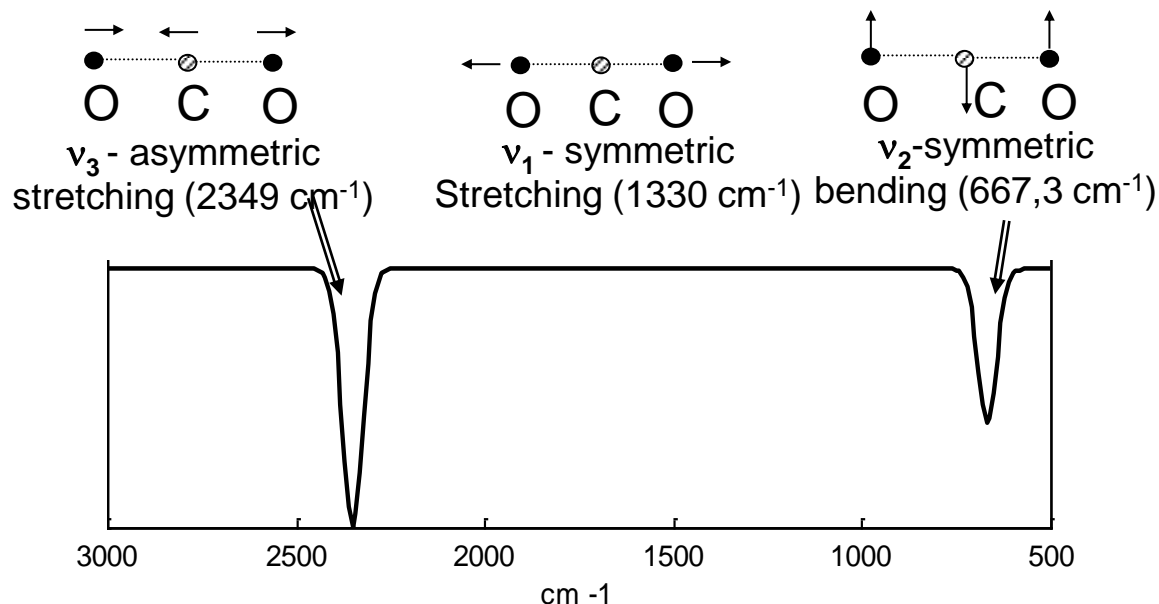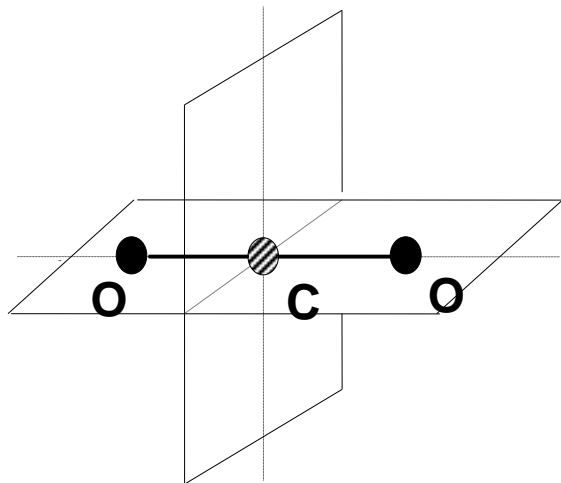
Convention rule:
Vibrations are note descending, firstly symmetric vibrations, then asymmetric vibrations
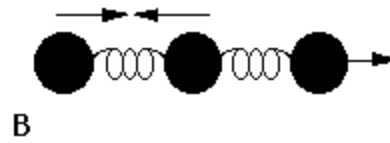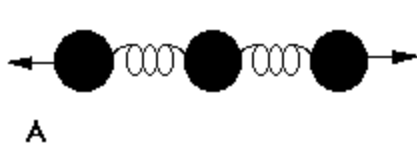
CO_2 vibrations
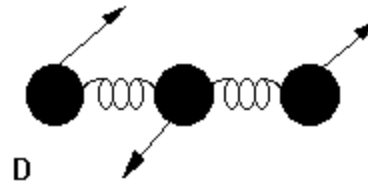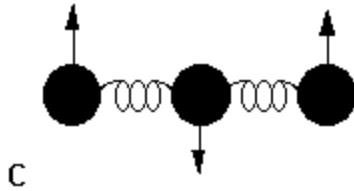
► The CO_2 vibrational modes, are responsible for the "*greenhouse*" effect in which heat radiated from the earth is absorbed (trapped) by CO_2 molecules in the atmosphere. The arrows indicate the directions of motion.

(A) – symmetric stretching

(B) – asymmetric stretching

(C), (D) - bending modes
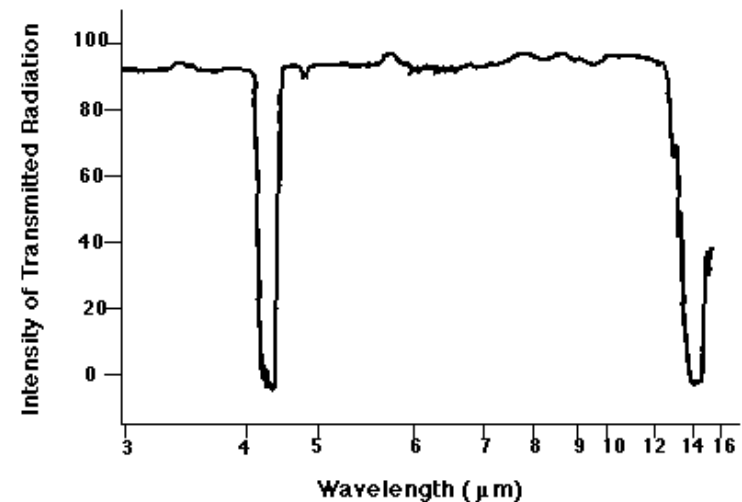
Nitrous Oxide, N_2O - Infrared Absorptions

bond stretching

bond bending

Vibrational Spectra

Transmittance (%)

$\triangle N2O$

Wavenumber (cm-1)

Molecules and Spectra by CAChe Molecular Modeling
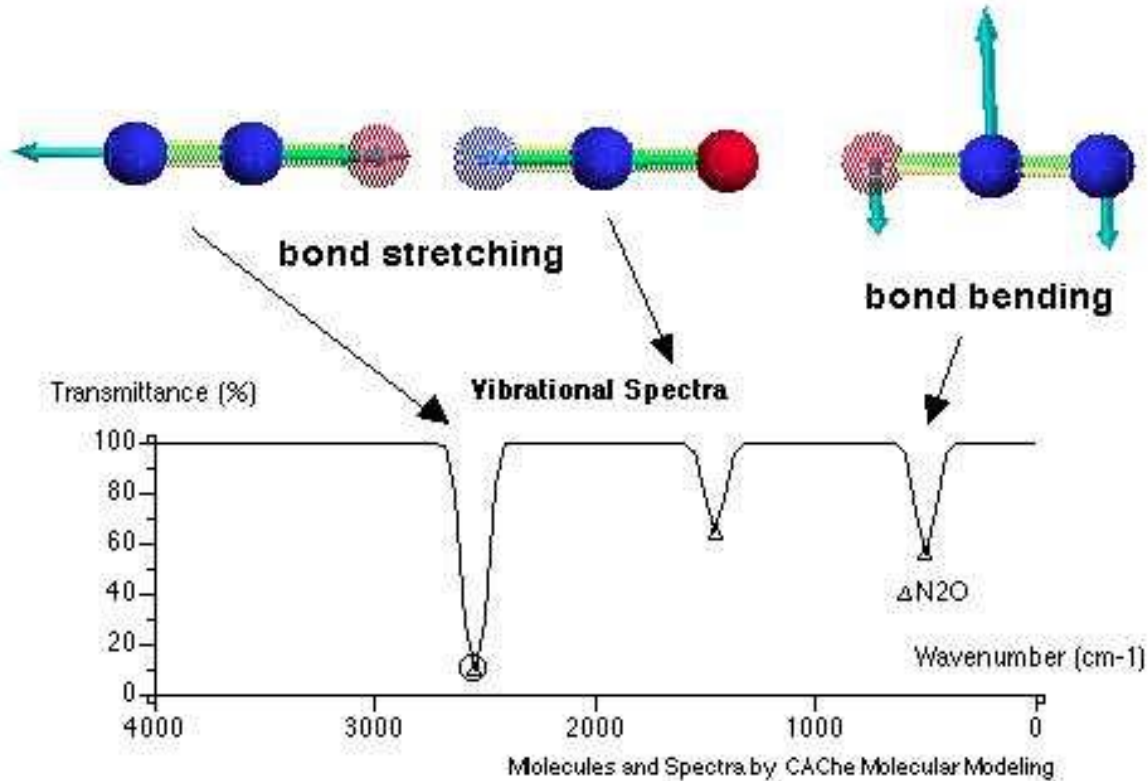
- linear,

- asymmetric

$N = 3 \rightarrow 3N - 6 = 3$ vibrations
(2 stretchings)

All three vibrations determine the change of the dipol moment, therefore all are IR active.

H_2O molecule: nonlinear, rotation axis, permanent dipol moment

$N = 3 \rightarrow 3N - 6 = 3$ vibrations
(2 stretchings)

Vibrations:

ν_1 - symmetric stretching
ν_3 - asymmetric stretching
ν_2 - bending (symmetric)

ν_3- asymmetric (3755,8cm^{-1})

ν_1-symmetric (3651,7cm^{-1})

ν_2- symmetric (1595cm^{-1})

Water - Infrared Absorptions

bond stretching

bond bending

Transmittance (%)

Vibrational Spectra

Δ water

Wavenumber (cm-1)

Molecules and Spectra by CAChe Molecular Modeling
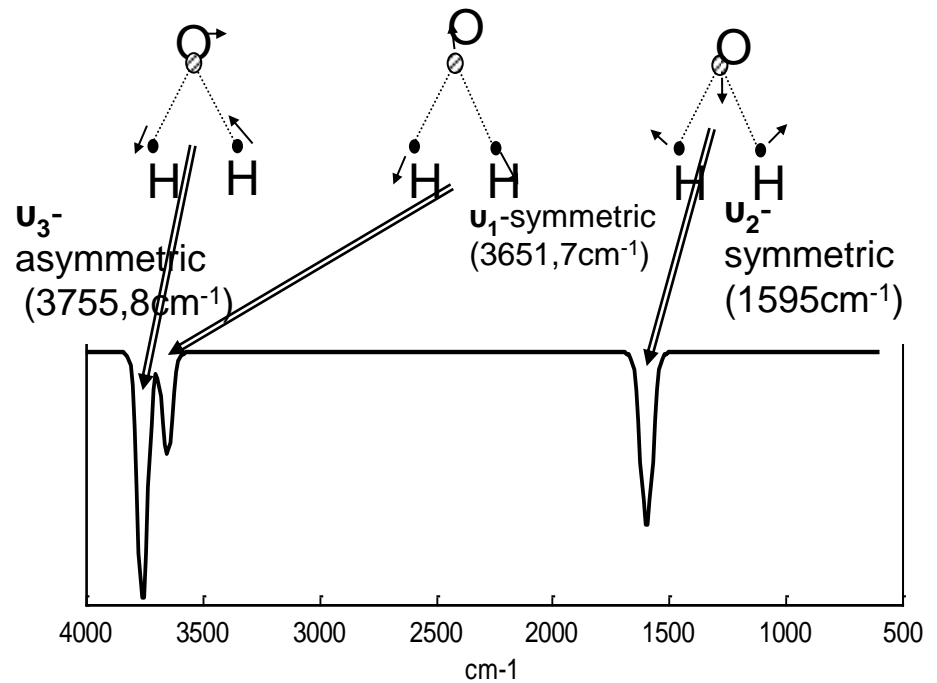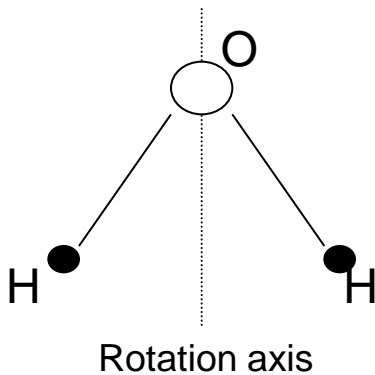
Rotation axis
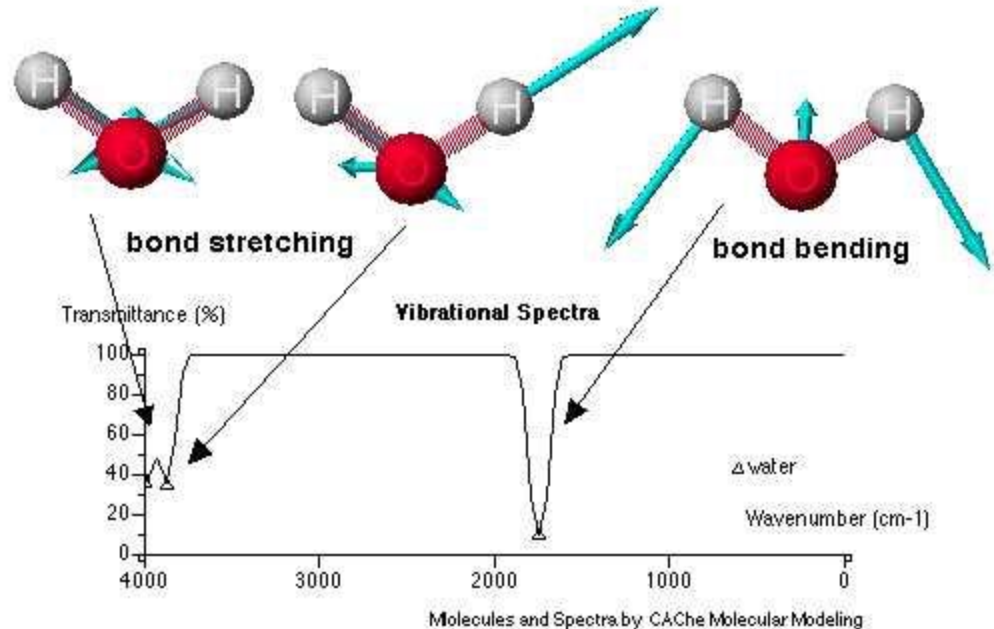
Hot bands

►A **hot transition** is a fundamental transition with $\Delta v = 1$ that start from an excited level! ($v_{initial} \neq 0$)

(a transition between two states of a single normal mode of vibration, neither of which is the overall ground state).

In IR or Raman spectroscopy "hot transitions" are known as **hot bands**, and specifically refer to those transitions for a particular vibrational mode which arise from a state containing thermal population of another vibrational mode.

Example (for a molecule with 3 normal modes):

The transition $001 \rightarrow 101$ is a hot band (the initial state has one quantum of vibrational excitation in the v_3 mode)

► At room temperature mostly molecules are in the ground state.

► At high temperature (150-200°C) we can not neglect the molecule population from lowers vibrational levels (< 800 cm⁻¹).

► The population of vibrational levels respect the Boltzmann distribution:

$$N_v = N_0 e^{-\frac{E_v}{kT}} = N_0 e^{-\frac{h\nu}{kT}} = N_0 e^{-\frac{hc\bar{\nu}}{kT}}$$
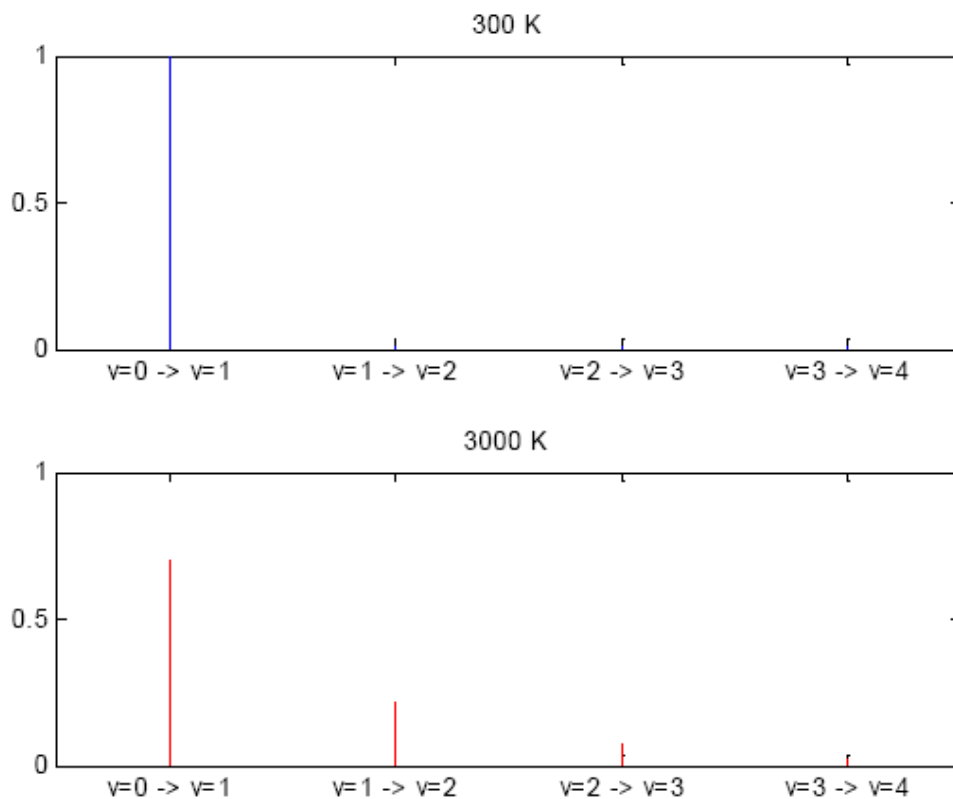
Fig. 1. Vibrational Boltzmann distribution for 300 K and 3000 K.

In the *harmonic approximation* all vibrational quantum levels are **equally spaced**, so hot bands would not be distinguishable from so-called "fundamental" transitions arising from the overall vibrational ground state.

$$E_v = hc\overline{v}(v + \frac{1}{2})$$
$$\overline{v}_{12} = \frac{E_2 - E_1}{hc} \qquad \overline{v}_{01} = \frac{E_1 - E_0}{hc}$$
$$\boxed{\overline{v}_{12} = \overline{v}_{01}}$$

Vibrations of real molecules always have some anharmonicity, and the energy levels **are not equally spaced**, so hot bands could be observed in vibrational spectra.

$$E_v = (v + \frac{1}{2})hc\overline{v}_0 - x_e(v + \frac{1}{2})^2 hc\overline{v}_0$$

$$\boxed{\overline{v}_{12} < \overline{v}_{01}}$$

Transition from an excited **level (**termal populated) (v = 1 → v = 2)
$$\overline{v}_{12} = \overline{v}_0(1 - 4x_e)$$

Transition from fundamental level (v = 0 → v = 1)
$$\overline{v}_{01} = \overline{v}_0(1 - 2x_e)$$

Hot bands appear at lower frequencies (exhibit red shifts) than the corresponding fundamental transitions.

The magnitude of the observed shift is correlated to the degree of anharmonicity in the corresponding normal modes.

Hot band

overtone bands

fundamental band

v=3
v=2
v=1
v=0
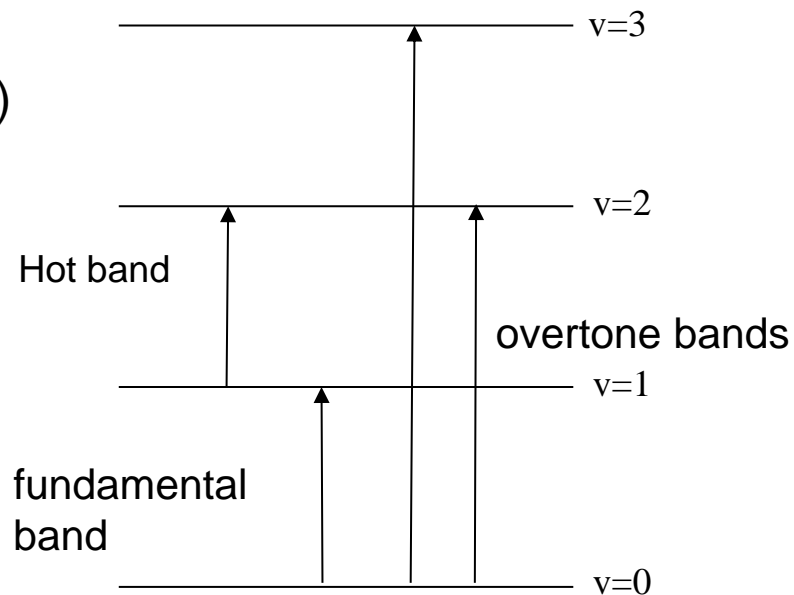
► Hot band frequencies is **lower** than fundamental corresponding band.

$$\bar{v}_{12} = \bar{v}_{01} - 2\bar{v}_0 x_e$$
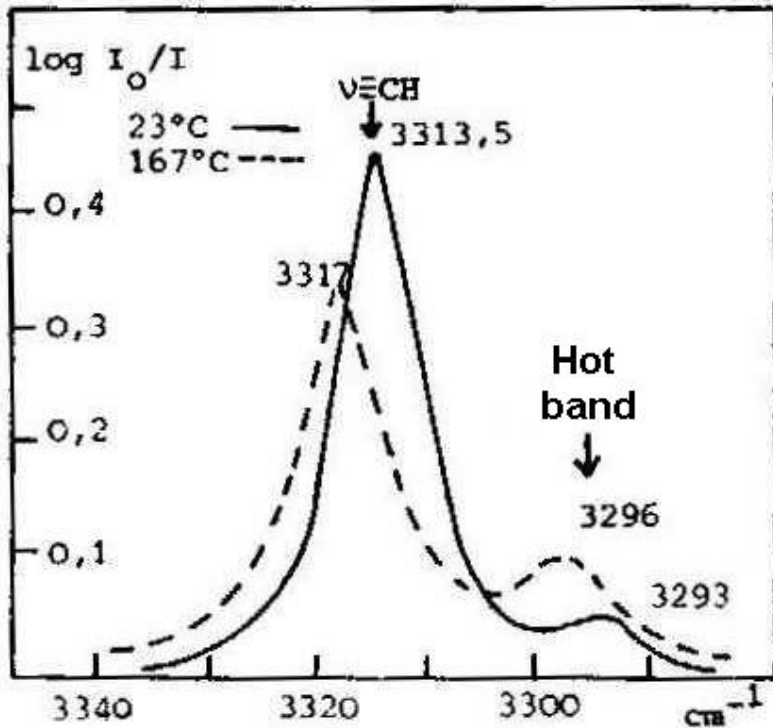
Hot band: a little asymmetry to lower wavenumbers of fundamental bands:

Hot band identification: when temperature rises, the hot band intensity increases due to increasing of the thermal population of excited level (v = 1).

Both 3.313 cm^{-1} and 3.293 cm^{-1} are due to the stretching vibration of $\equiv$C-H group
3.313 cm^{-1} fundamental band
3.293 cm^{-1} hot band (shoulder)

Fermi Resonance

► If a *fundamental vibration and an overtone* (or a combination of other vibrations) in a molecule are *comparable* in frequency, they **interact** by the anharmonic part of the Hamiltonian when allowed by symmetry.

►The results are *frequency shifts* and mixings of the wavefunctions with corresponding changes in the IR and Raman activities.

► Fermi resonance can occur when the frequency of one of the fundamental vibrations in a molecule is close to the frequency of overtone of other vibration of the molecule (*oscillations are mechanically coupled* each other).

► Fermi resonance most often occurs between normal and overtone modes, which are often nearly coincidental in energy.

► Fermi resonance determines *two effects*.

   - the high energy mode shifts to higher energy and the low energy mode shifts to still lower energy.

   - the weaker band gains intensity (becomes more allowed) and the more intense band decreases in intensity.

► The interaction between between a fundamental and an overtone vibrations (Fermi Resonance) appear only if the symmetries of the involved vibrations are the same.

► Usually Fermi Resonance interactions go unnoticed, but occasionally they produce "unexpected" doubling of important functional group bands.

► In order for Fermi Resonance to occur it requires that the fundamental band producing the overtone be relatively intense, and to be at a frequency approximately half that of the fundamental with which the overtone interacts

► In interpreting IR spectra it is useful to be aware of the possibility of Fermi Resonance.

► If you see a band that is "unexpectedly" two peaks you might look to see if there is a strong adsorption at about one half the frequency.

$h\nu$ $2h\nu'$ $h\nu'$

$h(\nu+x)$ $2h(\nu-x)'$
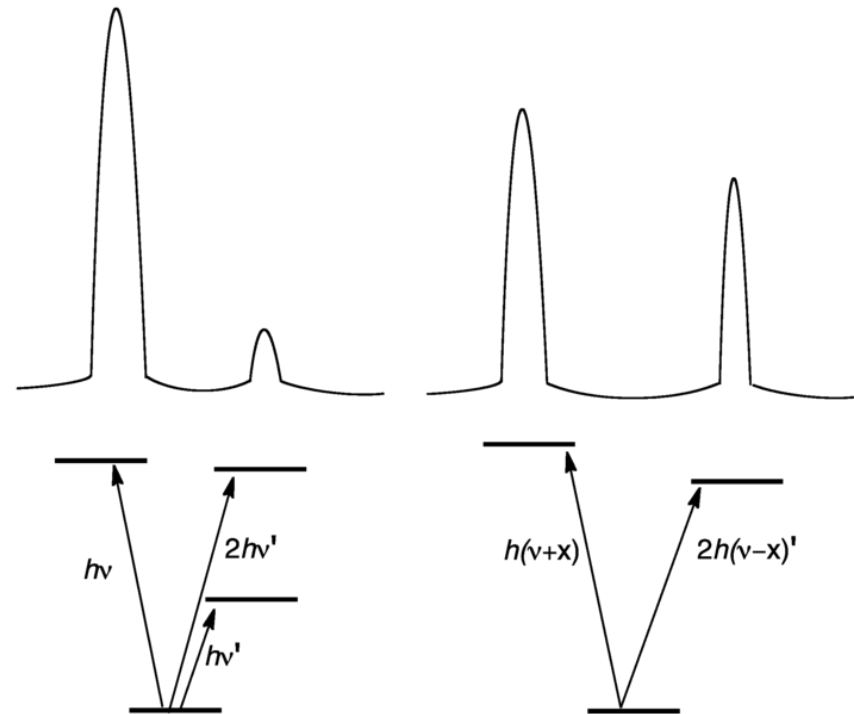
Ex.:

CO$_2$

The symmetric stretching vibration (1330 cm^{-1}) of CO$_2$ appears as **a doublet**. This splitting is caused by the first overtone of the deformation frequency (2 x 667 cm^{-1} = 1334 cm^{-1}).

As a result, the spectrum has two bands at 1286 cm^{-1} and 1389 cm^{-1}.

Cl-CN

Cyanogen chloride Cl-CN has a fundamental frequency of 378 cm^{-1} that generates the first overtone at 2 x 378 cm-1 = 756 cm^{-1}. Anharmonicity leads to a slight drop in energy so that the true value is 756 cm^{-1}.

