Infrared Spectroscopy

A Basic Introduction

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Molecular spectroscopy

- **Two types according to energy changes**
  - **Electronic transitions**: transitions between different electronic energy states, giving UV spectra.
  - **Vibrational and rotational transitions**: transitions between different vibrational or rotational levels with smaller energy changes, giving IR and Raman spectra.

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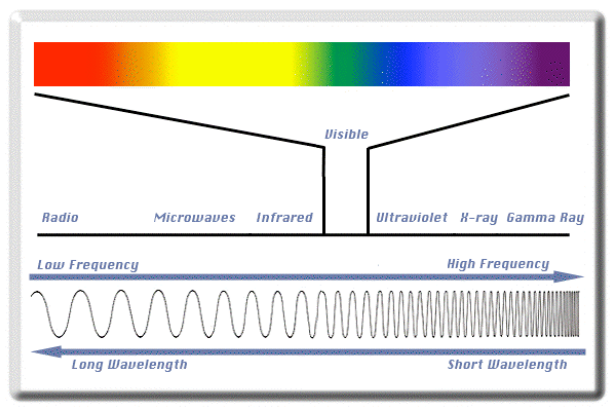
Electromagnetic Spectrum



- Frequency and wavelength are inversely proportional
- $c = \lambda\nu$, where c is the speed of light
- Energy per photon = $h\nu$, where h is Planck's constant

The Spectrum and Molecular Effects

Wavelength (λ) cm		Energy kcal/mol	Molecular effects
higher frequency, shorter wavelength			
ENERGY	10^{-9} gamma rays	10^{6}	
	10^{-7} X rays	10^{4}	ionization
	vacuum UV	10^{2}	
	10^{-5} near UV		electronic transitions
	10^{-4} visible	10	
	10^{-3} infrared (IR)	1	molecular vibrations
		10^{-2}	
	10^{-1} microwave	10^{-4}	rotational motion
	10^{2} 10^{4} radio	10^{-6}	nuclear spin transitions
lower frequency, longer wavelength			

IR spectra

- Appearance: many complex lines and bands.
- Reflect changes in dipole moment resulting from rotational and vibrational motions in molecules.
- Expression of spectra: %T vs. cm^{-1}
- Applications: useful in structural elucidation of functional groups in molecules, primarily in the area of natural products, organic syntheses.

IR spectra

- Fingerprint region : 1500 - 700 cm^{-1}, very useful in compounds identification by comparison of spectra, as two different compounds show different pattern in this region (except enantiomers).
- Stored in spectral catalogues or computer databases for comparison and identifications.

Vibration of Molecules

- IR spectra: reveal structural information through normal mode of vibration of molecule.
- Normal mode of vibration: each atom is connected to the molecule with bond acted like a spring undergoing harmonic oscillation about its equilibrium position. All atoms move in phase with the same frequency, v, and center of gravity does not move.

Normal Mode of Vibration

- Frequency : of a harmonic oscillator

$$= \frac{1}{2\#}\sqrt{\mu}$$

v is the frequency of oscillation, in unit of s^{-1},

k is the force constant in mdyne/Å

μ is the reduced mass in a.m.u. (atomic mass unit, Dalton)

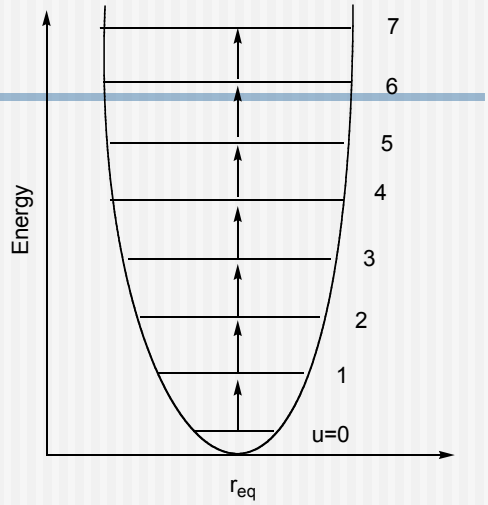
Simple harmonic oscillator

- **Force constant: derived from the Newton's equation, F = k·x , where k is the force constant and x is the displacement from equilibrium position.**
- **The force constant is very useful in predicting the frequency of a functional group.**