This value is in **Fermi resonance** with the C-Cl stretching frequency of 744 cm^{-1}. As a result, this frequency is split into two bands at 784 cm^{-1} + 714 cm^{-1}.

Fermi resonance would seem to have the potential to make IR and Raman spectra very complicated.

Fortunately, this is not the case because **only frequencies of the same symmetry can interact**.

Fermi resonance is commonly observed for Aldehydes!

► The look of Fermi doublet is changing with the solvent polarity.
  In the case of polar solvent *one of the band could disappeared*.

SOLVENT

pentane

cyclohexane

freon 113

carbon disulfide

acetonitrile

CHCl3
chloroform

1720   1700   1680   cm⁻¹

polar solvent
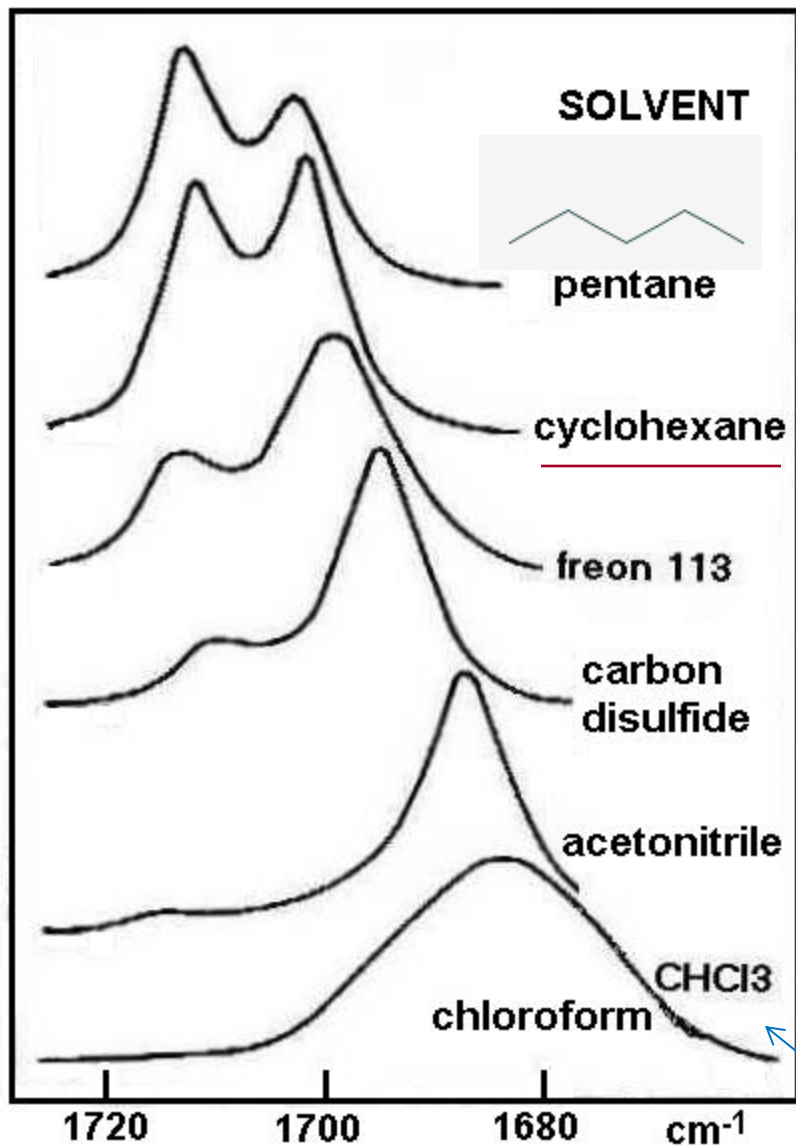
► diphenilformamide
    $HCON(C_6H_5)_2$
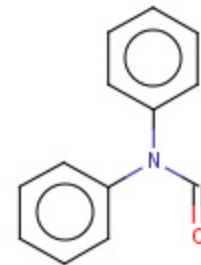
► C=O stretching vibration

► In cyclohexane the Fermi resonance is almost perfect

► The position and intensity of the Fermi bands allow the determination of fundamental transition wavenumber $\overline{\upsilon}_0$

$$\overline{\upsilon}_0 = \frac{\overline{\upsilon}_1 I_1 + \overline{\upsilon}_2 I_2}{\overline{\upsilon}_1 + \overline{\upsilon}_2}$$

I_1, I_2 intensities

The IR of **benzoyl chloride** is a good example:
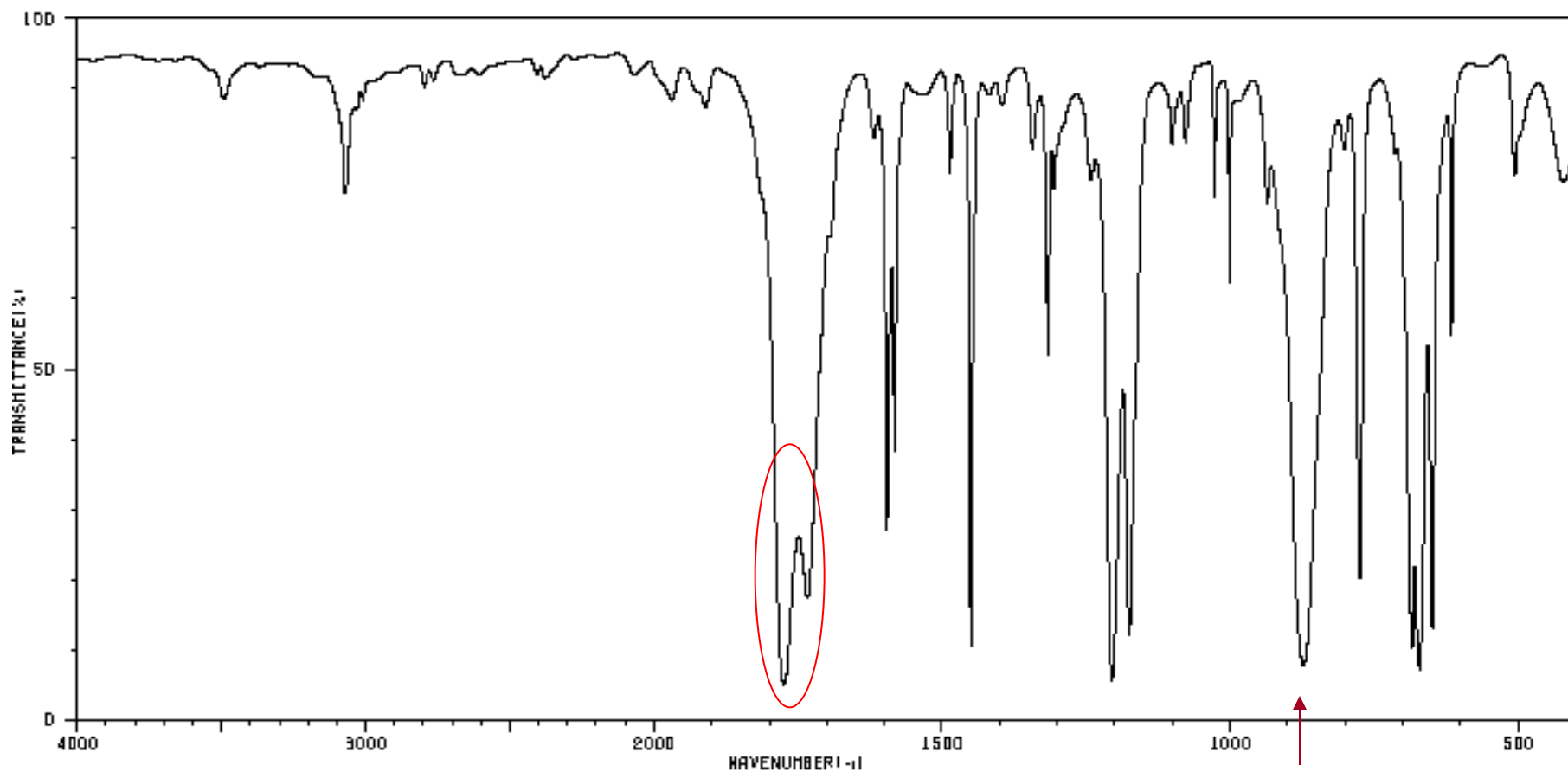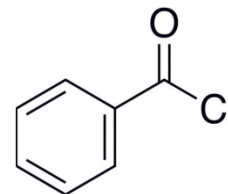
The $\overline{V}_{C=O}$ is at 1774 cm^{-1}
The Fermi Resonance band at 1730 cm^{-1} arises from coupling with the band at 872 cm^{-1} (this band has been variably assigned as a =C-C=, and sometimes a =C-Cl

- **Fermi Resonance** does not always occur in acid chlorides; it is absent in **hexanoyl chloride**:
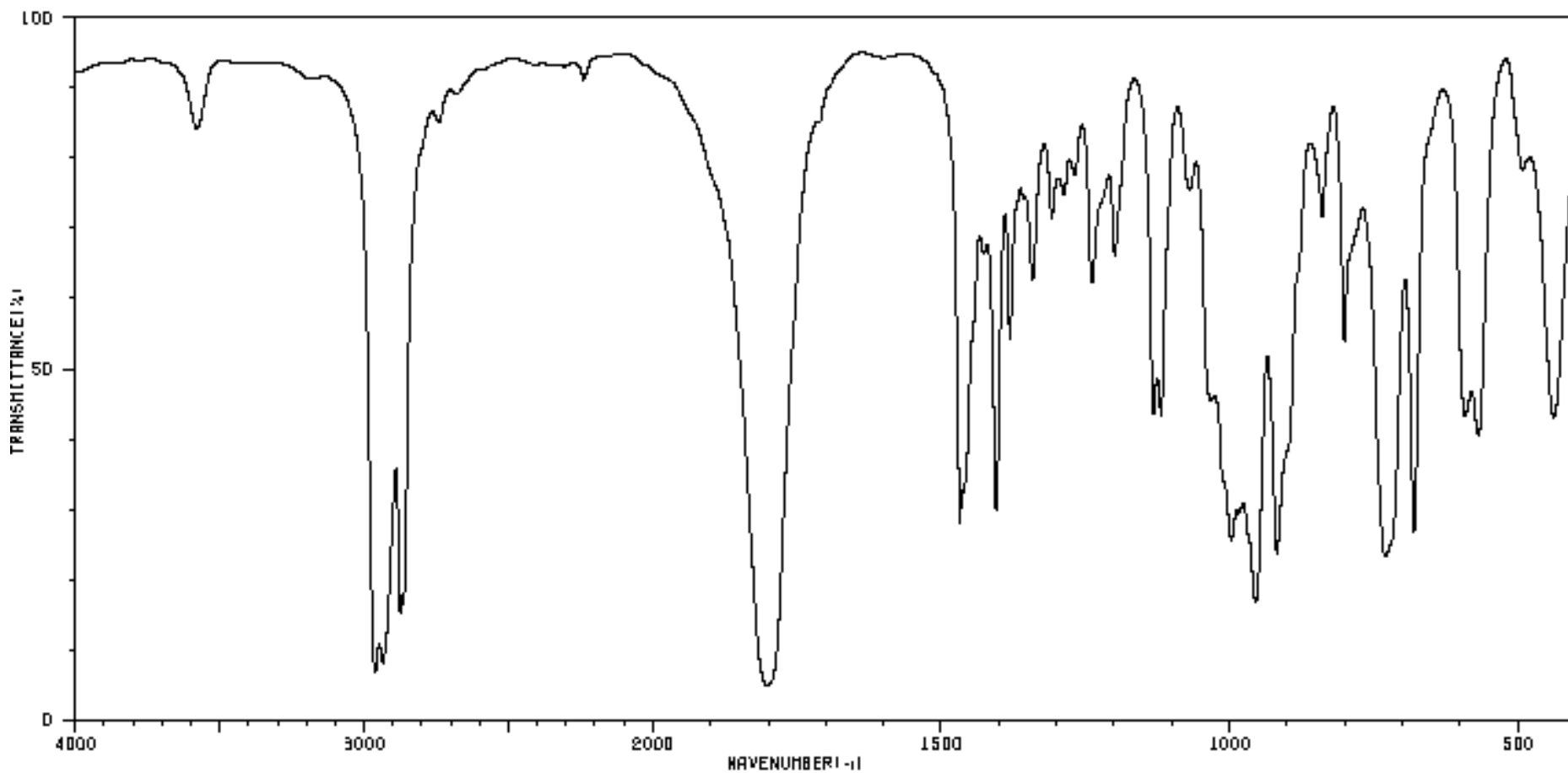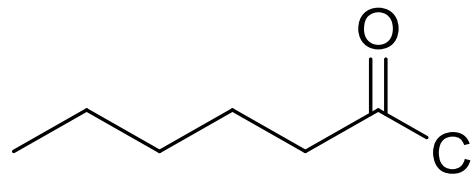
Fermi Resonance is present in **isobutyryl chloride**:
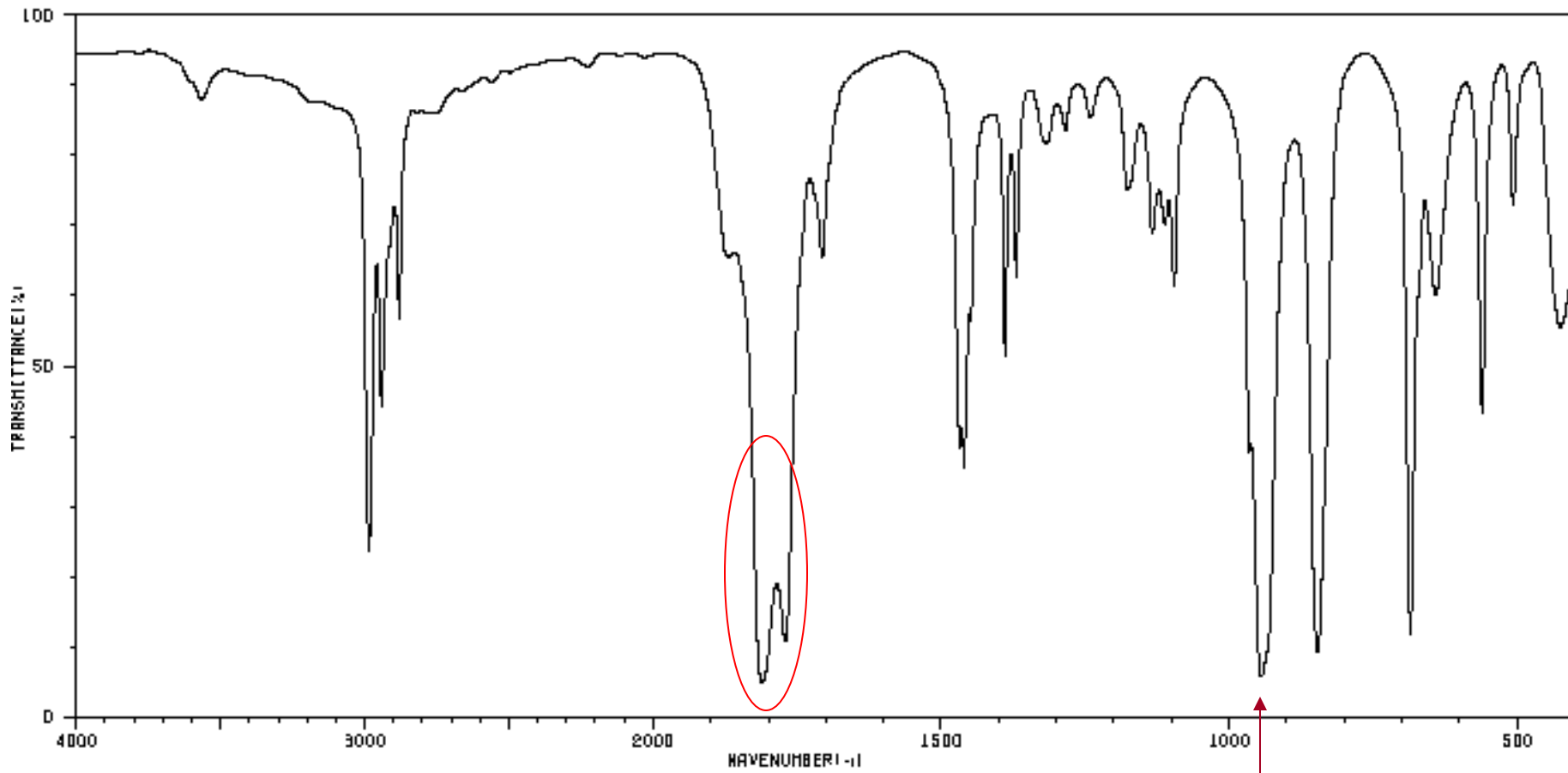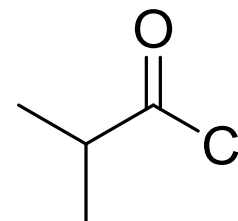
► *Harmonic approximation:* two close but different vibrational level E_i^0 and E_k^0 with ψ_i^0 and ψ_k^0 corresponding wave functions (independent!) → can not explain Fermi Resonance.   Schrodinger equations are: $H_0\psi_i^0 = E_i^0\psi_i^0$ and $H_0\psi_k^0 = E_k^0\psi_k^0$

► Anharmonic *approximation:* anharmonicity involve an perturbation Hamiltonian H':
total Hamiltonians is: $H = H_0 + H'$ (H_0 = equilibrium Hamiltonian).
► The perturbation wavefunction depend to unperturbed wavefunctions
 $\psi = c_i\psi_l^0 + c_k\psi_k^0$ $c_i^2 + c_k^2 = 1$ (coefficients obey the normalization condition)

► The energy difference between the two vibrational level is: $\Delta = E_i^0 - E_k^0$
► We can choose the energy origin between the two vibrational level, so: $E_{i,k}^0 = \pm\dfrac{\Delta}{2}$

► The energies and wavefunctions of coupled levels are:

$$\begin{cases} E_{+,-} = \pm\dfrac{1}{2}\sqrt{\Delta^2 + 4H_{ik}'^2} \\ \psi_+ = a\psi_i^0 + b\psi_k^0 \\ \psi_- = -a\psi_i^0 + b\psi_k^0 \end{cases} \qquad H_{ik}' = \int \psi_i^0 H'\psi_k^0 d\tau$$

$$\begin{pmatrix} a = \left[\dfrac{E_+ - \Delta/2}{2E_+}\right]^{1/2} \\ b = \left[\dfrac{E_+ - \Delta/2}{2E_+}\right]^{1/2} \end{pmatrix}$$

► <u>Fermi Resonance</u> is manifest when $\Delta \to 0$.   In this case $E_{+,-} = \pm H'_{ik}$ and a = b = $1/\sqrt{2}$.
► In the spectrum will appear two bands of slightly different intensity (Fermi doublet).
► An important contribution to one vibration from the other one could appear (because the perturbated wavefunctions ψ_+ and ψ_- depend on initially wavefunctions ψ_i^0 and ψ_k^0)

The IR Spectrum

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

In regions where the EM field of an oscilating bond interacts with IR light of the same ν – transmittance is low (light is absorbed)
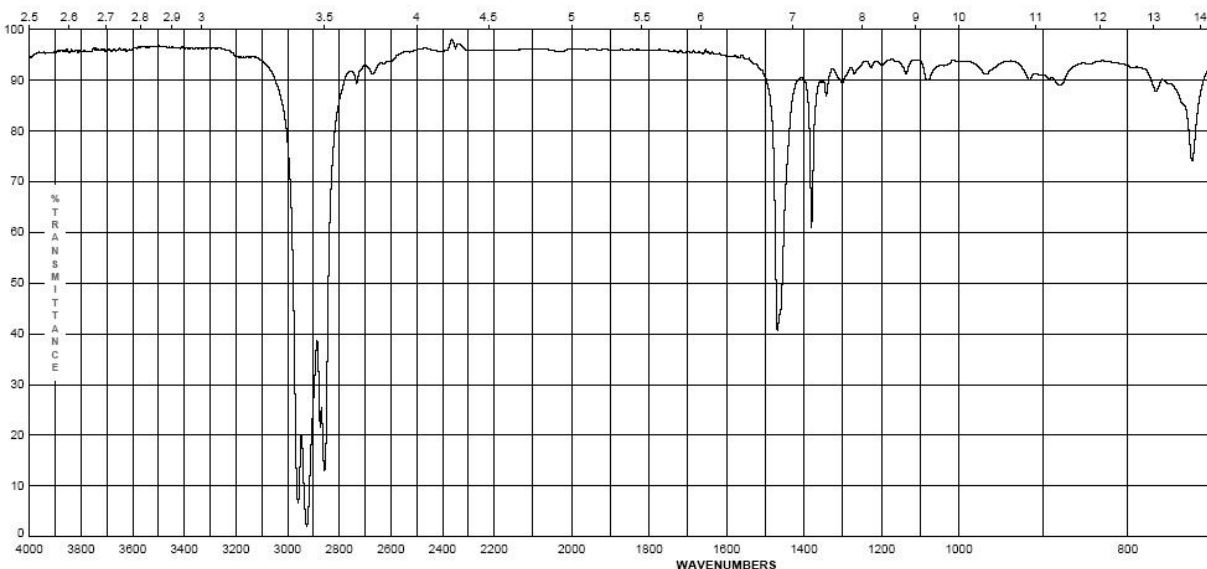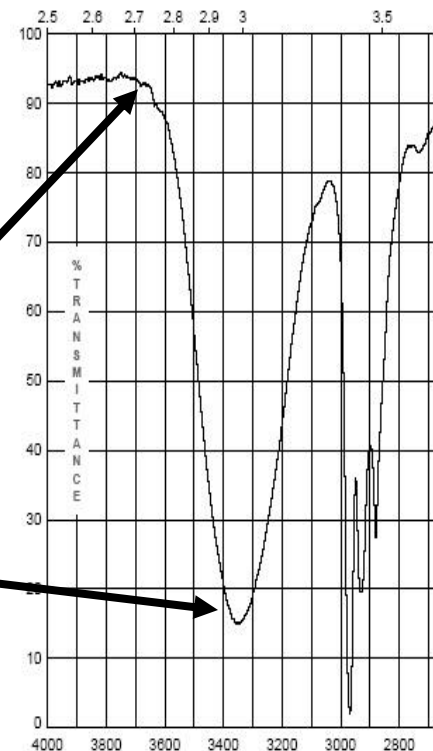
The x-axis of the IR spectrum is in units of wavenumbers, ν, which is the number of waves per centimeter in units of cm^{-1} (E = hc$\bar{\nu}$ or E = hc/λ).

In general:

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

$$\nu_{C-H} > \nu_{N-H} > \nu_{O-H}$$

Stronger bonds will have higher energy oscillations

Triple bonds > double bonds > single bonds in energy

Energy/ν of oscillation
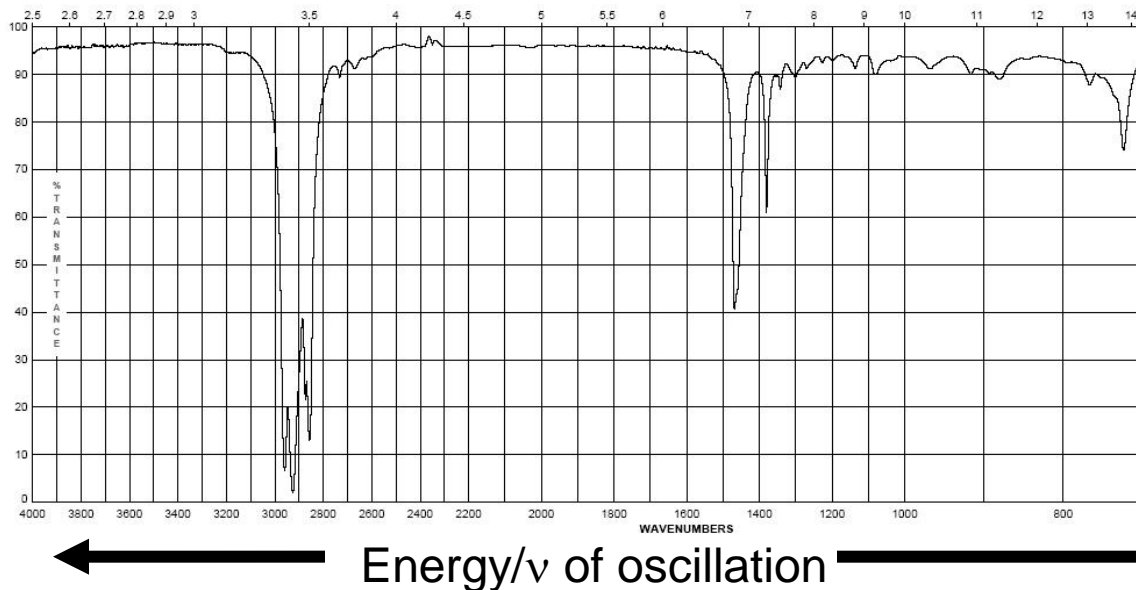
The intensity of an IR band is affected by two primary factors:

Vibration type (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, 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

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

- **Strong (s)** – peak is tall, transmittance is low (0-35 %)
- **Medium (m)** – peak is mid-height (75-35%)
- **Weak (w)** – peak is short, transmittance is high (90-75%)

Exact transmittance values are rarely recorded

All organic functional groups are made of multiple bonds and therefore show up as multiple IR bands (peaks)

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

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

Interpretation of IR spectra

►Because the IR spectrum of each molecule is unique, it can serve as a signature or *fingerprint* to identify the molecule.

Areas in which IR spectroscopy is used extensively include pharmaceutical analysis, quality control in industrial processes, environmental chemistry, geology and astronomy.

One difficulty is that the infrared (IR) spectra of molecules with more than a few atoms can be very complicated.

►How do we know to assign the vibrations to the absorption bands from the IR spectrum? There are really three possible answers.

1. It is possible to perform elaborate **chemical calculations** that allow us to develop pictures of each vibrational mode. How accurate these calculations are depends on the method used.

As with all modeling, these calculations are subject to a variety of errors, and so the quality of the results varies widely with the method and the complexity of the molecule being studied.

2. In many cases, it is not important to know the exact nature of each vibration. Rather, we might just want to find if certain ***functional groups*** (e.g. -COOH, -NH$_2$, etc.) are present in the molecule.

It turns out that the some molecular vibrations can be approximately described just in terms of the motions of a few of the atoms, while the other atoms move only slightly or not at all.

This approximation is called "functional group analysis".

It is particularly useful as a tool for *qualitative analysis of organic molecules*, and for *monitoring* the progress of *organic reactions*.

3. In other cases, we may not even care what the modes are! We may just want to obtain a spectrum of our sample, and *compare* it to a library of spectra of known compounds, in order to identify our sample.

This procedure is common in *environmental and forensic analyses*.

Infrared Functional Group Analysis

Looking for presence/absence of different functional groups

► Simple stretching: 1600 - 3500 cm^{-1} functional groups region

► Complex vibrations: 400 - 1400 cm^{-1}, "fingerprint region"

► A polar bond is usually IR-active!

► A nonpolar bond in a symmetrical molecule will absorb weakly or not at all!

►The stronger the bond, the more energy will be required to excite the stretching vibration:

$$\nu_{C \equiv C} > \nu_{C=C} > \nu_{C-C}$$
$$\nu_{C \equiv N} > \nu_{C=N} > \nu_{C-N}$$

►The heavier an atom, the lower the wavenumbers for vibrations that involve that atom.

$$\bar{\nu}_0 = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}}$$

The **four primary regions** of the IR spectrum
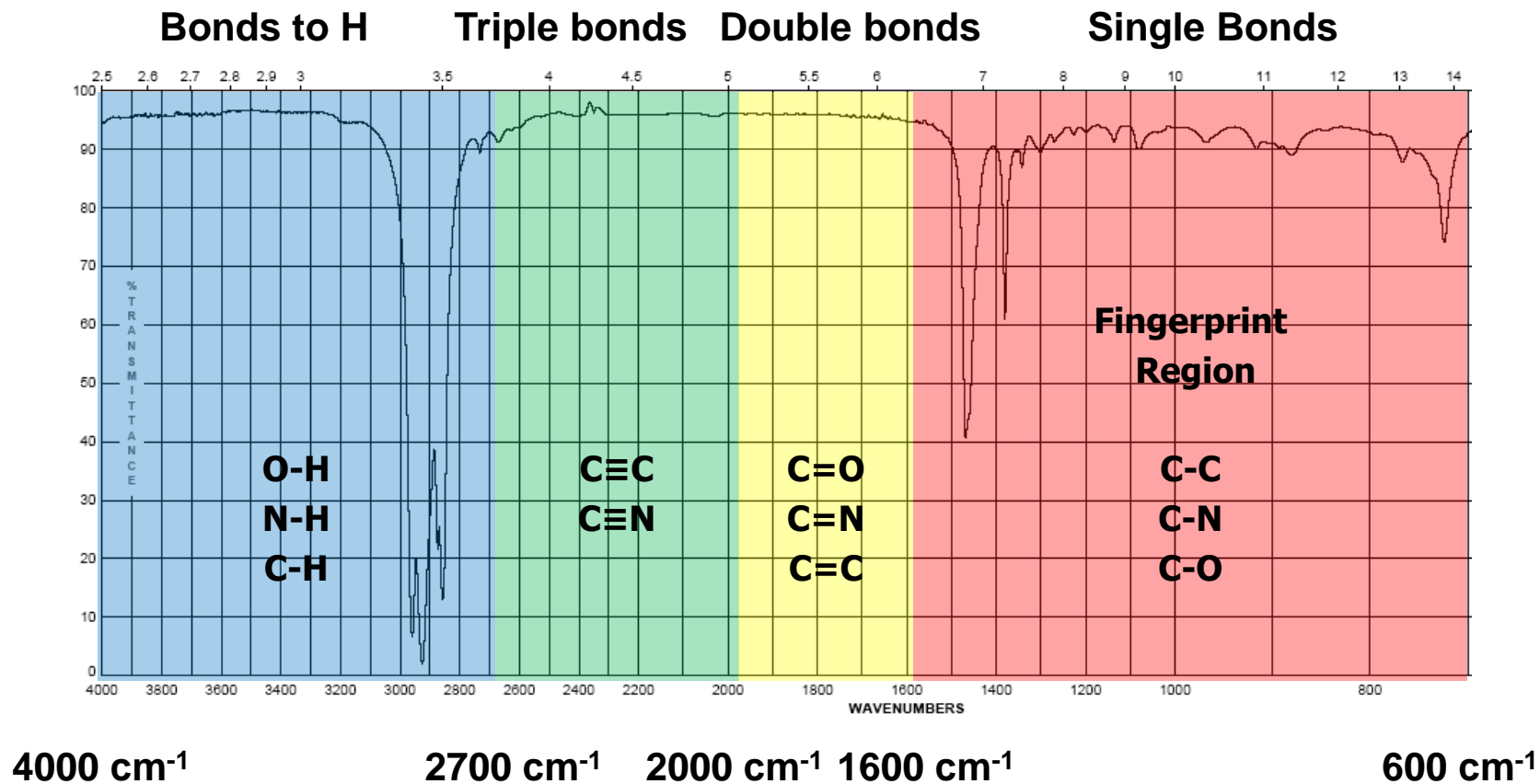
IR functional group analysis

► IR is absorbed when frequency of IR radiation is equal with frequency of molecule vibrations

$$\bar{v}_0 = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}}$$

► Covalent bonds vibrate at only certain allowable frequencies (associated with the nature of the bonds and the mass of vibrating atoms)

Stretching vibrations appear at higher wavenumbers than bending vibrations!

Asymmetric vibrations are strongest vibration from the IR spectrum.

► No two molecules will give exactly the same IR spectrum (except enantiomers)

Baseline

Absorbance/ Peak
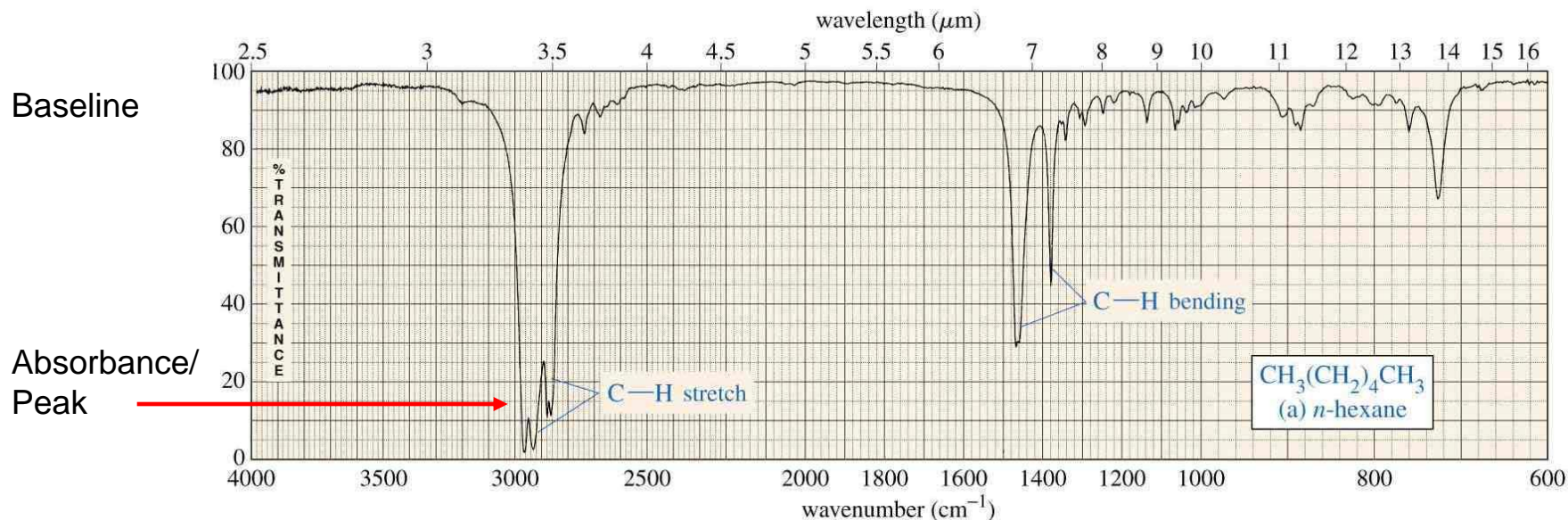
Alkanes
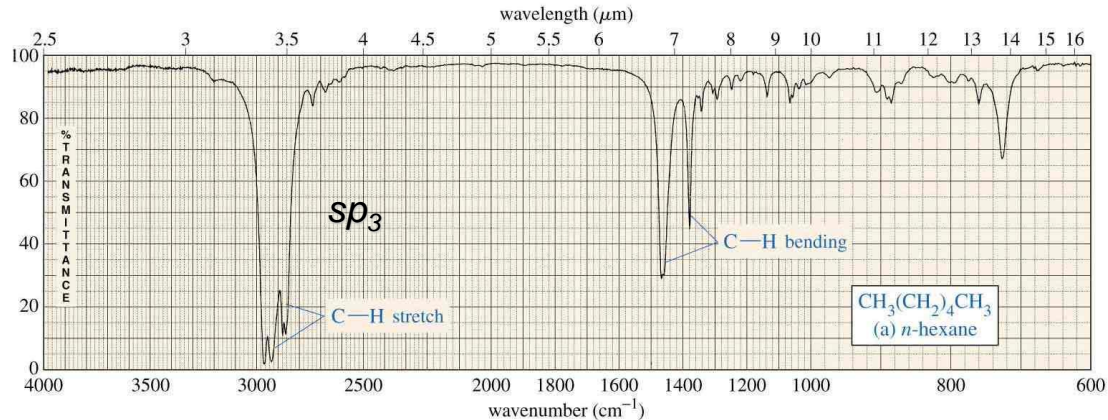
Combination of C-C and C-H bonds

- C-C stretches and bends 1360-1470 cm^{-1}
- CH_2-CH_2 bond 1450-1470 cm^{-1}
- CH_2-CH_3 bond 1360-1390 cm^{-1}
- sp^3 C-H between 2800-3000 cm^{-1}

Octane
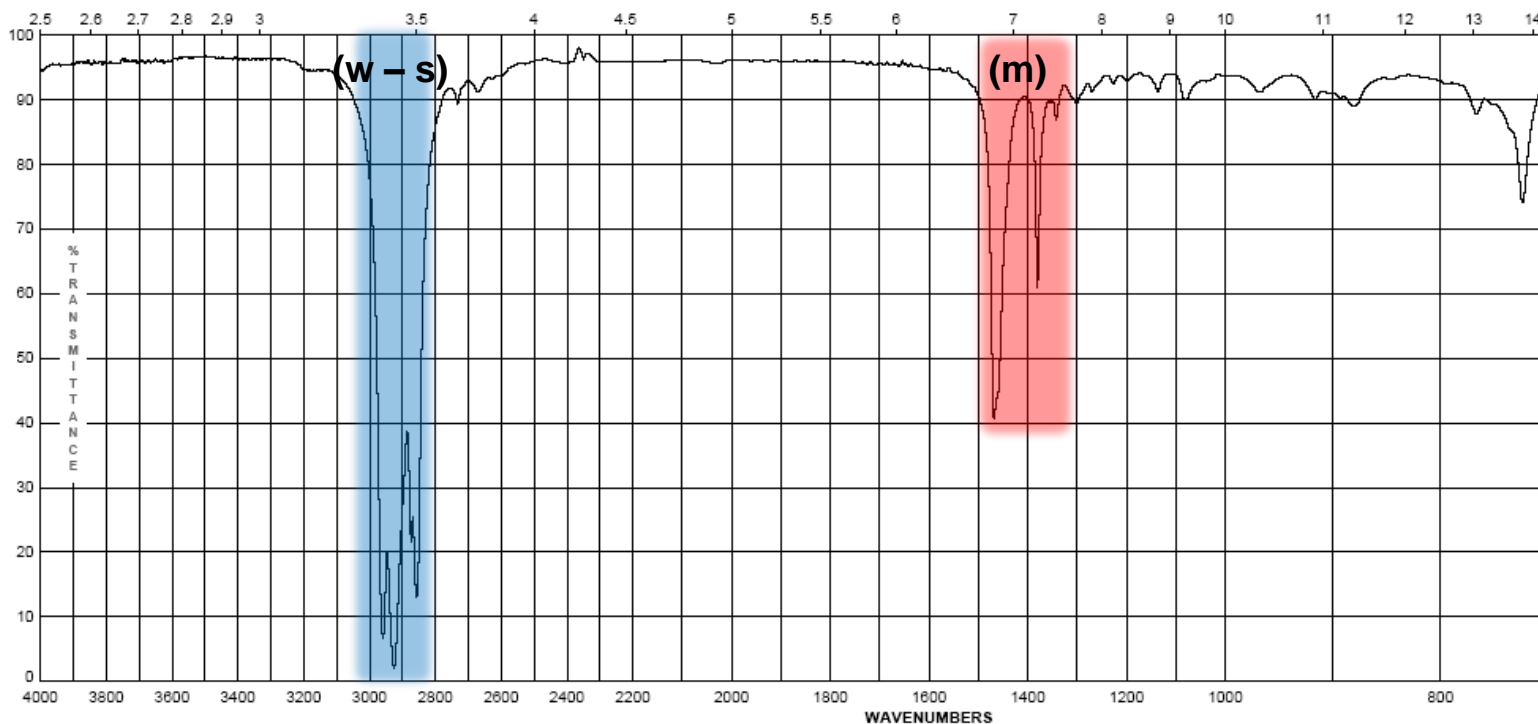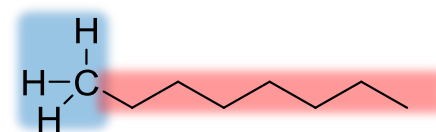
Alkenes

Addition of the C=C and vinyl C-H bonds

- C=C stretch at 1620-1680 cm^{-1} weaker as substitution increases
- vinyl C-H stretch (sp$_2$) occurs at 3000-3100 cm^{-1}

CH$_3$(CH$_2$)$_3$CH=CH$_2$
(b) 1-hexene

3080 =C—H stretch

sp$_2$

alkane C—H stretch

sp$_3$ 1642 C=C stretch

C—H bending
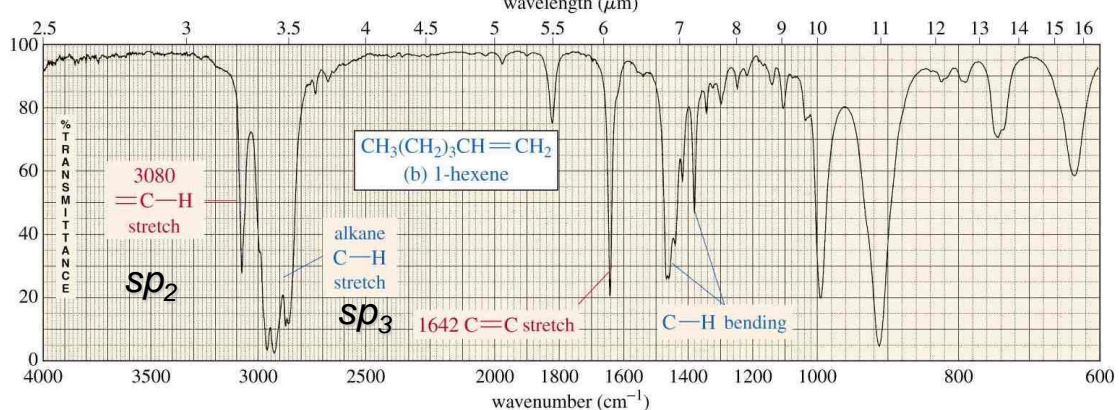
The difference between alkane, alkene or alkyne C-H is important!
If the band is slightly above 3000 it is vinyl **sp^2** C-H or alkynyl **sp** C-H
If the band is below 3000 it is alkyl **sp^3** C-H

1-Octene

(w – m)

(w – m)
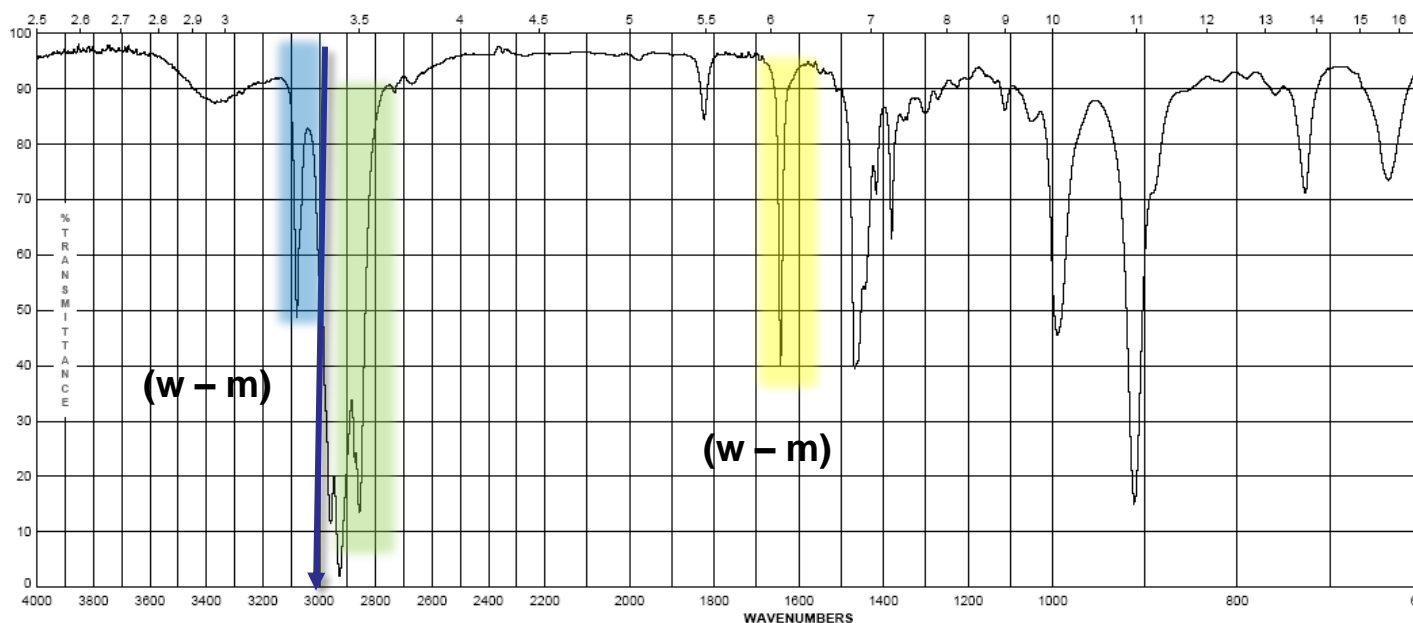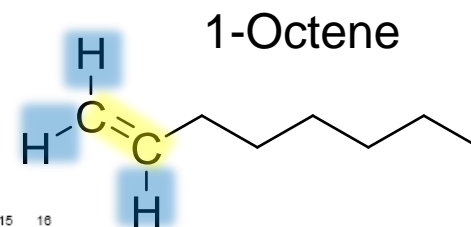
Alkynes Addition of the C ≡ C and vinyl C-H bonds

- C≡C stretch 2100-2260 cm^{-1}; strength depends on asymmetry of bond, strongest for terminal alkynes, weakest for symmetrical internal alkynes
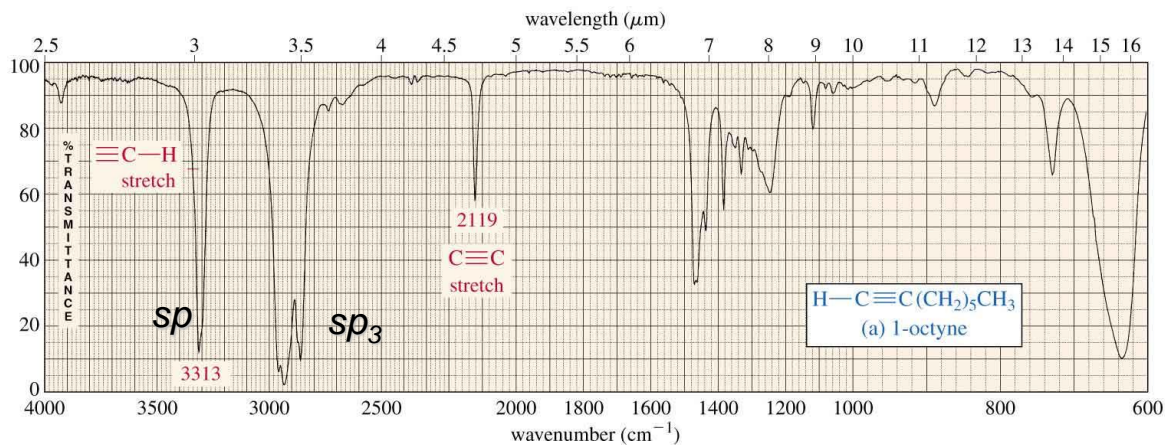
- C-H for **_terminal_** alkynes occurs at 3200-3300 cm^{-1}

1-Octyne
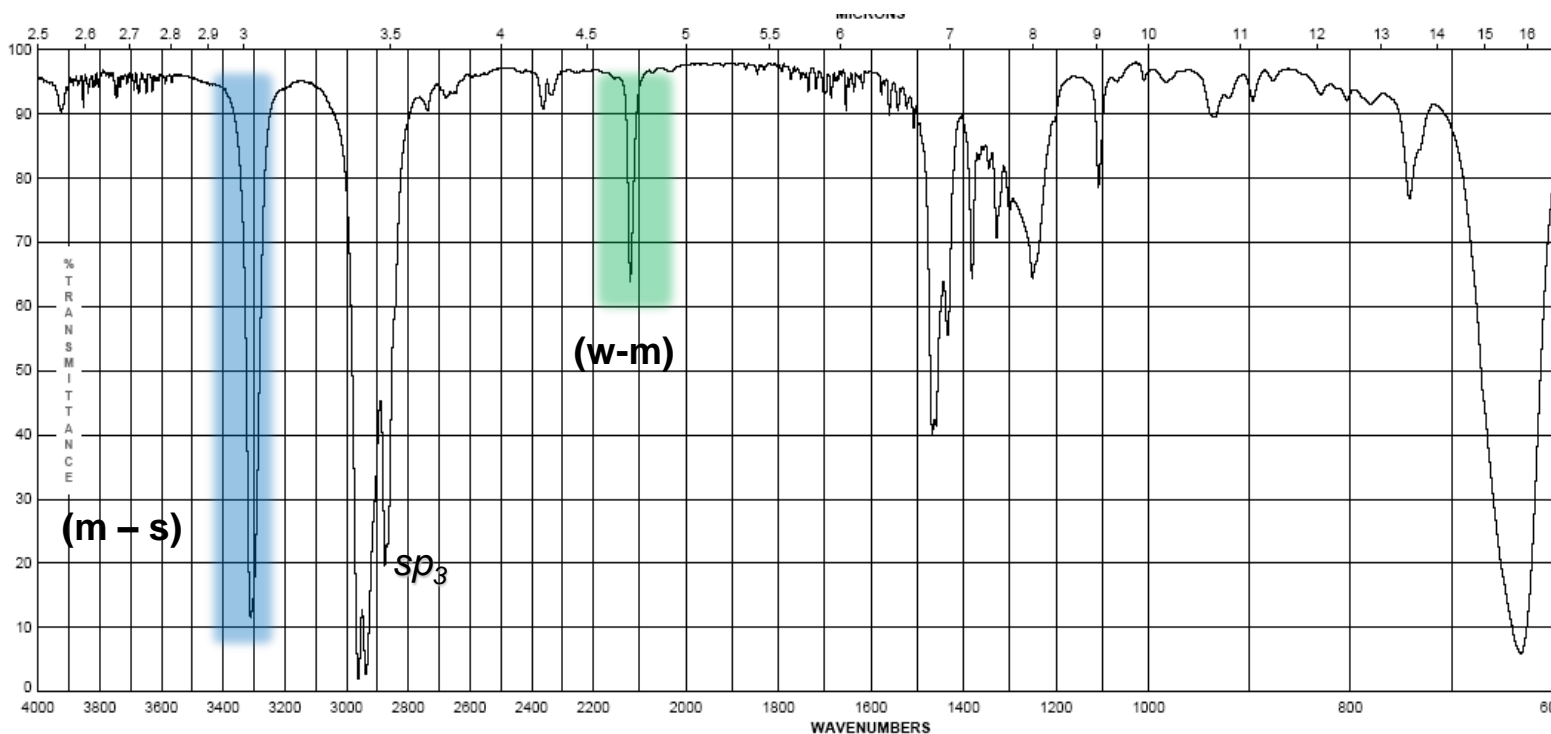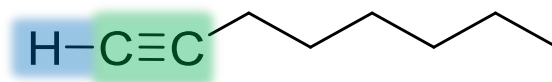
Internal alkynes (R-C≡C-R) would not have C ≡ C band!

(b) 4-octyne

$CH_3(CH_2)_2 - C \equiv C - (CH_2)_2CH_3$
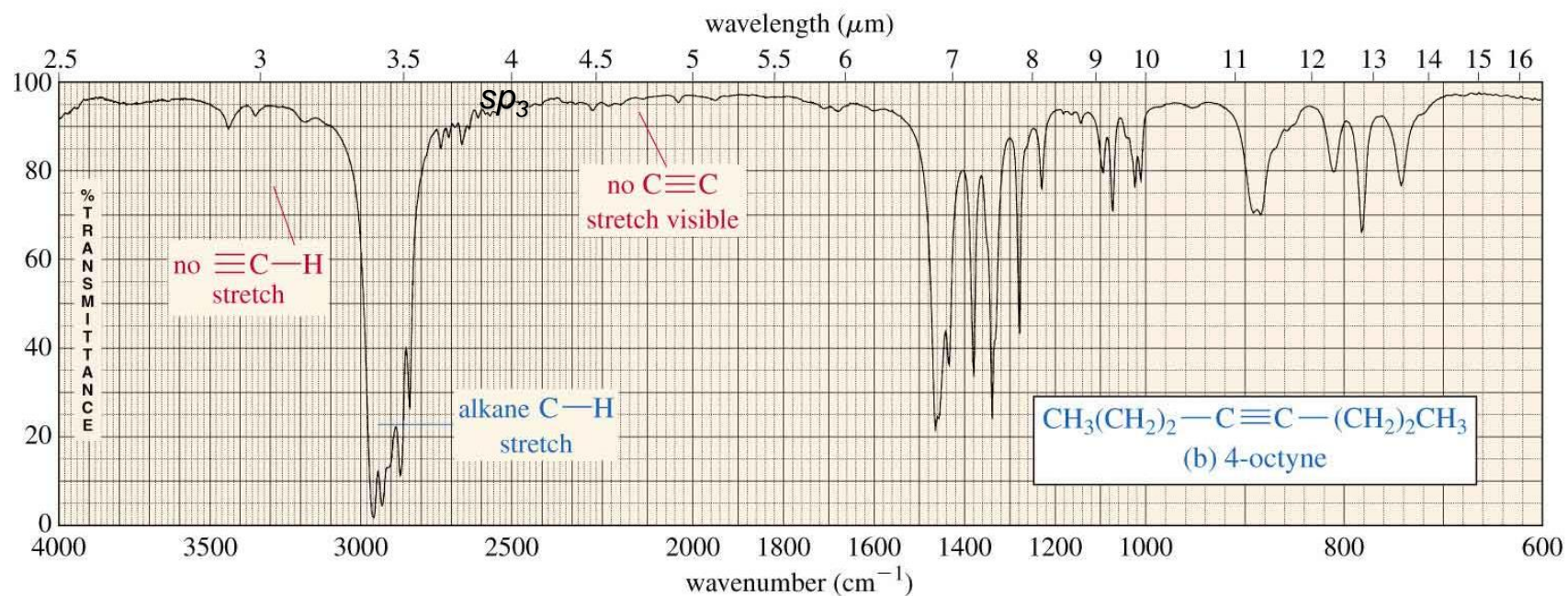
Aromatics

Ethyl benzene

- Due to the delocalization of e⁻ in the ring, C-C bond order is 1.5, the stretching frequency for these bonds is slightly lower in energy than normal C=C

- These show up as a *pair* of sharp bands, 1500 & 1600 cm^{-1}, (lower frequency band is stronger)

- C-H bonds off the ring show up similar to vinyl C-H at 3000-3100 cm^{-1}

overtone of bending region
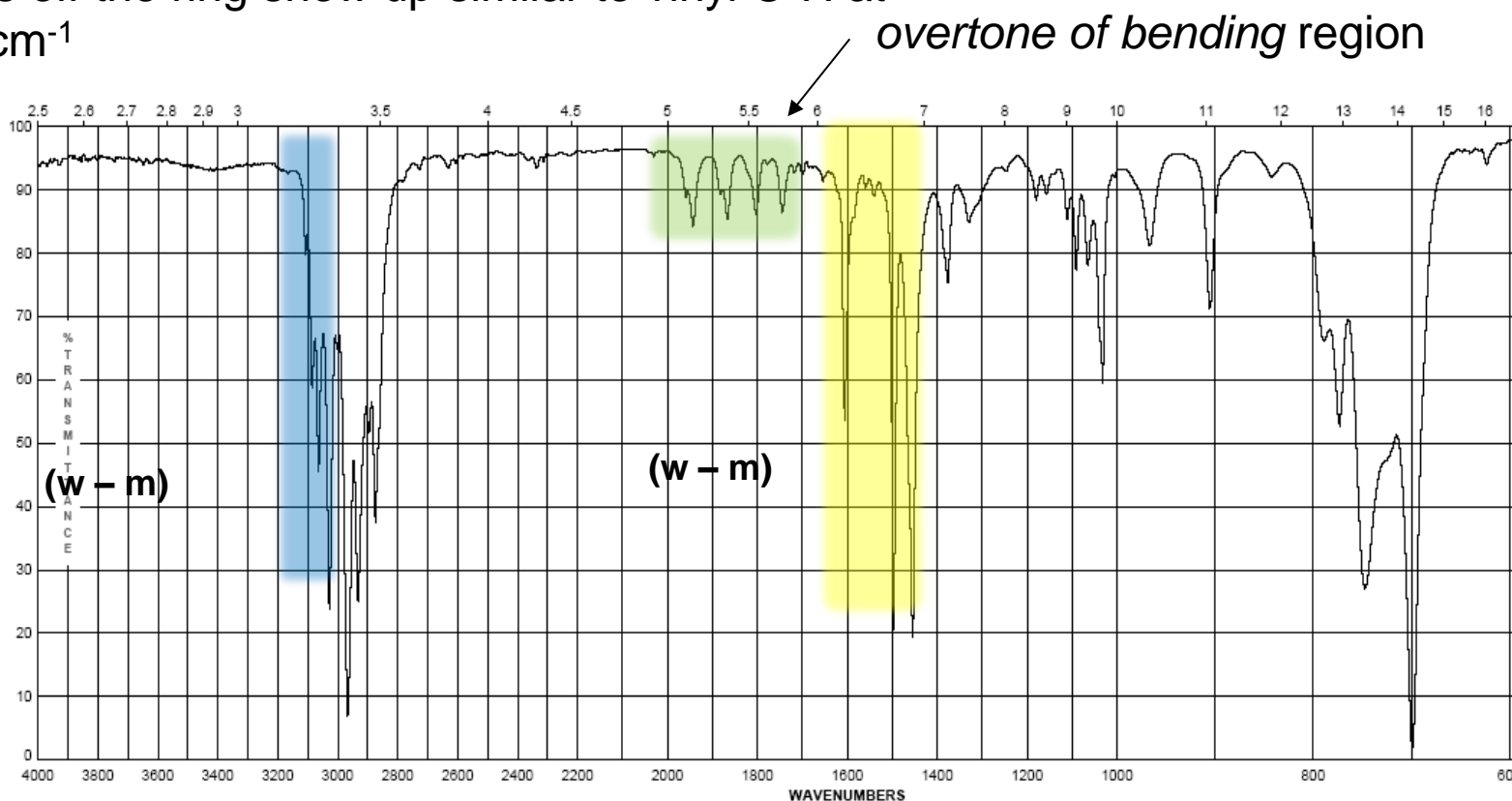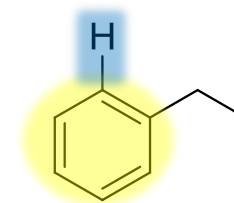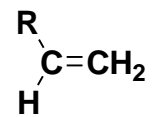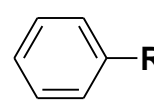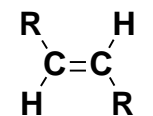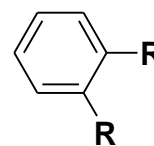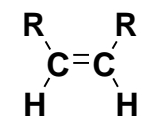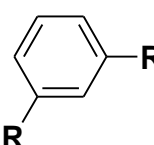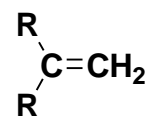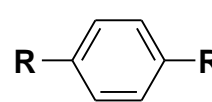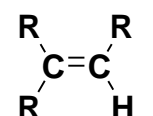
Aromatics

• 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-*)
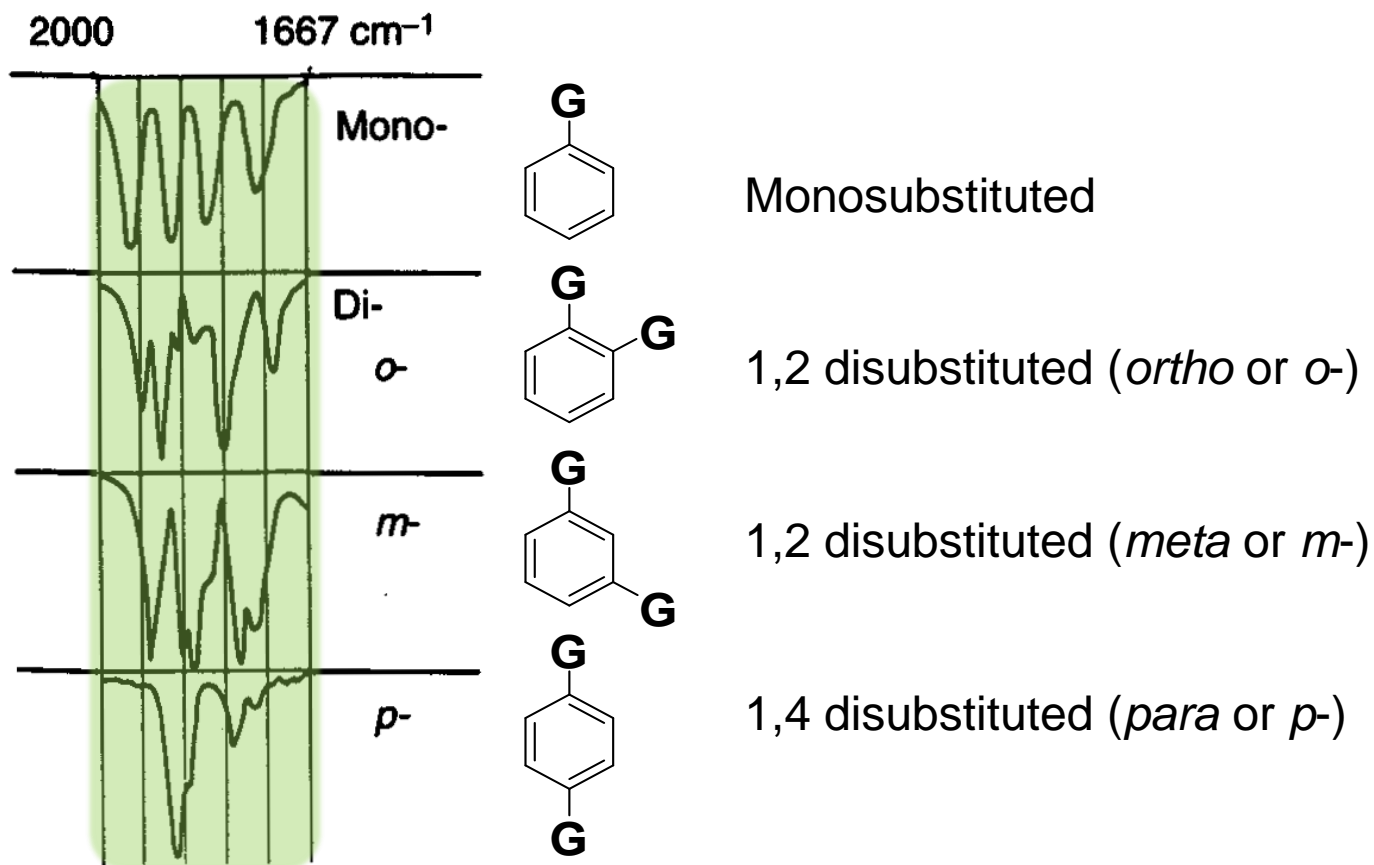
Unsaturated Systems – substitution patterns

• 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}		cm^{-1}
R–C=CH$_2$ (H)	985-997 / 905-915	Ph–R	730-770 / 690-710
R,H–C=C–H,R	960-980	ortho-R,R	735-770
R,H–C=C–R,H (cis)	665-730	meta-R,R	860-900 / 750-810 / 680-725
R,R–C=CH$_2$	885-895	para R–R	800-860
R,R–C=C–R,H	790-840		

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
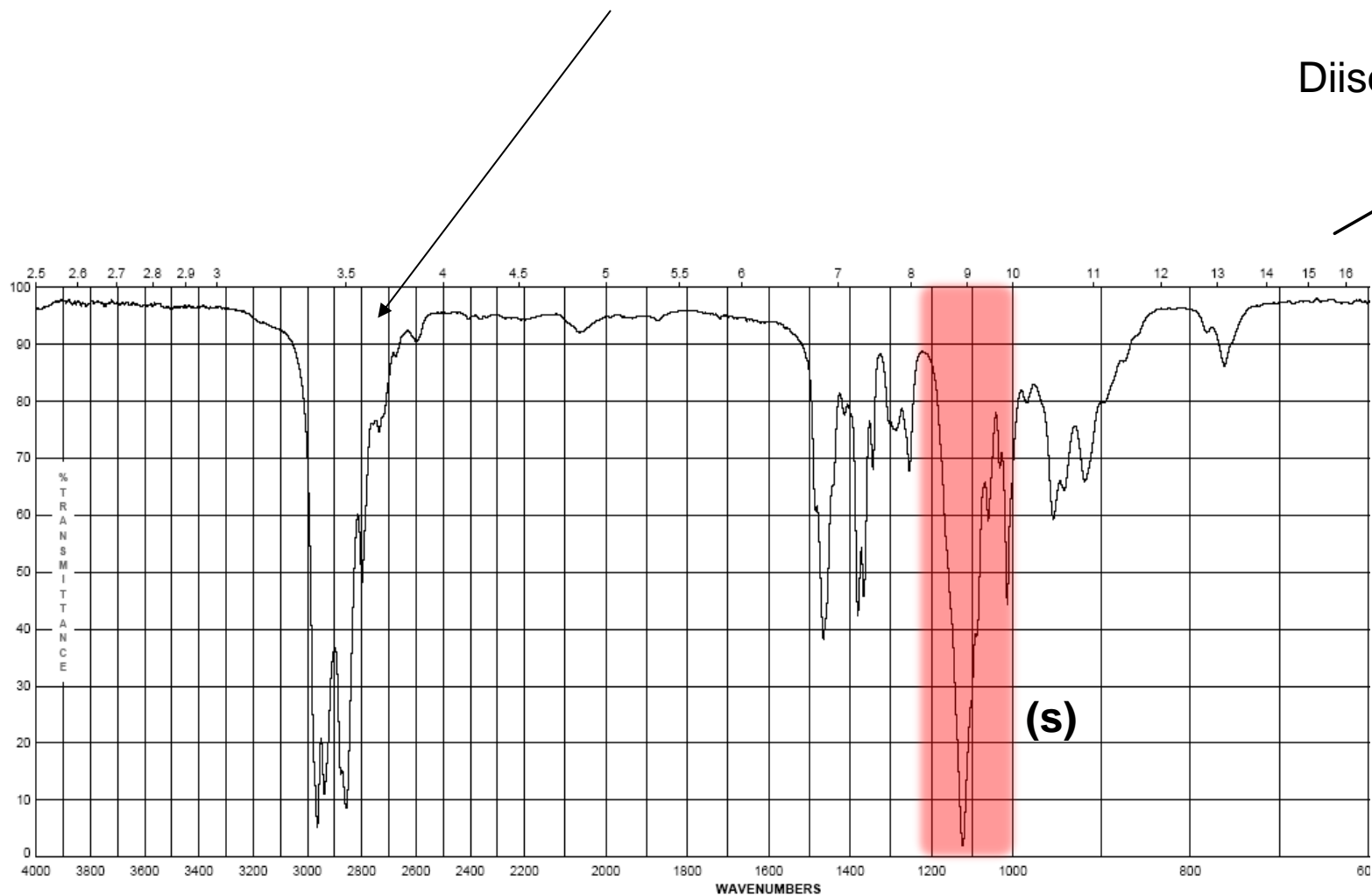
Diisopropyl ether
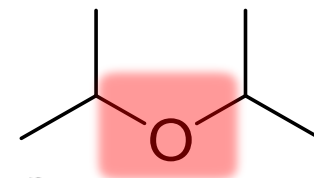
Alcohols

• Strong, broad with rounded tip
O-H stretch from 3200-3400 cm^{-1}

The shape is due to the
presence of hydrogen bonding

1-butanol
$CH_3(CH_2)_3OH$

O—H stretch

saturated C—H stretch

C—O stretch (unreliable)
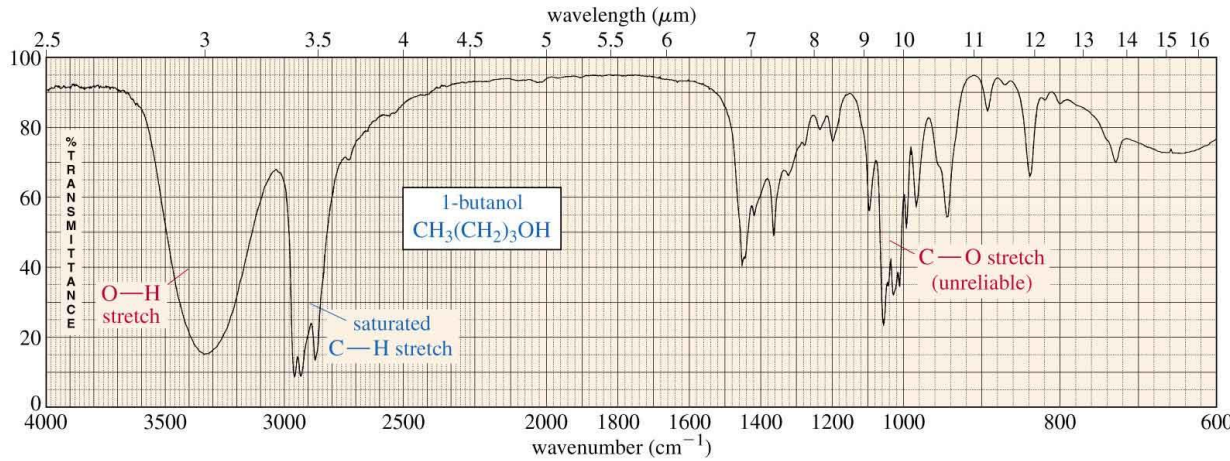
• C-O stretch from 1050-1260 cm^{-1} (like ethers)
Band position changes depending on the alcohols substitution:
1° 1075-1000; 2° 1075-1150; 3° 1100-1200; phenol 1180-1260)

(m– s) br

(s)

NICOLET 20SX FT-IR
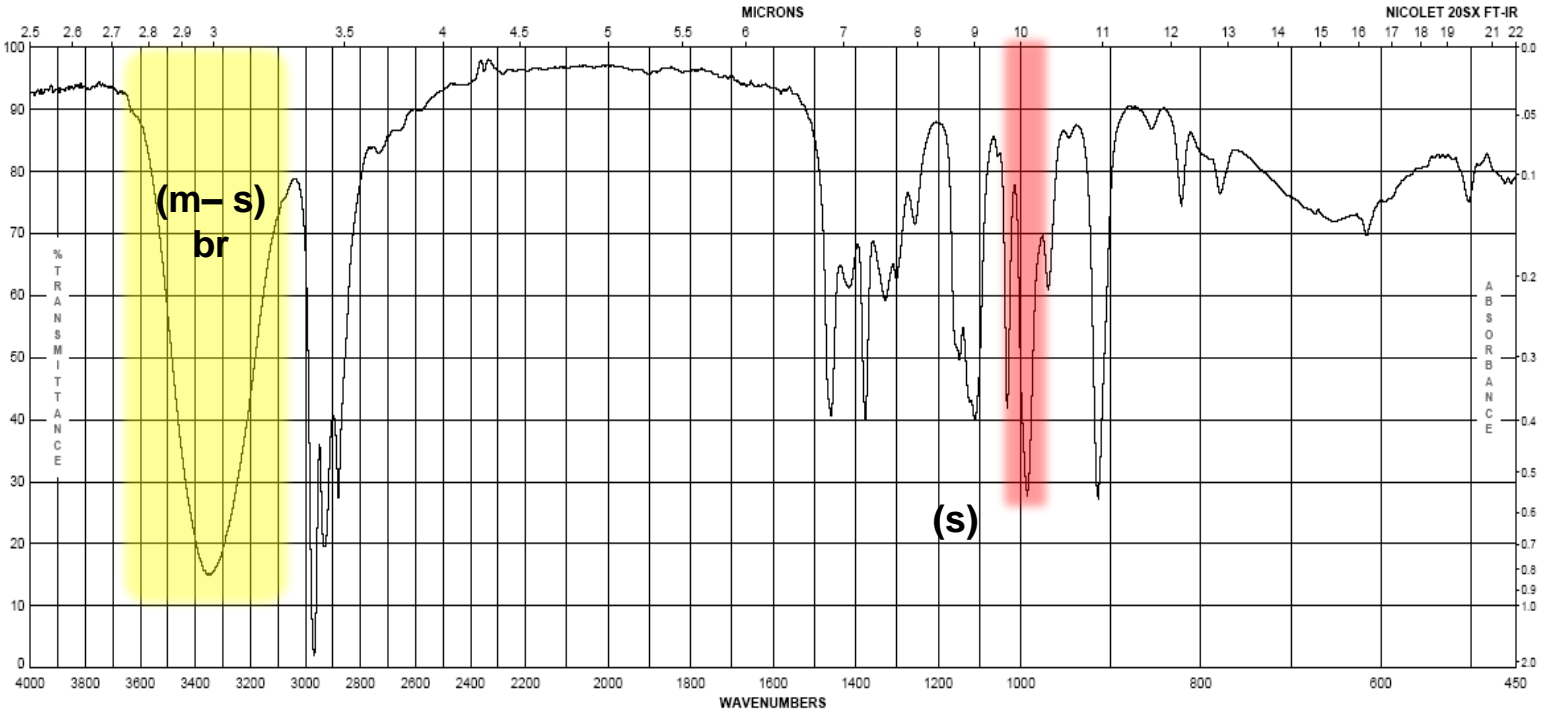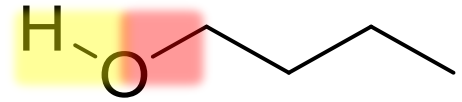
Primary amine (R-NH$_2$):

- The –N-H stretching band for NH$_2$ occur between 3200-3500 cm^{-1}

- Broad band with two sharp spikes (dublet: symmetric and anti-symmetric modes)

- NH$_2$ deformation band: 1590-1650 cm^{-1}

2-aminopentane
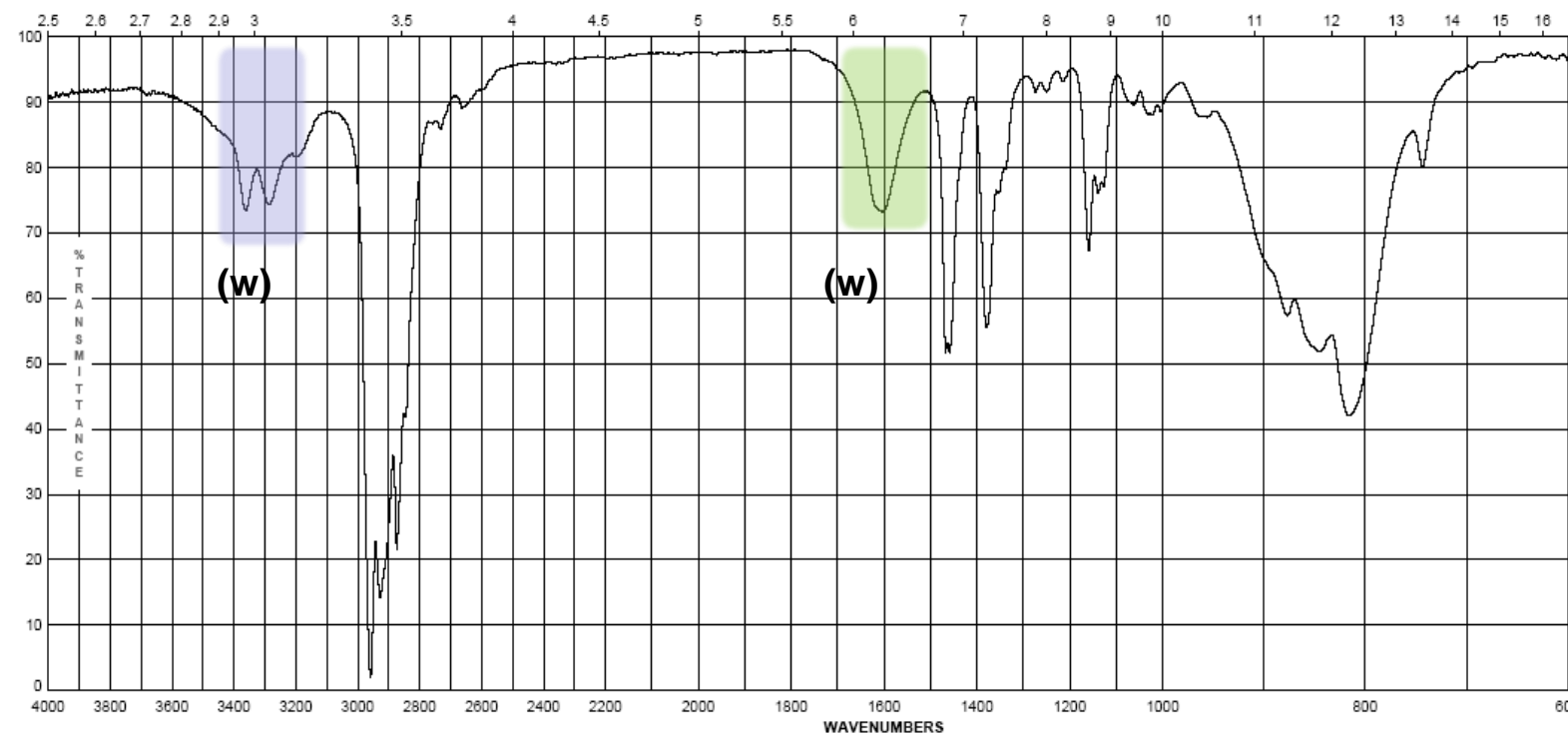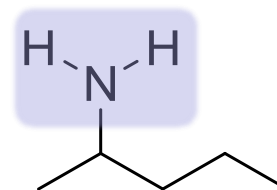
Secondary amine (R$_2$-NH):

- The – N-H stretching band occurs at 3200-3500 cm^{-1} as a single sharp peak weaker than –O-H band
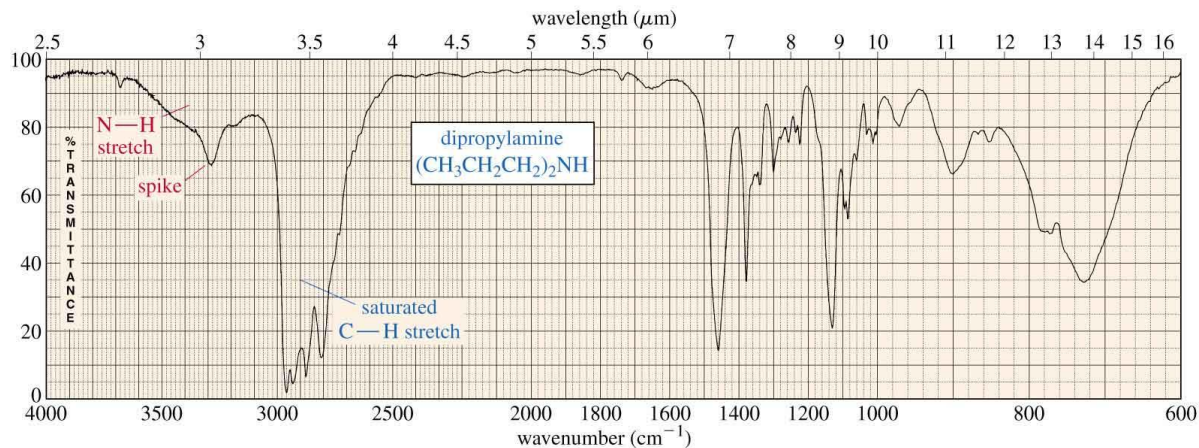
► Both O-H and N-H stretching bands occur around 3300 cm^{-1}, but they look different!

pyrrolidine
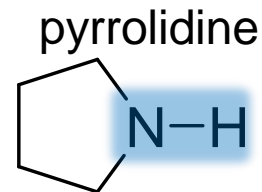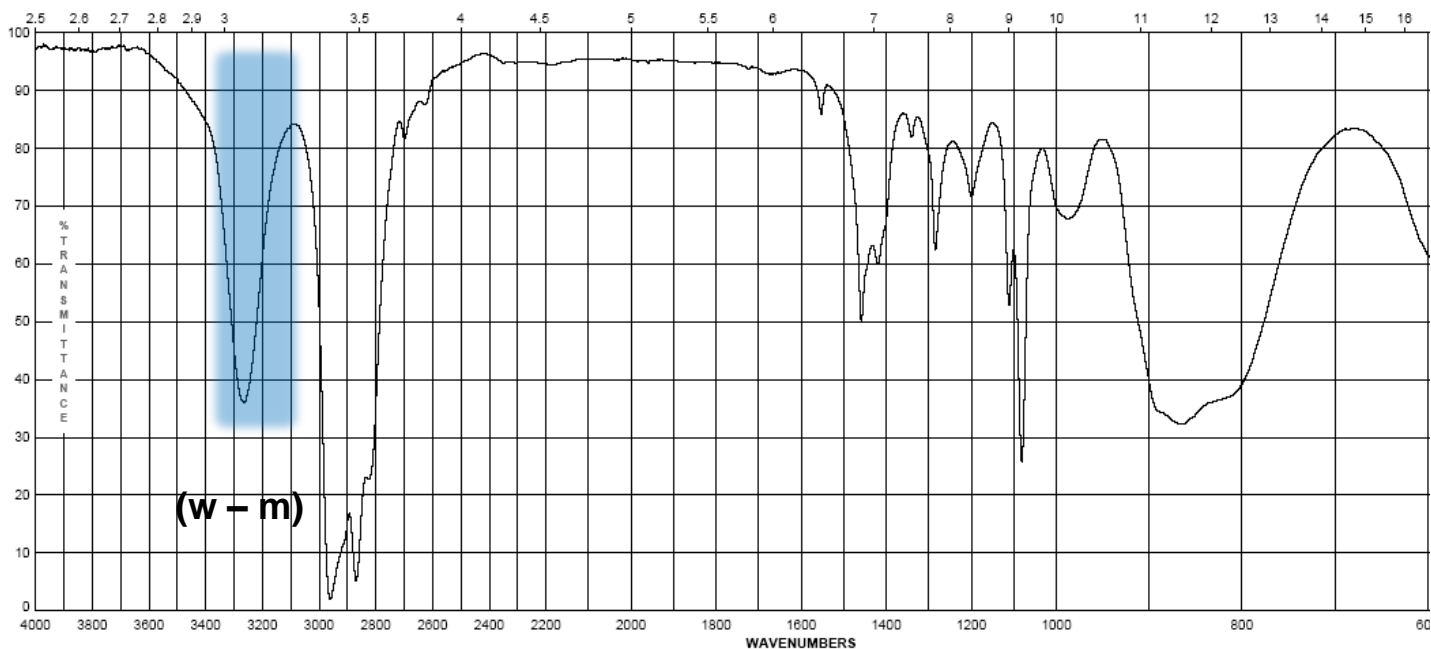
Tertiary amines (R$_3$N) have no N-H bond and *will not* have a band in this region

H region review

- Inspect the bonds to H region (2700 – 4000 cm^{-1})

- Peaks from 2850-3000 are simply sp^3 C-H in most organic molecules

- Above 3000 cm^{-1} *Learn shapes, not wavenumbers!:*

V-shape peak
-N—H bond for 2° amine (R$_2$**N—H**)

Broad U-shape peak
-**O—H** bond

W-shape peak
-N—H bond for 1° amine (R**NH**$_2$)

Sharp spike
-C≡**C—H** bond
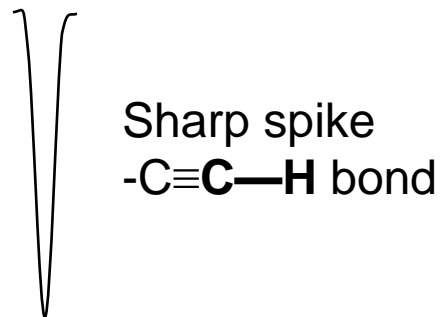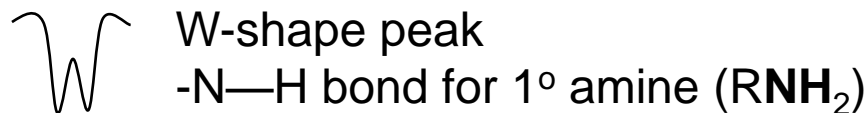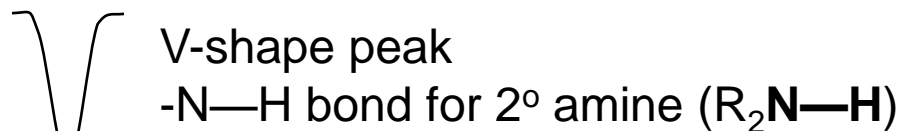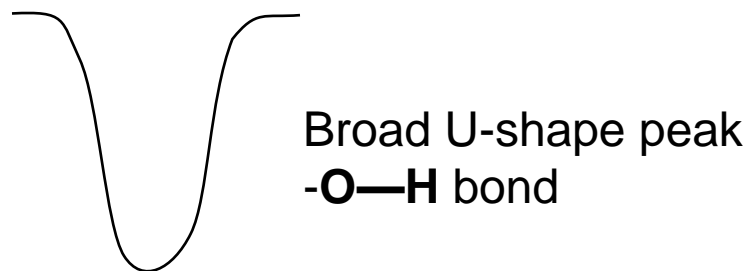
Small peak shouldered
just above 3000 cm^{-1}
C=**C—H** or Ph**—H**

3000 cm^{-1}
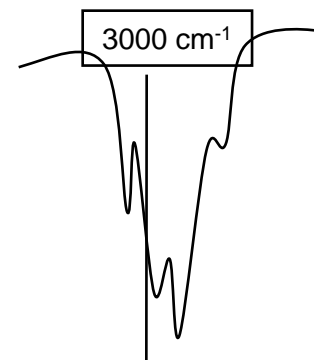
Carbon-Carbon Bond Stretching

► Stronger bonds absorb at higher frequencies ($v \sim k$!):

   C-C   1200 cm^{-1}
   C=C   1660 cm^{-1}
   C≡C   2200 cm^{-1} (weak or absent if internal)

► Conjugation lowers the frequency:

   isolated C=C   1640-1680 cm^{-1}
   conjugated C=C   1620-1640 cm^{-1}
   aromatic C=C   approx. 1600 cm^{-1}

Carbon-Hydrogen Stretching

► Bonds with more *s* character absorb at a higher frequency:

   sp^3 C-H, just below 3000 cm^{-1} (CH$_3$)
   sp^2 C-H, just above 3000 cm^{-1} (CH$_2$)
   sp C-H, at 3300 cm^{-1} (CH)

Carbonyl Stretching (C=O)

▶ The C=O bond of simple *ketones, aldehydes, and carboxylic acids* absorb around 1710 cm^{-1}

▶ Usually, it's the strongest IR signal.

▶ Aldehydes have two C-H signals around 2700 and 2800 cm^{-1}

▶ Carboxylic acids will have O-H also.

Aldehydes

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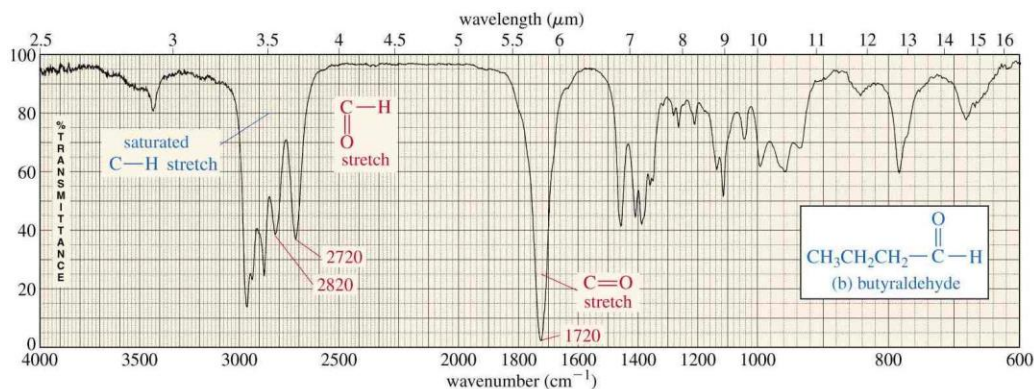
- A highly unique sp^2 C-H stretch appears as a doublet, 2720 & 2820 cm^{-1} called a "*Fermi doublet*"

Cyclohexyl carboxaldehyde

(w-m)

(s)

(a) 2-heptanone
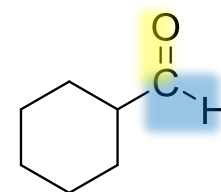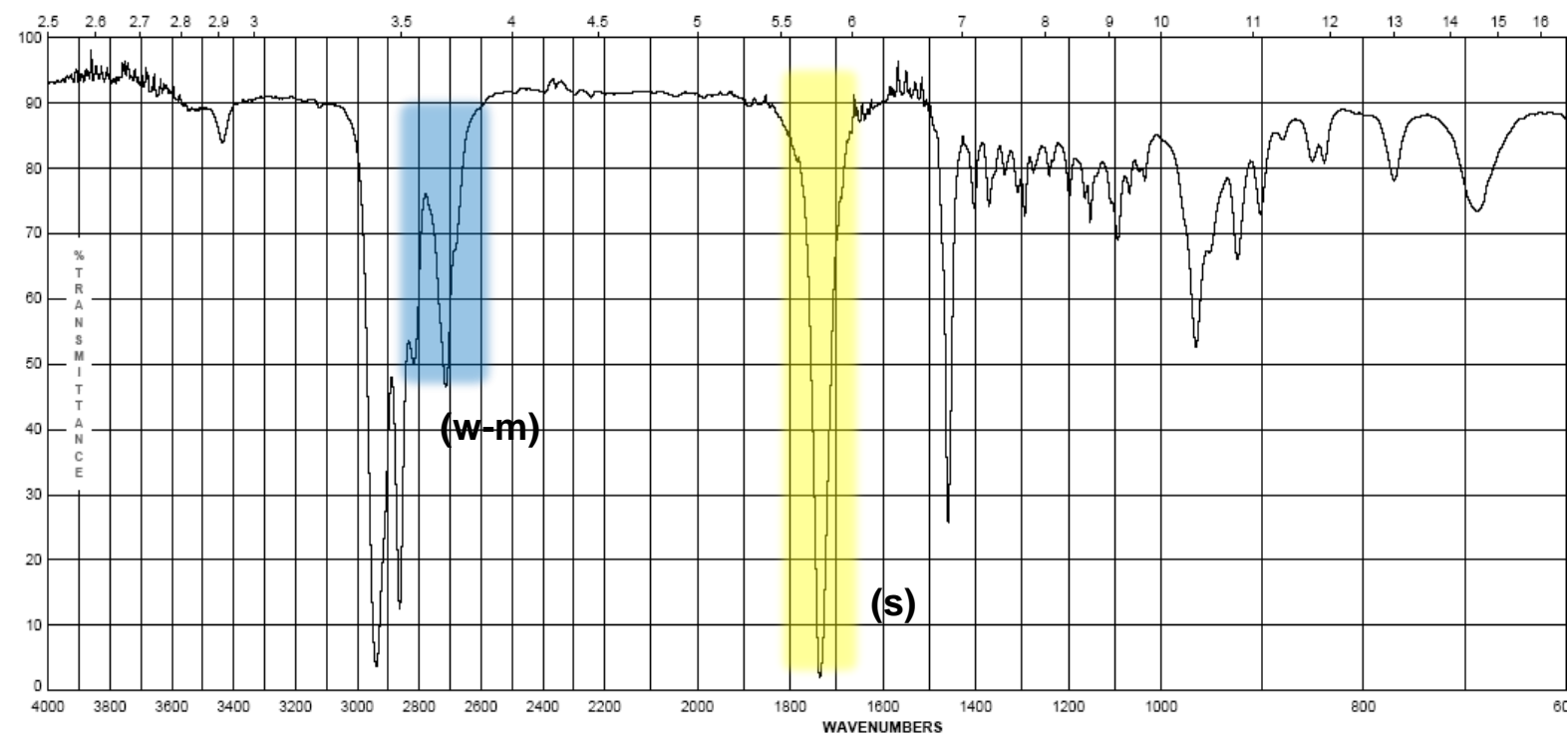
Ketones
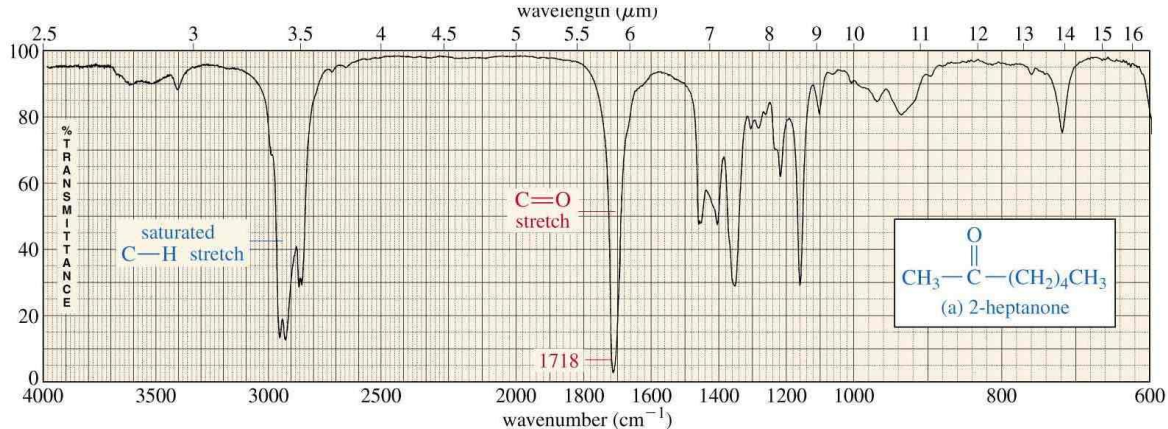
- C=O stretch occurs at 1705-1725 cm^{-1}

- Simplest of the carbonyl compounds as far as IR spectrum – carbonyl only

3-methyl-2-pentanone

(s)
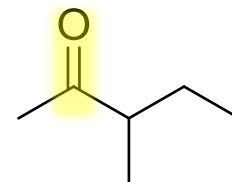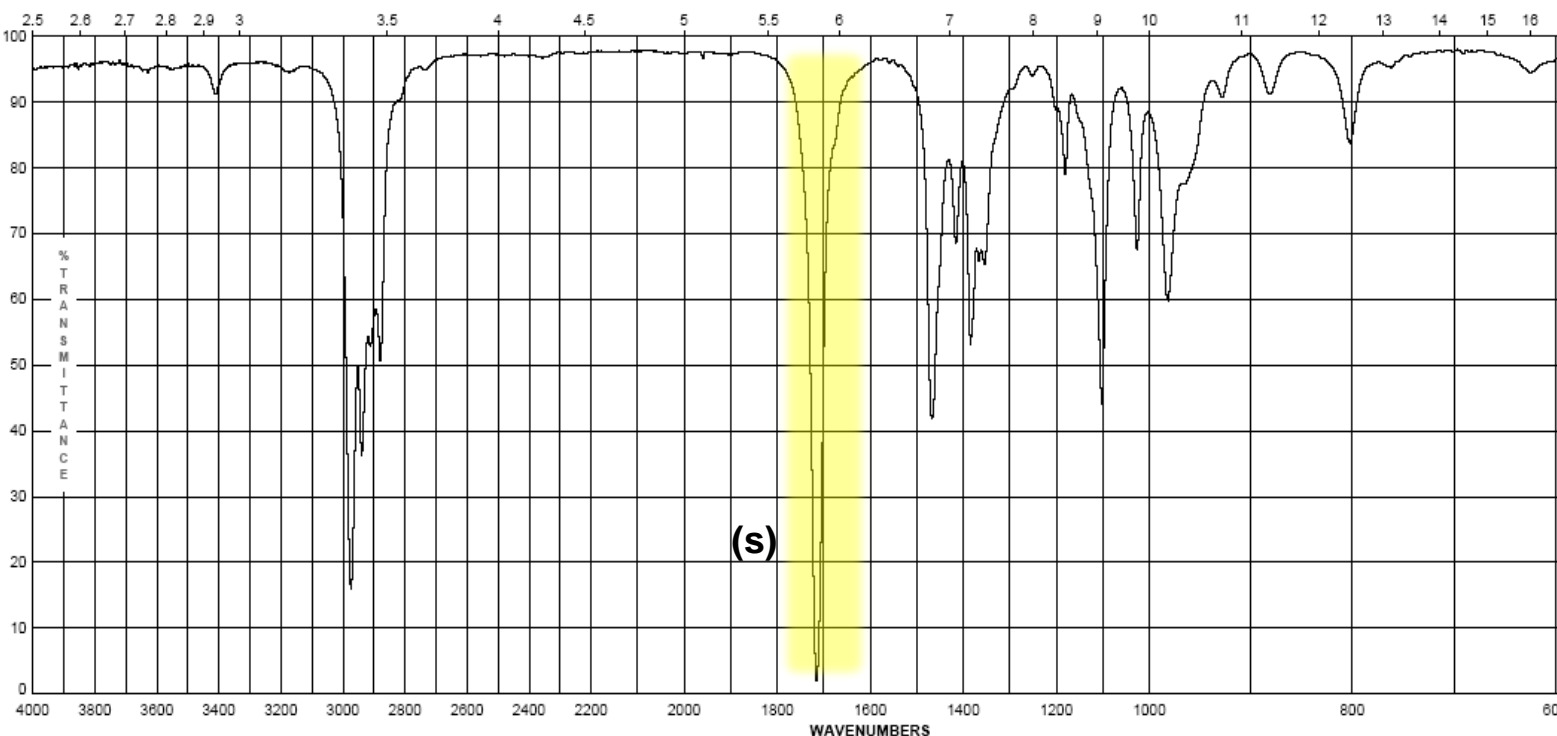
Esters

• C=O stretch at 1735-1750 cm^{-1}

• Strong band for C-O at a higher frequency than ethers or alcohols at 1150-1250 cm^{-1}

Ethyl pivalate
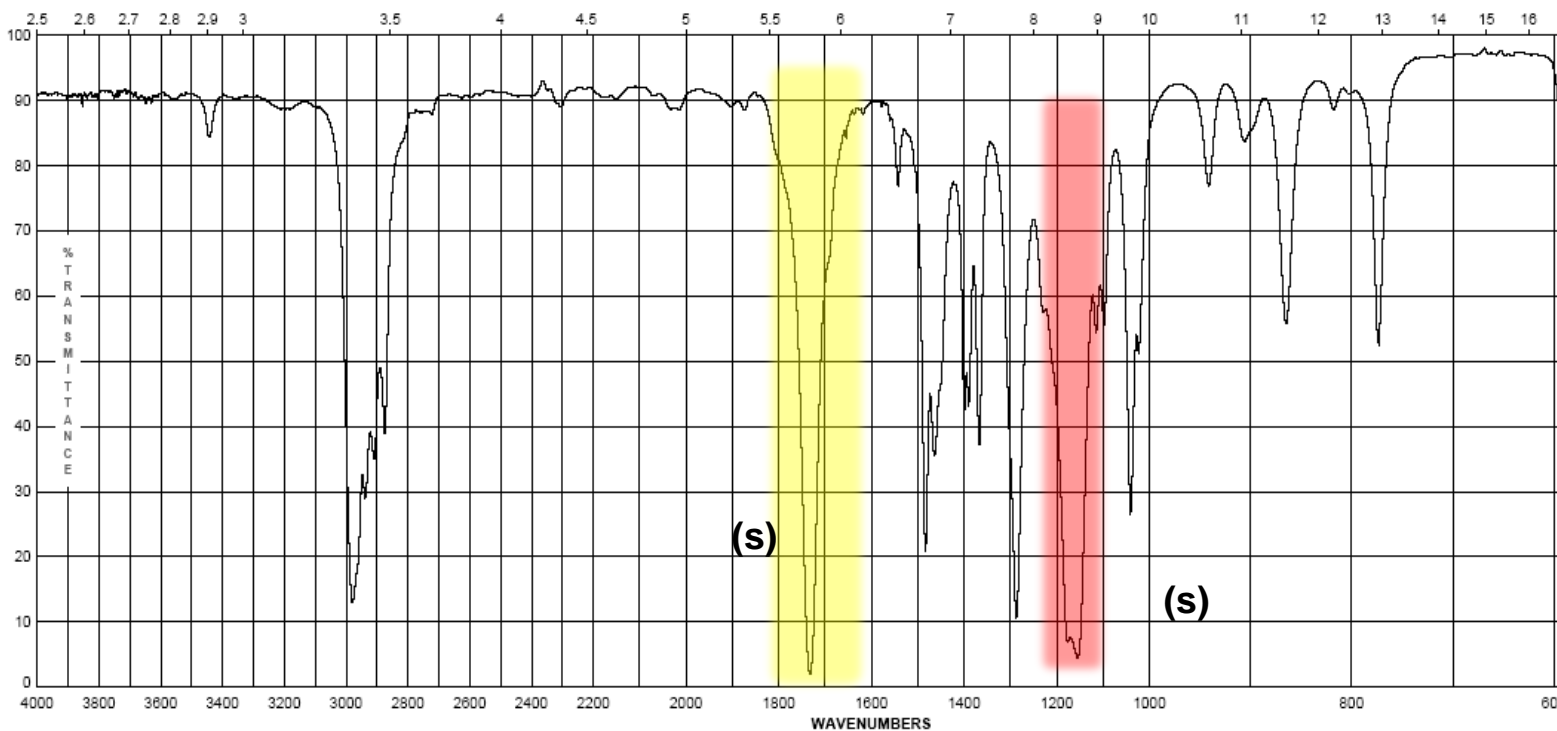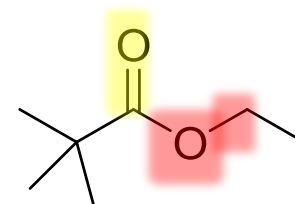
Carboxylic Acids:

- 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} covering up to half the IR spectrum in some cases

This O-H absorbs broadly due to strong hydrogen bonding

1710 cm^{-1}
broad, about 3000 cm^{-1}
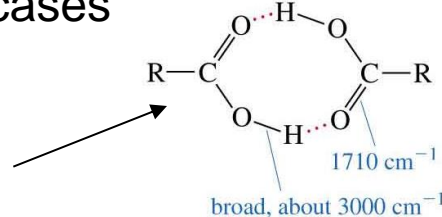
4-phenylbutyric acid

(w – m)
br

(s)

(s)
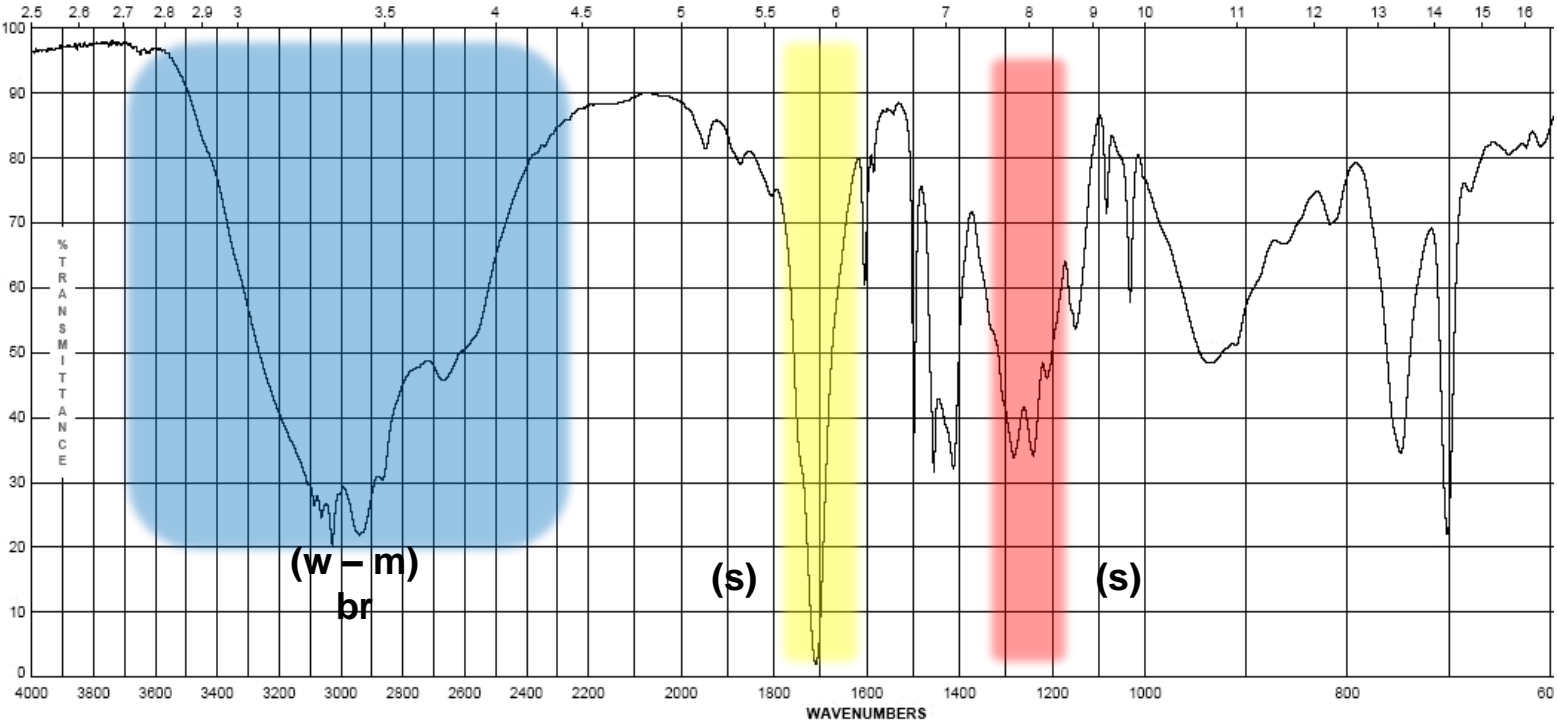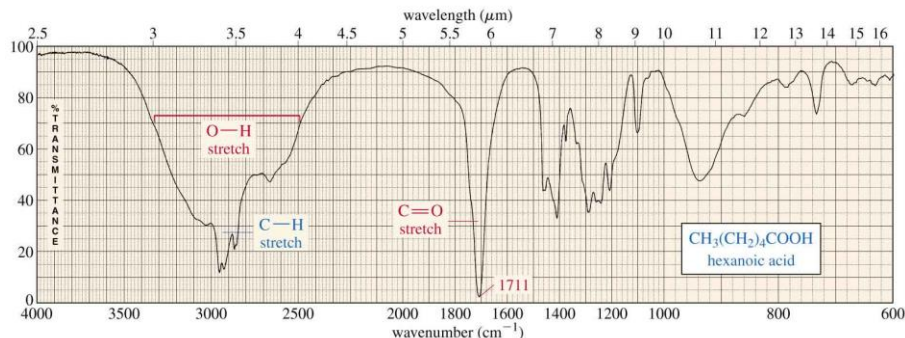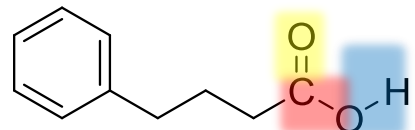
Acid anhydrides

- 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}

- Mixed mode C-O stretch at 1000-1100 cm^{-1}

Propionic anhydride
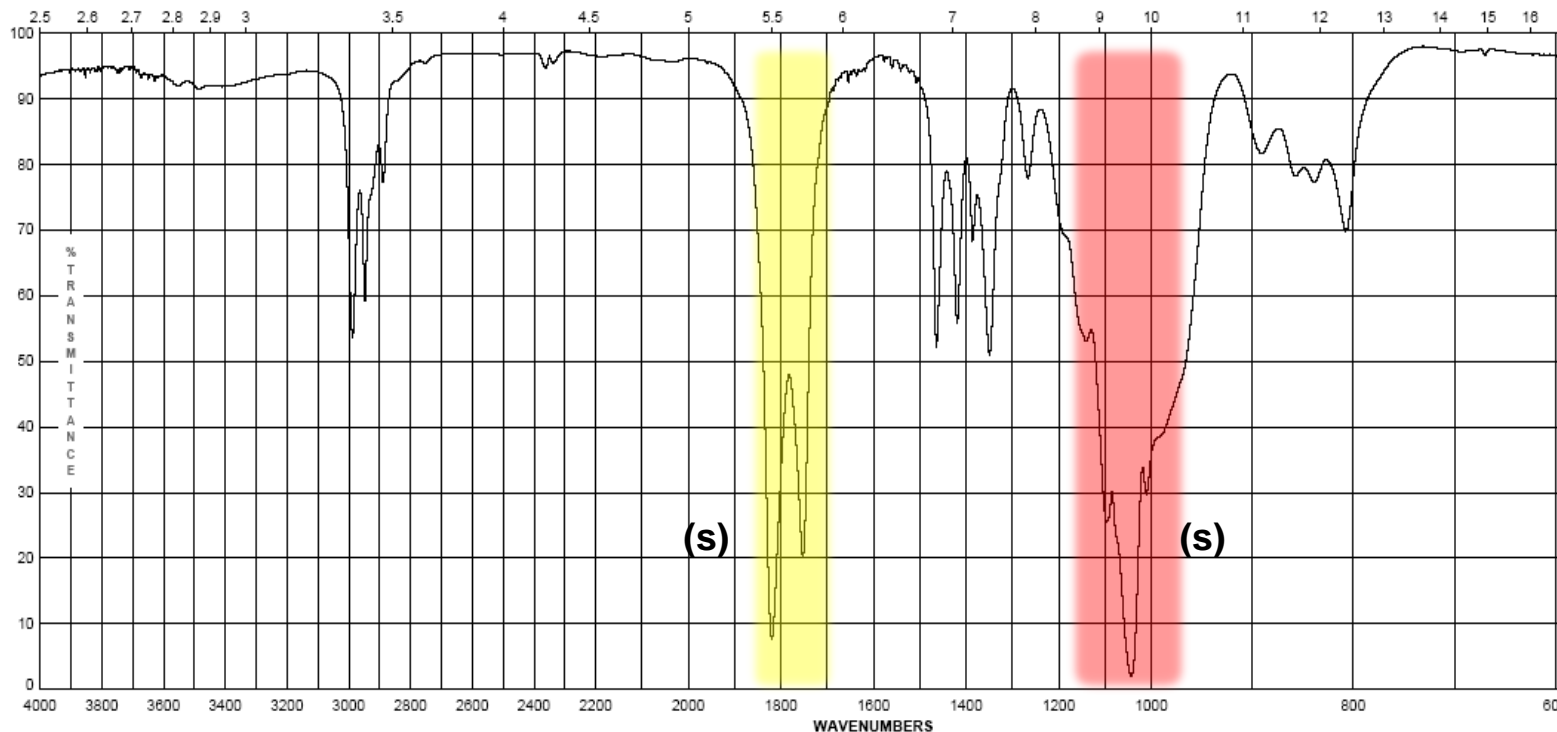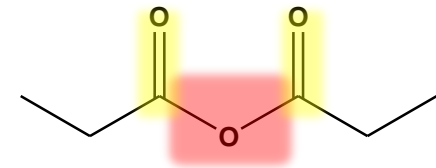
Acid halides

• Clefted band at 1770-1820 cm^{-1} for C=O

• Bonds to halogens, due to their size (see Hooke's Law derivation) occur at low frequencies, only Cl is light enough to have a band on IR, C-Cl is at 600-800 cm^{-1}

Propionyl chloride
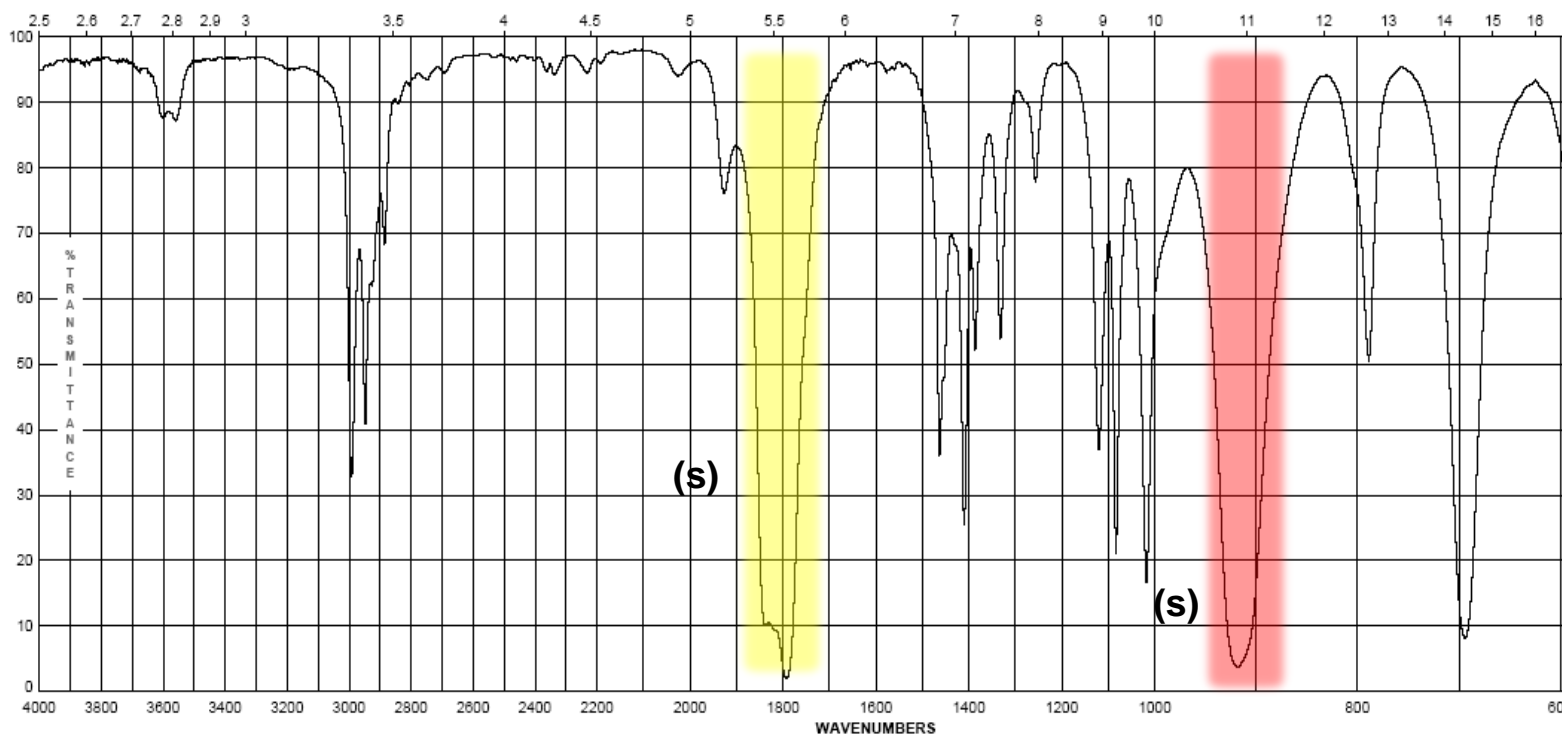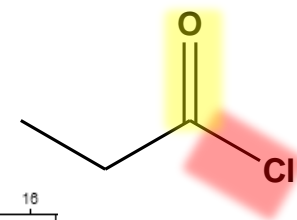
Amides

- Display features of amines and carbonyl compounds

(a) $CH_3CH_2CH_2C\overset{O}{\overset{\|}{-}}NH_2$

- C=O stretch at 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

(m – s)

(s)
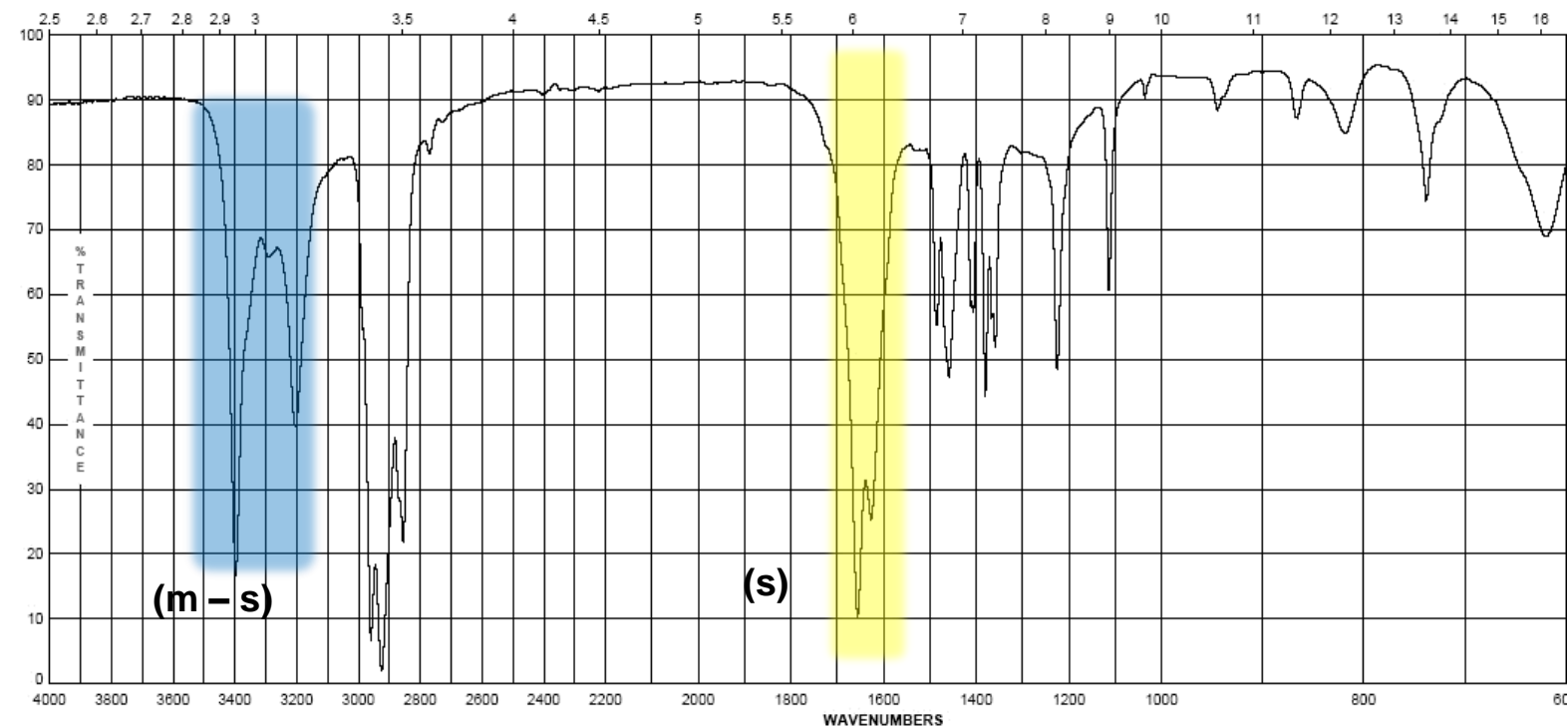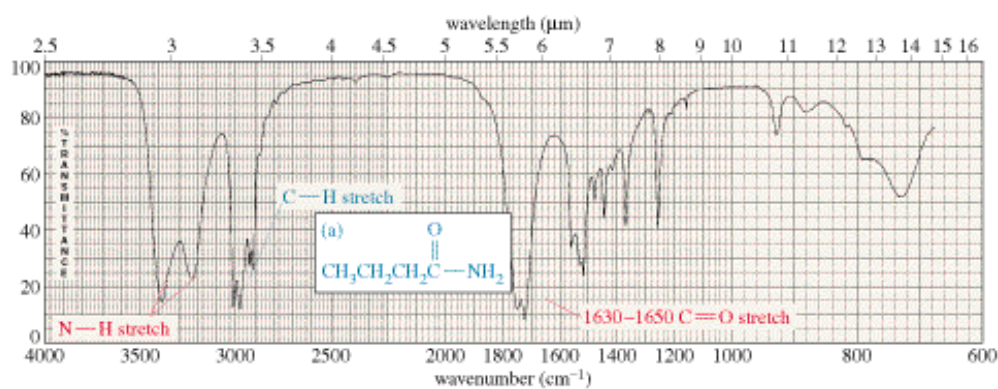
pivalamide
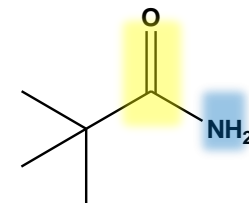
Nitro group (-NO$_2$)

• 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} and 1500-1570 cm^{-1}

• This group is a strong resonance withdrawing group and is itself vulnerable to resonance effects
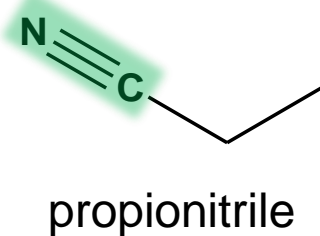
2-nitropropane
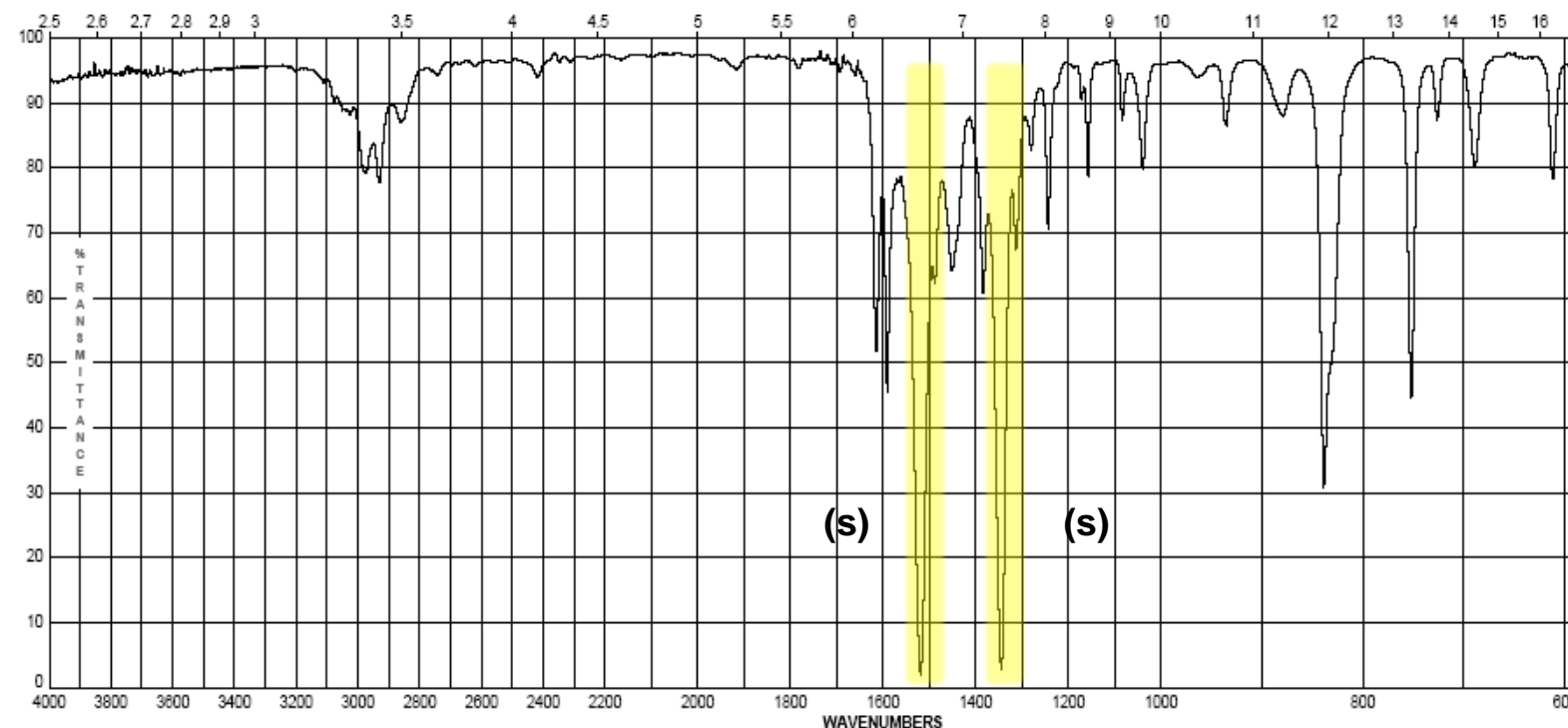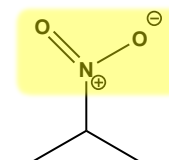
Nitriles (the cyano- or –C≡N group)

• Principle group is the carbon nitrogen triple bond at 2100-2280 cm^{-1}

C≡N stretch 2249

butyronitrile
$CH_3CH_2CH_2C≡N$
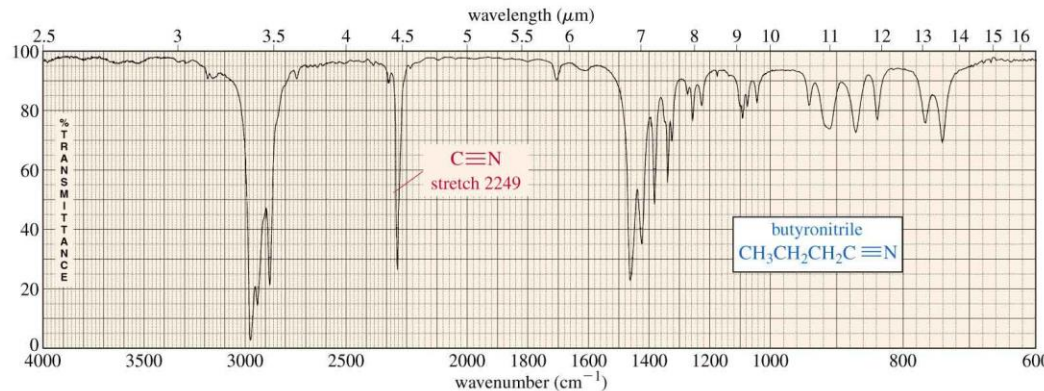
• This peak is usually much more intense than that of the alkyne due to the electronegativity difference between carbon and nitrogen

(s)

propionitrile
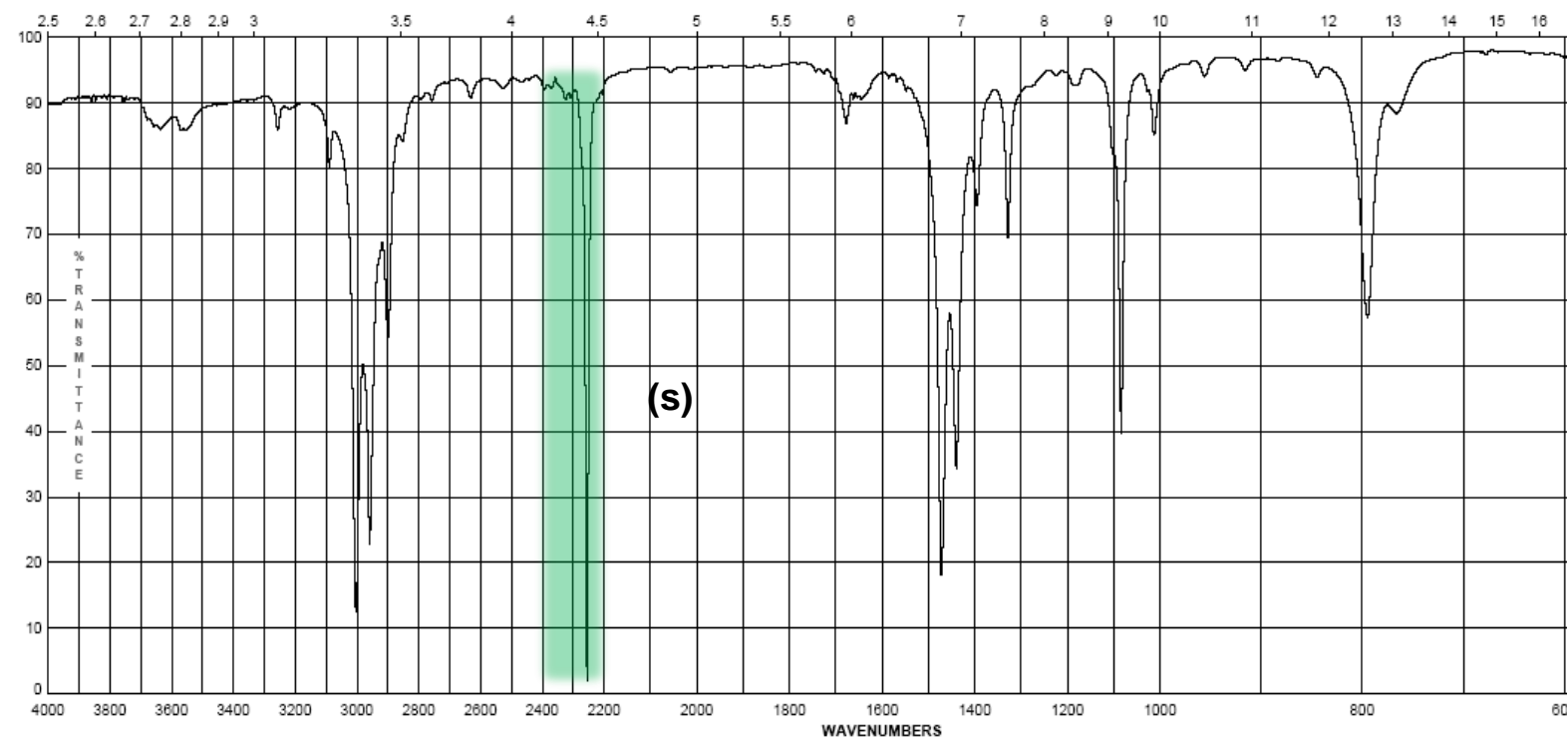
Variations in C=O Absorption

► Conjugation of C=O with C=C lowers the stretching frequency to ~1680 cm^{-1}

► The C=O group of an amide absorbs at an even lower frequency, 1640-1680 cm^{-1}

► The C=O of an ester absorbs at a higher frequency, ~1730-1740 cm^{-1}

► Carbonyl groups in small rings (5 C's or less) absorb at an even higher frequency

Carbon - Nitrogen Stretching

► C - N absorbs around 1200 cm^{-1}
► C = N absorbs around 1660 cm^{-1} and is much stronger than the C = C absorption in the same region
► C $\equiv$ N absorbs strongly just *above* 2200 cm^{-1}.

The alkyne C $\equiv$ C signal is much weaker and is just *below* 2200 cm^{-1}

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:
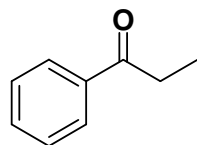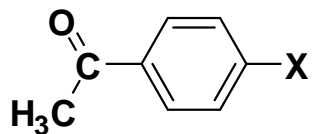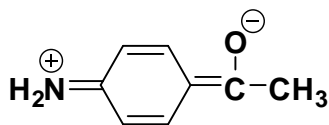

1684 cm^{-1}
C=O
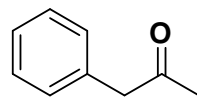
1715 cm^{-1}
C=O

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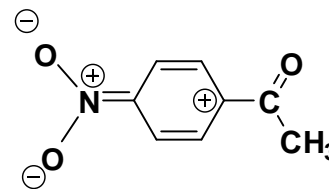

| X =	NH$_2$	CH$_3$	Cl	NO$_2$	
	1677	1687	1692	1700	cm^{-1}

 vs.

Strong resonance contributor
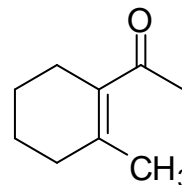
Poor resonance contributor (cannot resonate with C=O)

- Inductive effects are usually small, unless coupled with a resonance contributor (note –CH$_3$ and –Cl above)

Effects on IR bands

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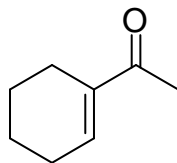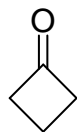

C=O: 1686 cm^{-1} C=O: 1693 cm^{-1}

•   Here the methyl group in the structure at the right causes the carbonyl group to be slightly out of plane, interfering with resonance
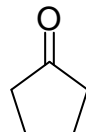
3.   Strain effects – changes in bond angle forced by the constraints of a ring will cause a slight change in hybridization, and therefore, bond strength
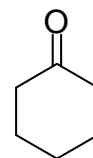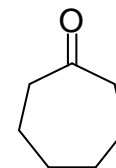

1815 cm^{-1} 1775 cm^{-1} 1750 cm^{-1} 1715 cm^{-1} 1705 cm^{-1}

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

Effects on IR bands

4.   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:
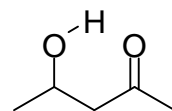
Gas phase spectrum of 1-butanol
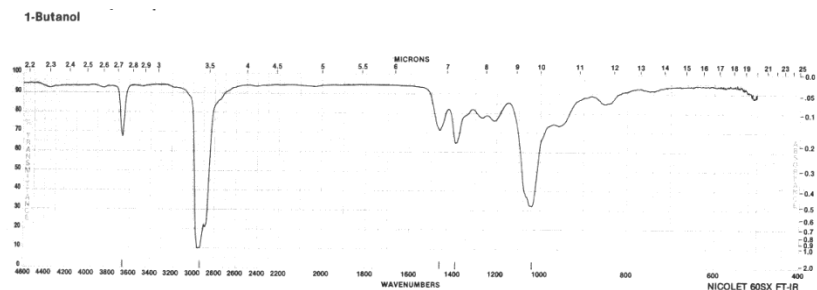
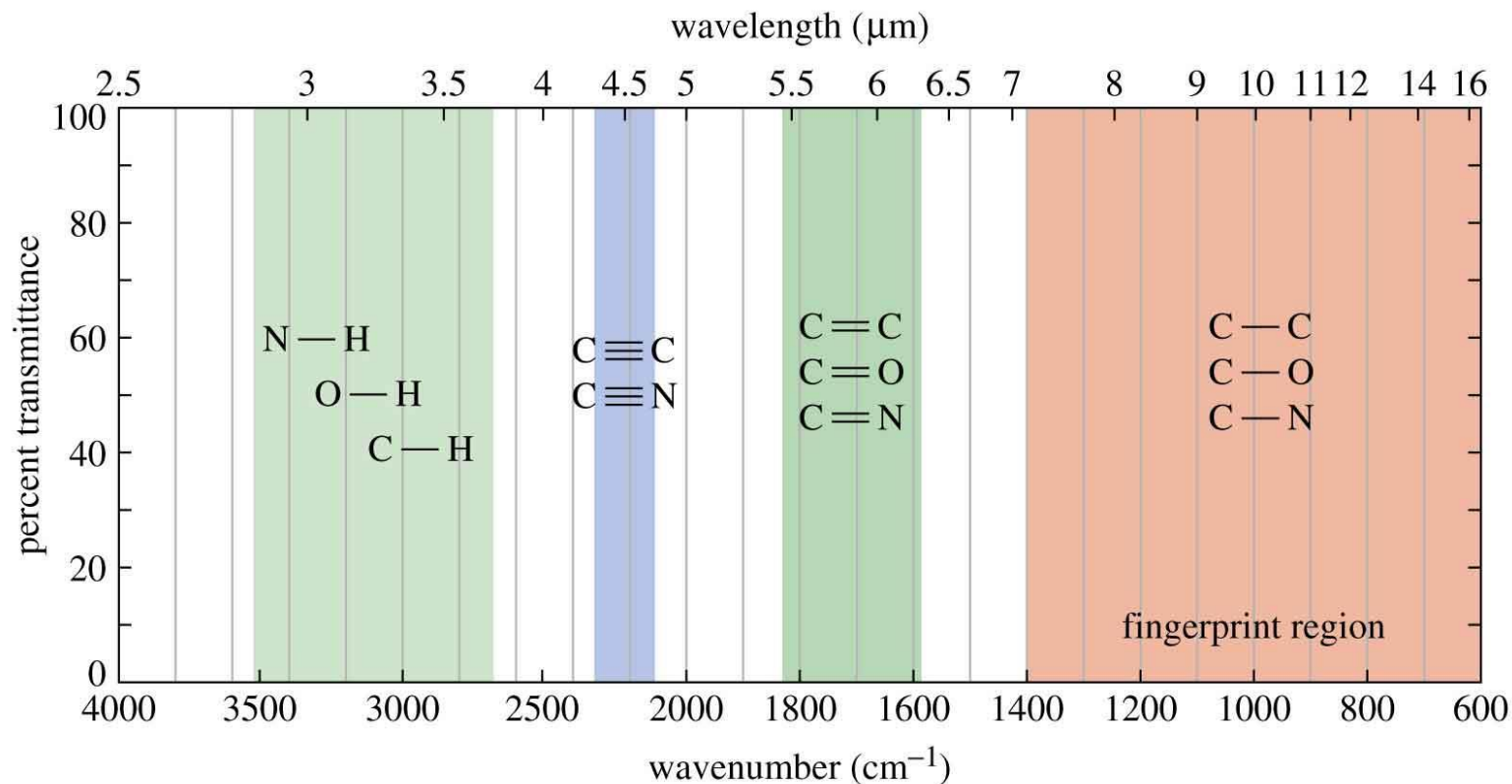Steric hindrance to H-bonding in a di-*tert*-butylphenol
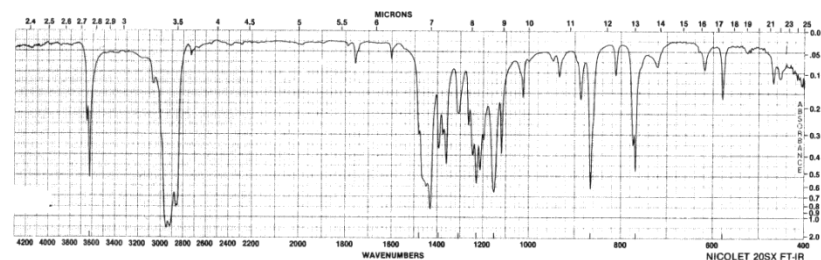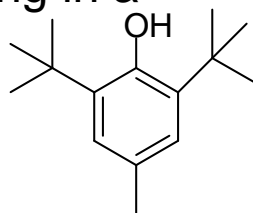
•   H-bonding can interact with other functional groups to lower frequencies

C=O; 1701 cm^{-1}

Summary of IR Absorptions

Strengths and Limitations

► IR alone cannot determine a structure

► Some signals may be ambiguous

► The presence of a *functional group* is usually indicated by a signal in IR spectrum

► The *absence* of a signal is definite proof that the functional group is absent

► Correspondence with a known sample's IR spectrum confirms the identity of the compound

http://www.chem.ualberta.ca/~orglabs/Interactive%20Tutorials/ir/IR%20Quiz.swf

Procedure:

START

1. are there absorptions above 2700 cm^{-1}

--YES: very broad and intense?

--YES: probably -OH

--NO: go to #2

--NO: go to #5

2. is there a weak absorption from 3000-3100 cm^{-1}?

--YES: could be aromatic ring hydrogen or alkene hydrogen stretch

--NO: go to #3

3. is there a sharp absorption from 2700-3000 cm^{-1}?

--YES: could be simple alkane hydrogen stretch

--NO: go to #4

4. is there a medium, sharp absorption from 3300-3500 cm^{-1}?

--YES: NH (if singlet) or NH2 (if doublet) stretch

--NO: go to #5

5. are there absorptions between 2000 and 1500 cm^{-1}?

--YES: intense, from 1660-1770 cm-1?

--YES: probably C=O

--NO: go to #6

--NO: C=O, aromatic and secondary amine probably absent; go to #8

6. is there a sharp, medium absorption close to 1500 or 1600 cm^{-1}?

--YES: could be aromatic or secondary amine

--NO: go to #7

7. **is there a sharp, medium absorption from 1640-1840 cm^{-1}?**
--YES: probably an alkene
--NO: go to #8
8. **are there absorptions between 1500-1100 cm^{-1}?**
--YES: intense between 1050-1300 cm-1?
--YES: could be C-C, C-O, or C-N stretches
--NO: go to #11
--NO: C-O, C-N, CH$_2$, CH$_3$ probably absent; go to #11
9. **is there a medium, sharp absorption at 1375 cm^{-1}?**
--YES: could be -CH$_3$
--NO: go to #10
10. **is there a medium, sharp absorption at 1450 cm^{-1}?**
--YES: could be -CH$_2$- or -CH$_3$
--NO: go to #11
11. **are there <u>strong </u>absorptions below 900 cm^{-1}?**
--YES: sharp at 720 cm-1 could be -CH$_2$-
--OTHERS: aromatic*, alkene or monochloro C-Cl possible
END
* aromatic substitution patterns (may not show):   mono 710-690 cm-1
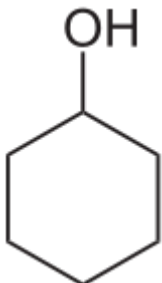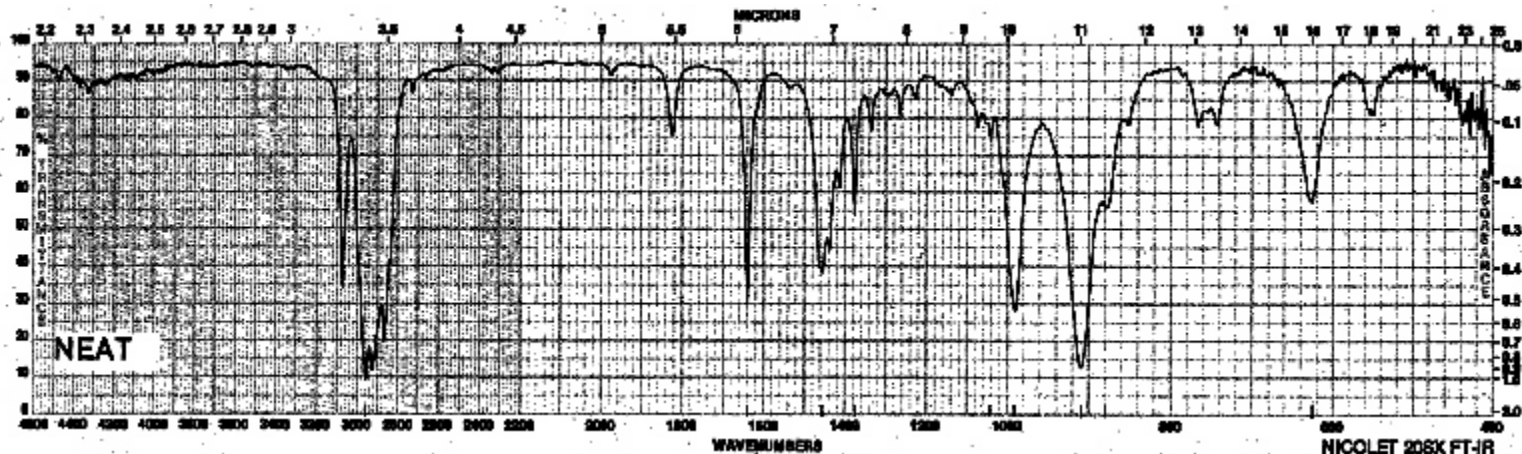   770-730 cm-1
                                                                      1,2-di 770-735 cm-1
                                                                      1,3-di 735-680 cm-1
   810-750 cm-1
                                                                      1,4-di 860-800 cm-1

Exercises:

Alkene - Pentene

Frequency in cm^{-1}	Assignment
3035, 3060, 3090	C-H (sp^2, aromatic)
1479	C=C (stretch)
1036	=C-H (bending in ring plane)
673	=C-H (oop bending)

NEAT

MICRONS

WAVENUMBERS

NICOLET 20SX FT-IR

OH

Alcohols - Cyclohexanol

Frequency in cm^{-1}	Assignment
3600-3100	O-H (stretch)
2930, 2850	CH$_2$ (sp^3, stretch)
1067	C-O (stretch)

NEAT

MICRONS

WAVENUMBERS

NICOLET 20SX FT-IR
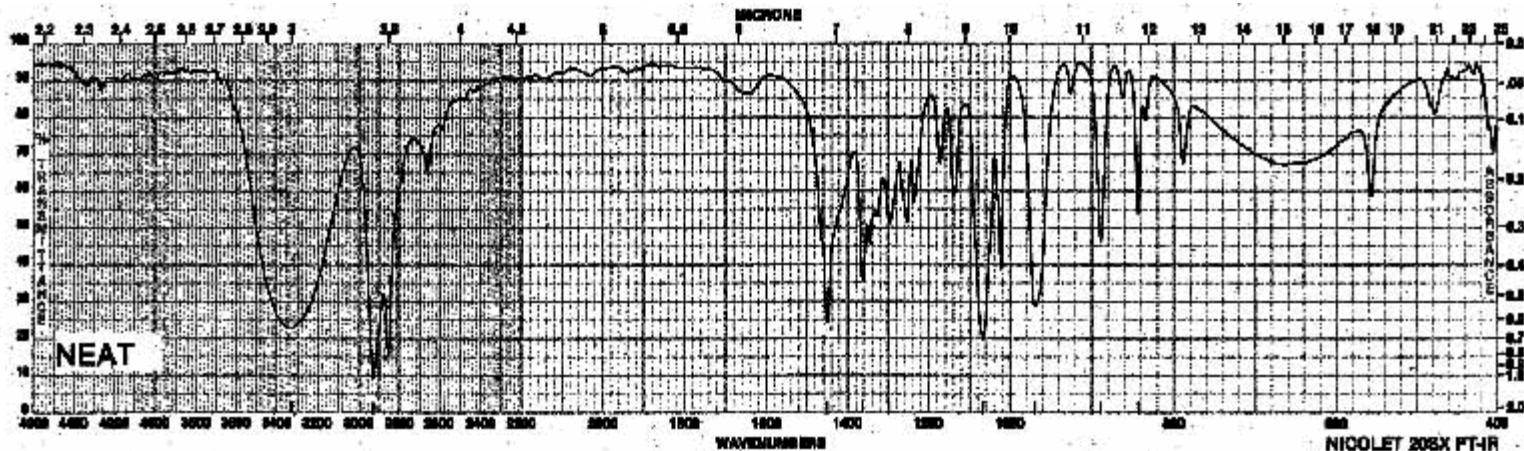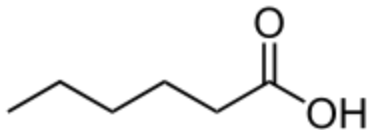
Carboxylic Acid - Hexanoic Acid

Frequency in cm⁻¹	Assignment
3500-2400	O-H (stretch, O-H bridges)
2932	C-H (sp³, stretch)
1711	C=O (stretch)

NEAT

MICRONS

WAVENUMBERS

NICOLET 205X FT-IR
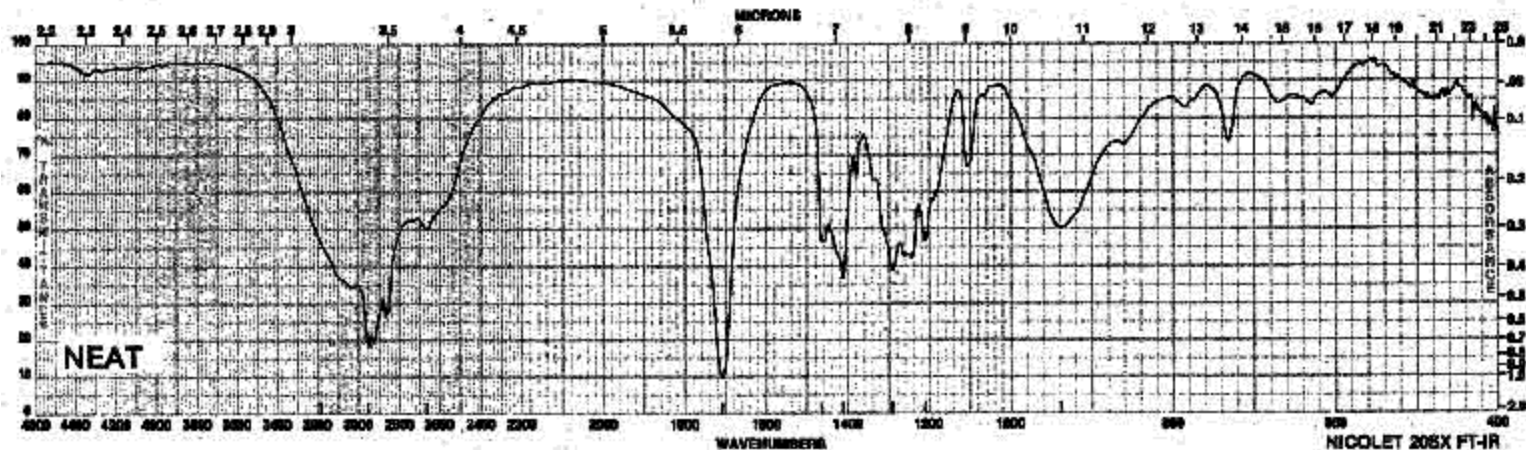
Frequency in cm⁻¹	Assignment
3367, 3280	N-H (stretch, two peaks !)
2958	C-H (sp³, stretch)
1607	N-H (broad, scissoring)
816	N-H (broad, oop bending)

Primary Amine - Propylamine

NEAT

MICRONS

WAVENUMBERS

NICOLET 205X FT-IR
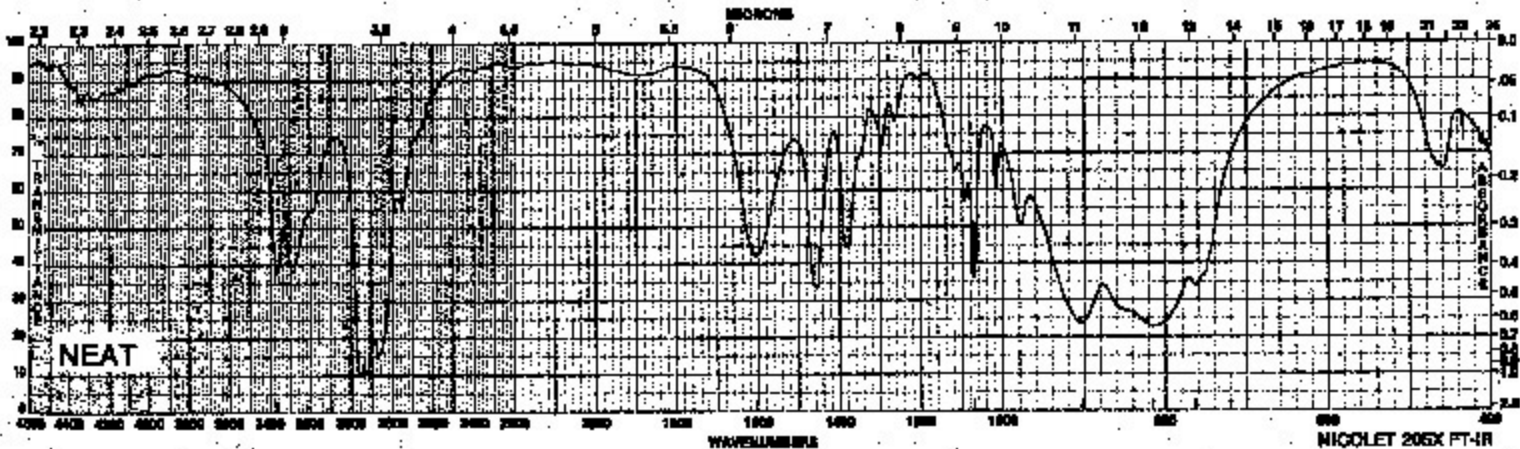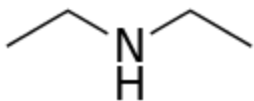
Secondary Amine - Diethylamine

Frequency in cm^{-1}	Assignment
3280	N-H (stretch, one peak only)
2964	C-H (sp^3, stretch)
1452	CH$_3$ (bend)
1378	CH$_2$, CH$_3$ (bend)
776	N-H (oop bending)

NEAT

NICOLET 20SX FT-IR

Frequency in cm^{-1}	Assignment
3560	overtone from C=O peak
2963	C-H (sp^3, stretch)
1801	C=O (stretch)
753	C-Cl (stretch)
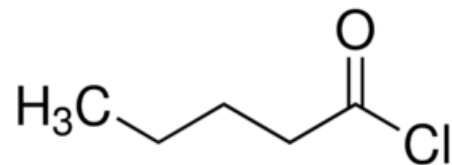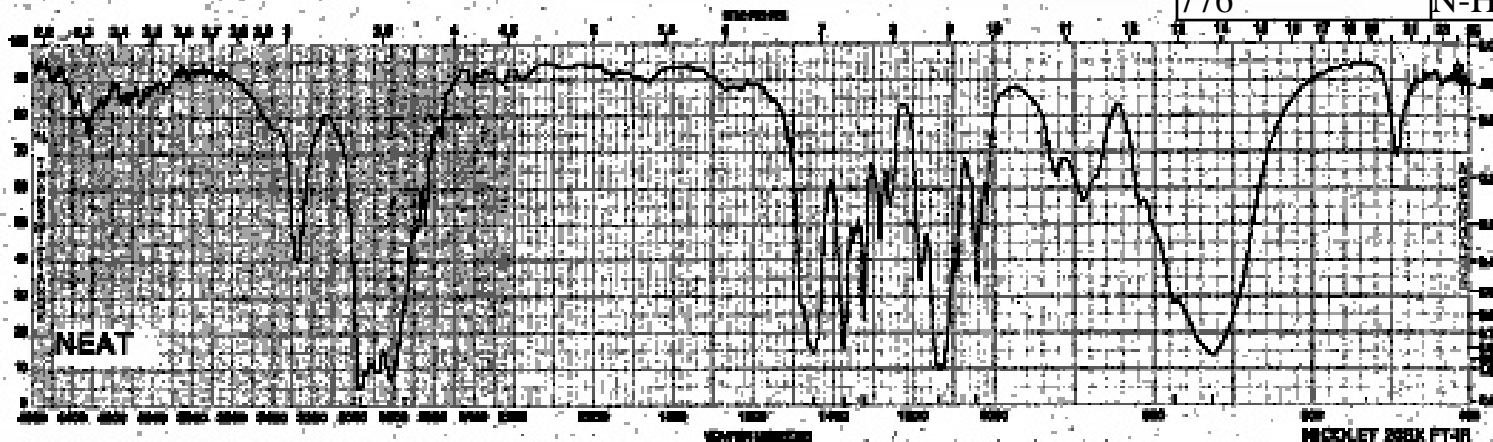
Carboxylic Acid Chloride

NEAT

NICOLET 20SX FT-IR
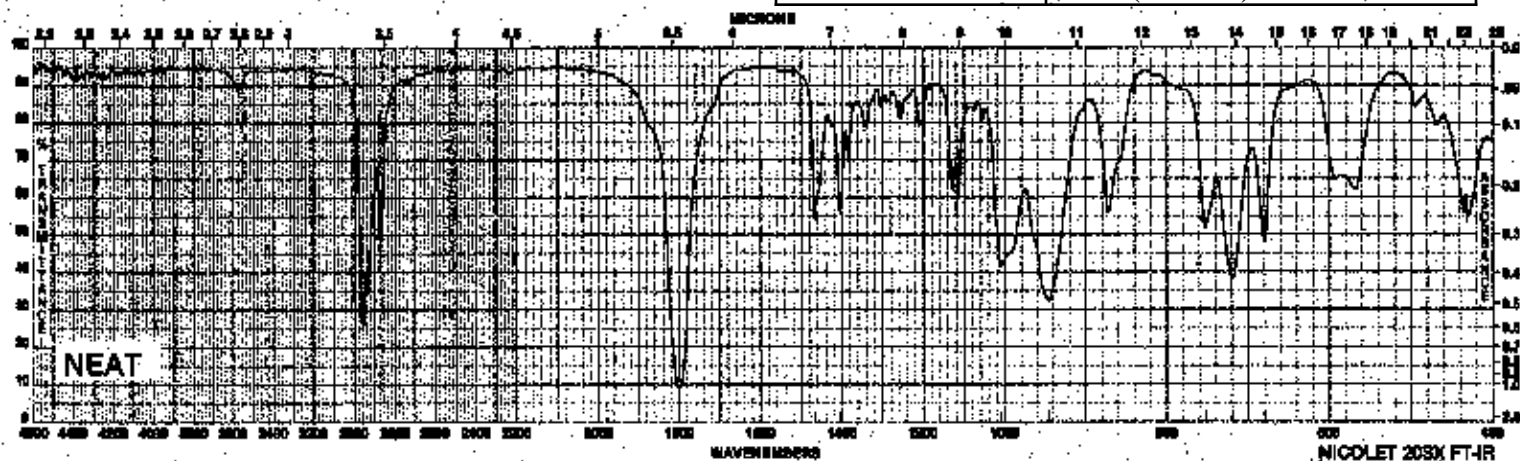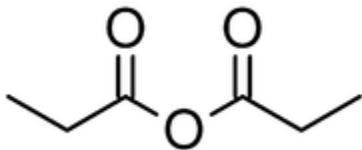
Carboxylic Acid Anhydrides

Frequency in cm^{-1}	Assignment
2987	C-H (sp^3, stretch)
1819	C=O (asym. stretch)
1751	C=O (sym. stretch)
1094	C-O (stretch)

NEAT

NICOLET 20SX FT-IR
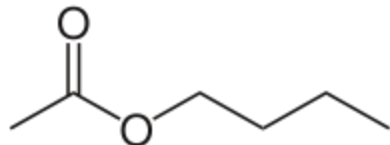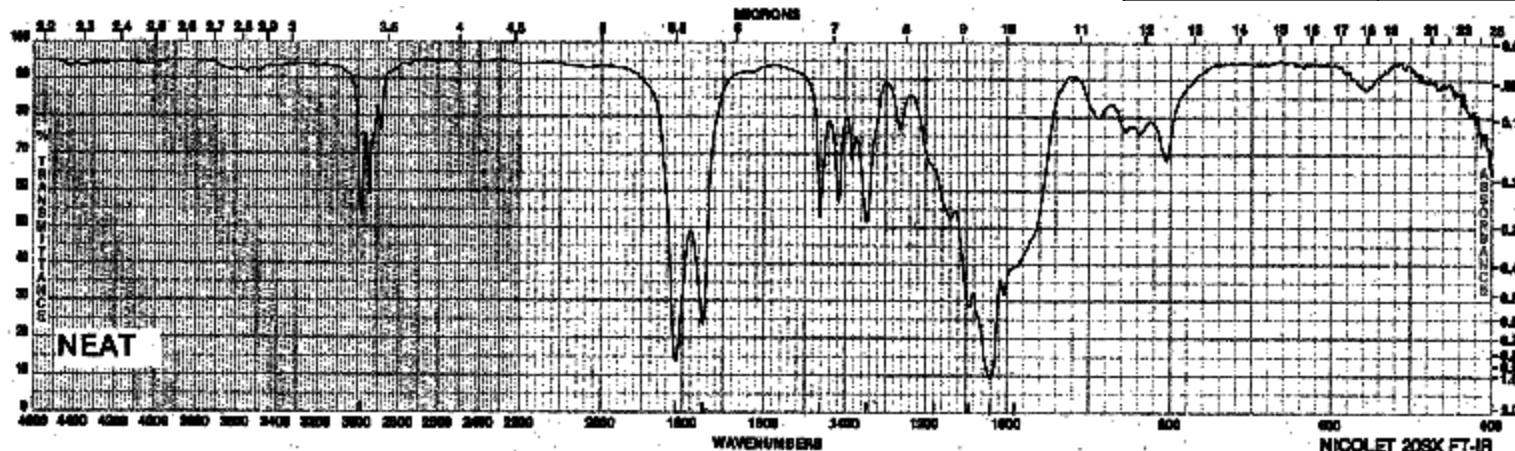
Ester - Butyl acetate

Frequency in cm^{-1}	Assignment
2962	C-H (sp3, stretch)
1743	C=O (stretch)
1243, 1031	C-O-C (stretch)

NEAT

NICOLET 20SX FT-IR
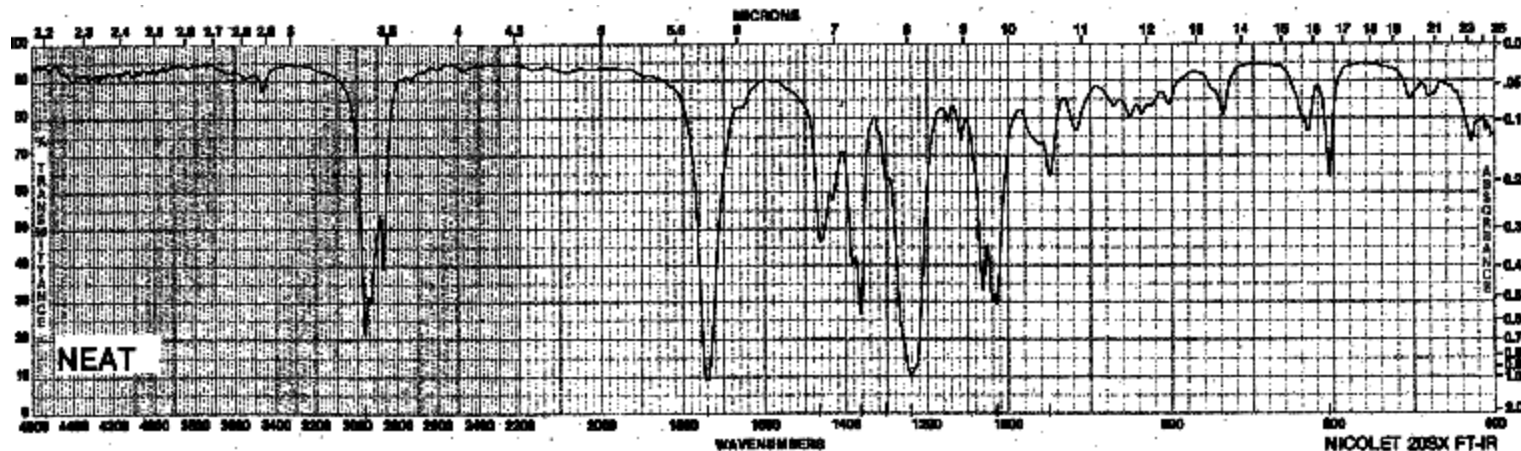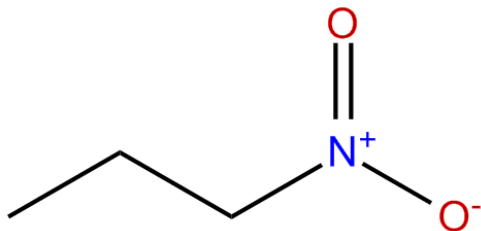
1-Nitropropane

Frequency in cm⁻¹	Assignment
2978	C-H (sp³, stretch)
1554	NO₂ (asym. stretch)
1387	NO₂ (sym. stretch)

NEAT

NICOLET 20SX FT-IR
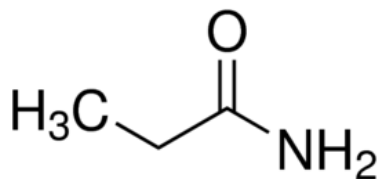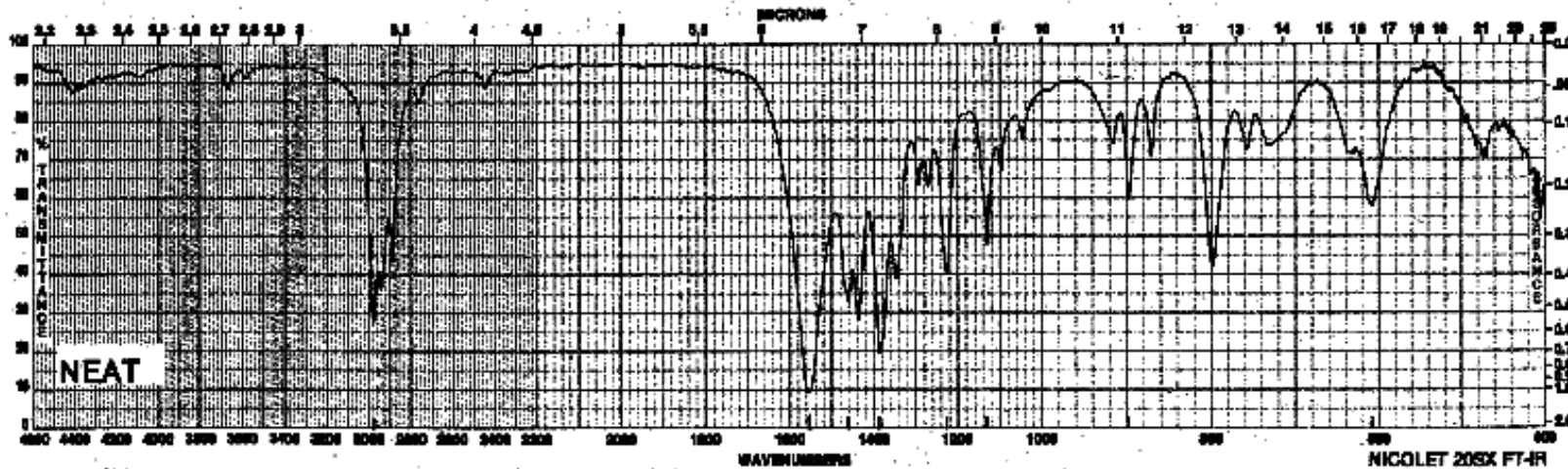
Propionamide

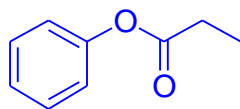| Frequency in cm⁻¹	Assignment
3362, 3200	N-H (stretch, two peaks for a primary amide)
2920	C-H (sp³, stretch)
1661	C=O (stretch)

NUJOL

NICOLET 20SX FT-IR
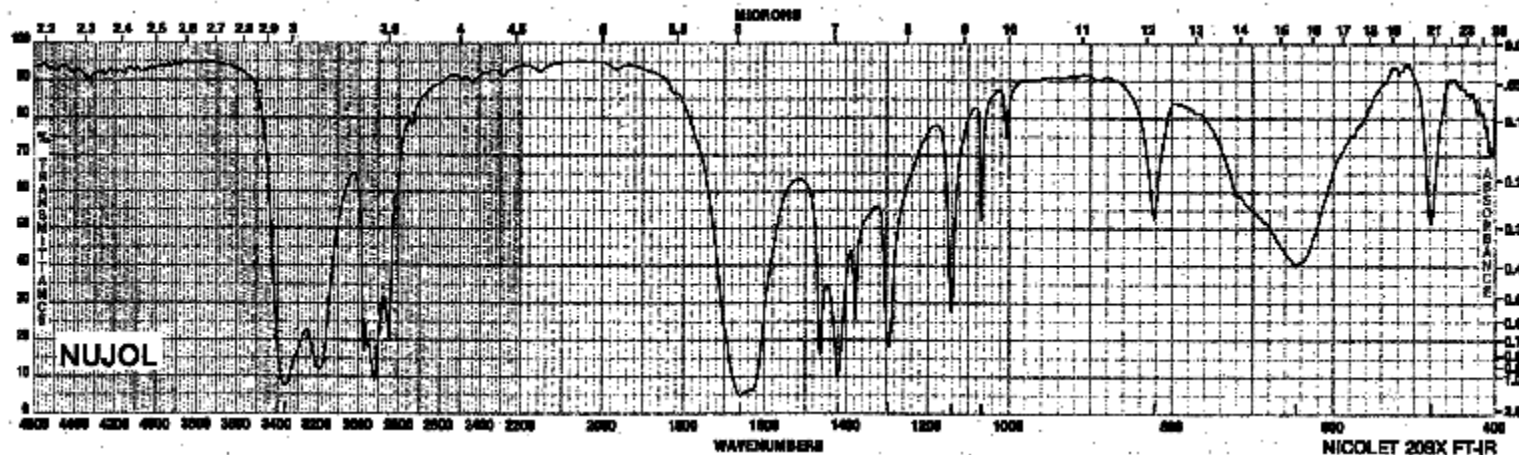
Which of the following substances correspond to given IR spectra?
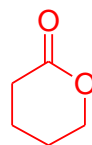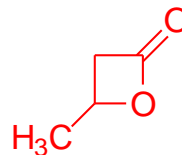## Indicate at least two IR bands related to functional groups from chosen substance:

A   B   C   D   E

1

2

3

4

5
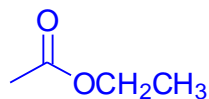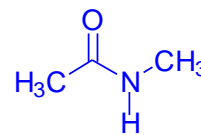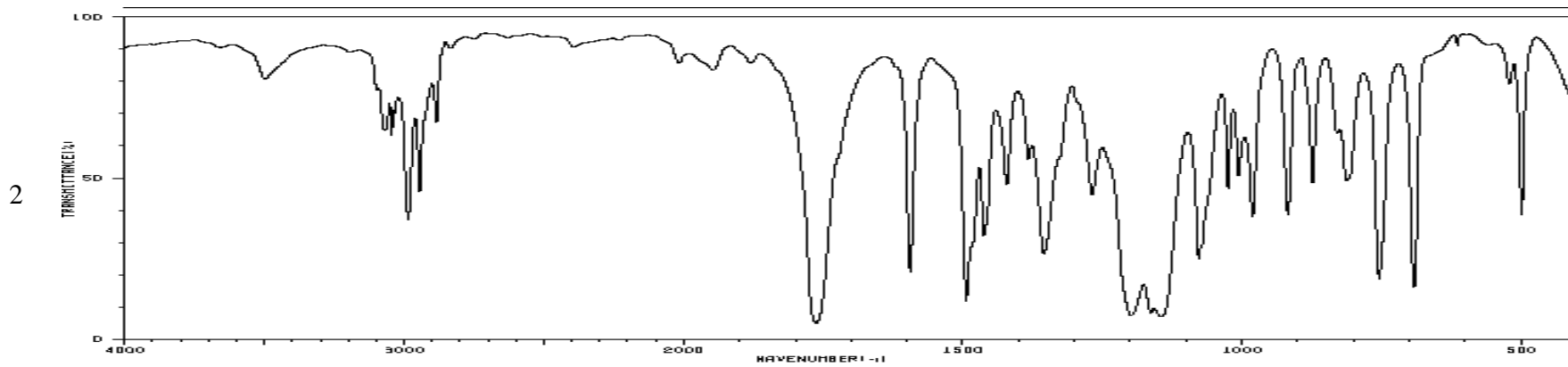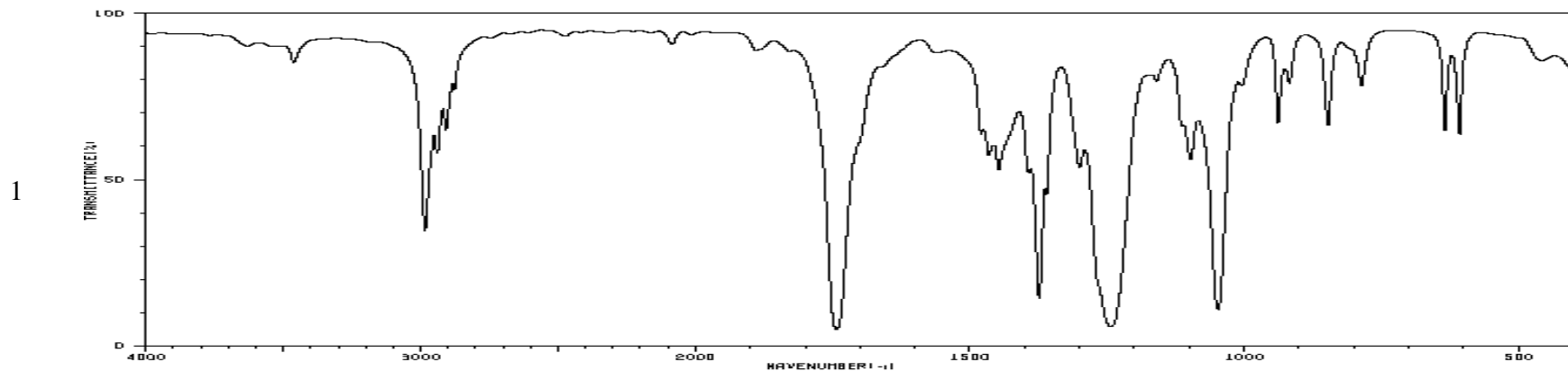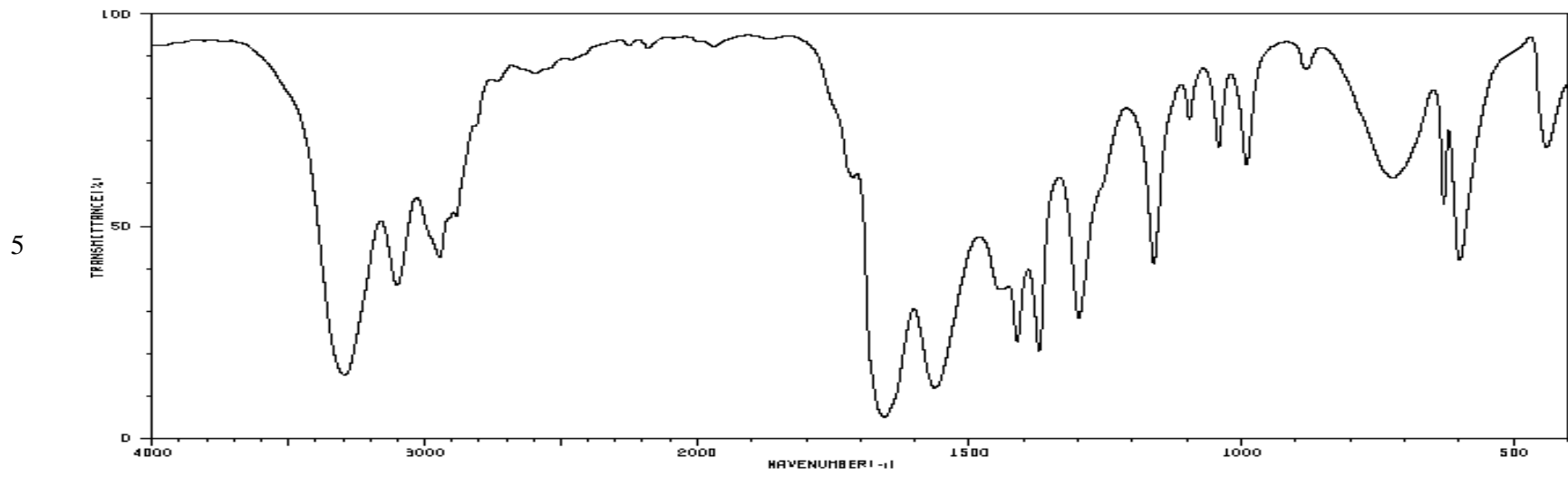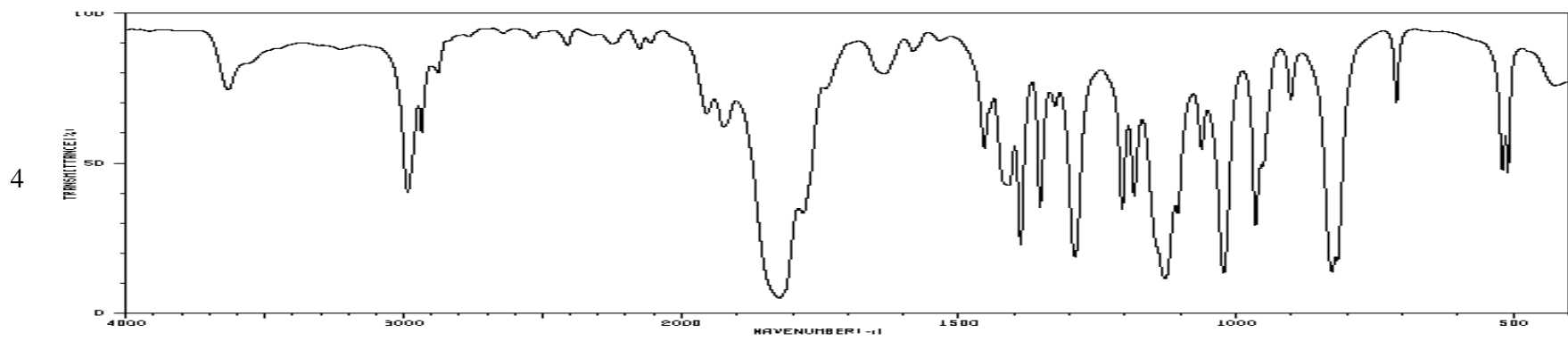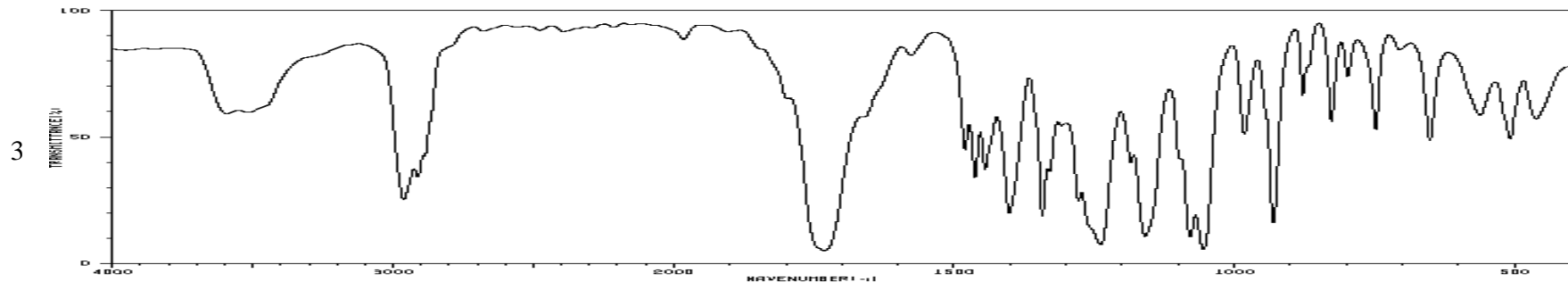
The three next infrared spectra are from compounds whose elemental composition is given at the upper left hand corner of each plot (C_3H_3Br, $C_4H_4O_3$, $C_3H_5O_2Cl$). From the spectra and the summary tables of characteristic vibrational frequencies, deduce the structure of each compound, explaining your reasoning throughout.

C_3H_3Br

$C_4H_4O_3$

$C_3H_5O_2Cl$

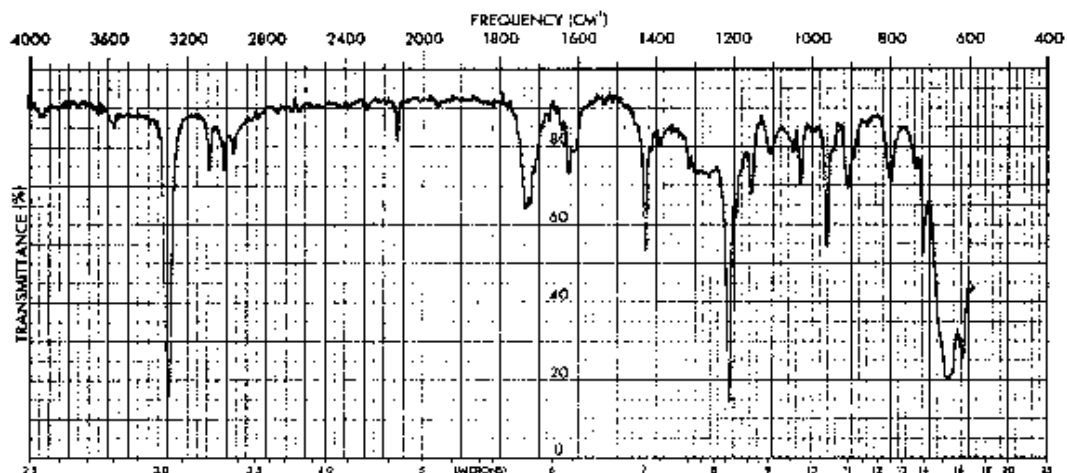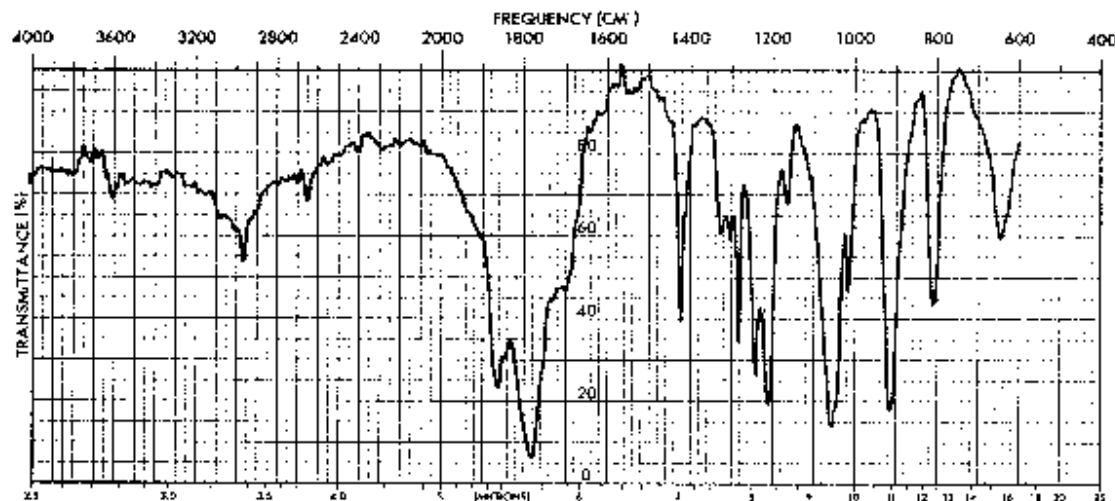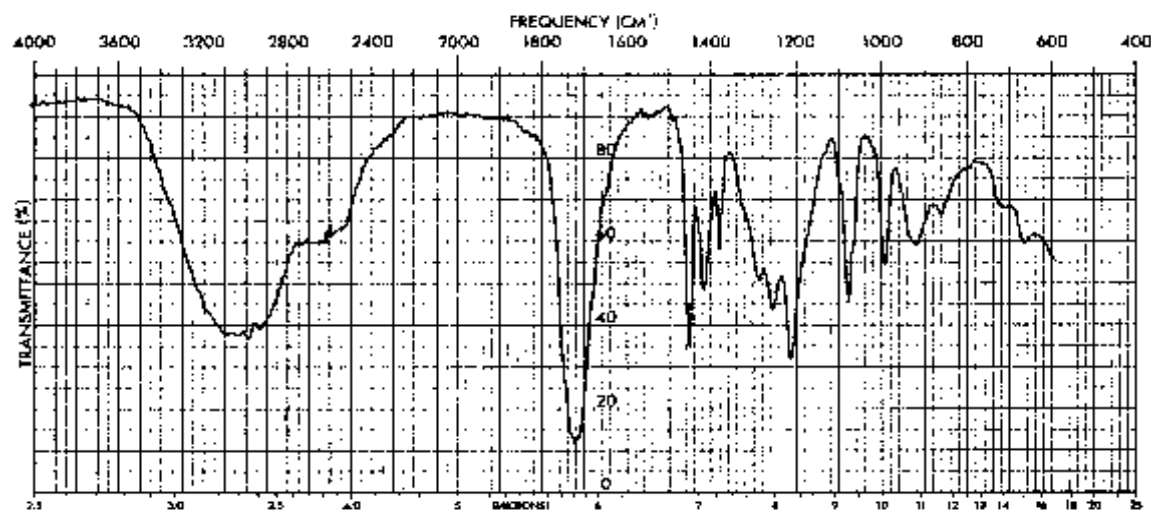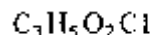| Carbonyl Derivative	Carbonyl Absorption	Comments
Acyl Halides (RCOX) X = F X = Cl X = Br	C=O stretch 1860 ± 20 cm^{-1} 1800 ± 15 1800 ± 15	Conjugation lowers the C=O frequencies reported here, as with aldehydes & ketones. In acyl chlorides a lower intensity shoulder or peak near 1740 cm^{-1} is due to an overtone interaction.
Acid Anhydride, (RCO)$_2$O acyclic 6-membered ring 5-membered ring	C=O stretch (2 bands) 1750 & 1820 cm^{-1} 1750 &1820 1785 & 1865	Conjugation lowers the C=O frequencies reported here, as with aldehydes & ketones. The two stretching bands are separated by 60 ± 30 cm^{-1}, and for acyclic anhydrides the higher frequency (asymmetric stretching) band is stronger than the lower frequency (symmetric) absorption. Cyclic anhydrides also display two carbonyl stretching absorptions, but the lower frequency band is the strongest. One or two -CO-O-CO- stretching bands are observed in the 1000 to 1300 cm^{-1} region.
Esters & Lactones (RCOOR')	C=O stretch 1740 cm $\pm$ 10 cm	Conjugation lowers the C=O frequencies reported here, as with aldehydes & ketones Strong CO-O stretching absorptions (one ot two) are found from 1150 to 1250 cm^{-1}

	Stretching Vibrations			**Bending Vibrations**		
Functional Class	**Range (nm)**	**Intensity**	**Assignment**	**Range (nm)**	**Intensity**	**Assignment**
Alkanes	2850-3000	str	CH_3, CH_2 & CH 2 or 3 bands	1350-1470 1370-1390 720-725	med med wk	CH_2 & CH_3 deformation CH_3 deformation CH_2 rocking
Alkenes	3020-3100 1630-1680 1900-2000	med var str	=C-H & =CH_2 (usually sharp) C=C (symmetry reduces intensity) C=C asymmetric stretch	880-995 780-850 675-730	str med med	=C-H & =CH_2 (out-of-plane bending) cis-RCH=CHR
Alkynes	3300 2100-2250	str var	C-H (usually sharp) C≡C (symmetry reduces intensity)	600-700	str	C-H deformation
Arenes	3030 1600 & 1500	var med-wk	C-H (may be several bands) C=C (in ring) (2 bands) (3 if conjugated)	690-900	str-med	C-H bending & ring puckering
Alcohols & Phenols	3580-3650 3200-3550 970-1250	var str str	O-H (free), usually sharp O-H (H-bonded), usually broad C-O	1330-1430 650-770	med var-wk	O-H bending (in-plane) O-H bend (out-of-plane)
Amines	3400-3500 (dil. soln.) 3300-3400 (dil. soln.) 1000-1250	wk wk med	N-H (1°-amines), 2 bands N-H (2°-amines) C-N	1550-1650 660-900	med-str var	NH_2 scissoring (1°-amines) NH_2 & N-H wagging (shifts on H-bonding)
Aldehydes & Ketones	2690-2840 (2 bands) 1720-1740 1710-1720 1690 1675 1745 1780	med str str str str str str	C-H (aldehyde C-H) C=O (saturated aldehyde) C=O (saturated ketone) aryl ketone α,β-unsaturation cyclopentanone cyclobutanone	1350-1360 1400-1450 1100	str str med	α-CH_3 bending α-CH_2 bending C-C-C bending
arboxylic Acids & Derivatives	2500-3300 (acids) overlap C-H 1705-1720 (acids) 1210-1320 (acids) 1785-1815 (acyl halides) 1750 & 1820 (anhydrides)	str str med-str str str	O-H (very broad) C=O (H-bonded) O-C (sometimes 2-peaks) C=O C=O (2-bands)	1395-1440	med	C-O-H bending