$$\# \sqrt{\quad}$$

Harmonic oscillator

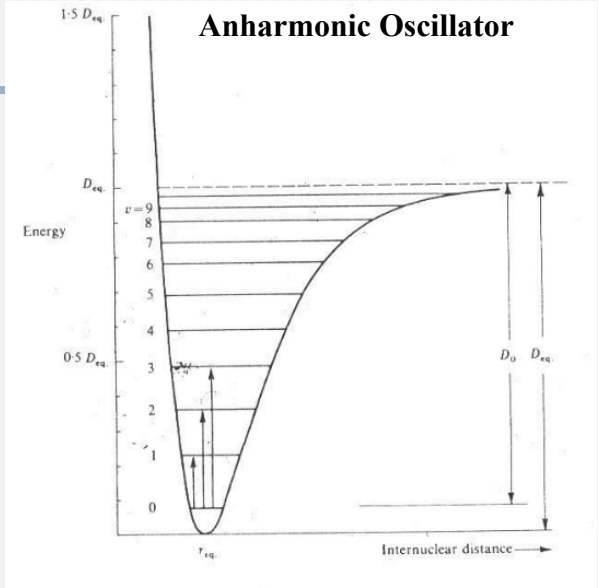
- **Energy levels: according to quantum mechanics, solution of wave equation of a molecular system gives *N* energy levels.**
- **Each level is assigned a corresponding quantum number:**
- **u = 0, 1, 2,.....**
- **Equally spaced energy levels:**
- **$\Delta E = E_1 - E_0 = E_2 - E_1 = ... = hv$**



Harmonic oscillator

Anharmonic oscillator

- For real molecules: there exist nonideal anharmonicity, i.e. vibration of an anharmonic oscillator.
- ΔE is different for each level, and the energy levels are getting narrower and squeezed nearing the point where the bond dissociation occurs.



Energy Level Transitions

- Most molecules exists in the ground state
- The most probable transition is E_0 --> E_1
- The energy-frequency relationship:

  $\Delta E = E_1 - E_0 = h\ v$

  h is Planck's constant 6.624×10^{-34} J·S

  v is frequency in s^{-1}

Different Transitions

- Fundamental Transition: transition from $u_i = 0$ to $u_i = 1$ is an allowed transition.
- Overtone: transition from $u_i = 0$ to $u_i = 2$ is forbidden transition.
- Combination Transition: a transition from ground state to two different levels, i.e. a combination band of fundamentals or overtones.

Rule of Transitions

- Allowed transition: $\Delta v = 1$, fundamental band is allowed transition line.
- Forbidden transition: $\Delta v > 1$

  Overtones and combination lines are forbidden in simple harmonic oscillator, which become allowed transitions in anharmonic oscillator, giving weak absorption bands in IR spectra.

Units and Notations in IR

- The spectrum is recorded graphically with wavelength, frequency, or wave number as the abscissa, vs. the amount of absorption (or transmission) as the ordinate scale.
- As the frequency of vibration in a molecule is very large (near 10^{13} s^{-1}), so a more convenient unit is the wave number obtained by dividing the frequency with the light speed.

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

Different Relationships

- Wave number vs. frequency:

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

$\bar{\nu}$: Wave number in cm^{-1}

ν : Frequency in s^{-1}

c : velocity of light (3×10^{10} cm s^{-1})

Wave length vs. wave number:

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

Energy difference:

$$\Delta E = h\nu = hc\bar{\nu}$$

Appearance of Spectra

- In modern data or catalogues they are expressed in wave numbers in (cm^{-1}).
- In old IR literatures the spectra were expressed in micrometers: micron (μ) .
- The ordinate scale can be % transmittance (%T) or absorbance (A).

Beer-Lambert Law

- Transmittance:

$$T = \frac{I}{I_0} \qquad \%T = 100 \times \frac{I}{I_0}$$

I : intensity after absorption

I_0 : intensity of incidence beam

Absorbance: $A = \log_{10}\frac{I_0}{I} = \log_{10}\frac{1}{T} = \log_{10}\frac{100}{\%T}$

Calculated by **Beer-Lambert Law**:

$A = CL$ concentration C is in $mol.L^{-1}$, cell length L is in cm, and the molar absorption coefficient ε is in $L.mol^{-1}cm^{-1}$.

IR Spectroscopy: Measurement of Spectra

- **In early days: dispersive spectrometer is used,**
- **Nowadays: interferometric spectrometer coupled with Fourier transform, FTIR.**
- **Dispersive spectrometer: use grating or prism to resolve source light into component wavelength spectrum. Composed of three parts:**
  - IR source: SiC heated at high T.
  - monochromator: disperse the light beam into spectrum.
  - detector: sensitive thermocouple transforms heat into electricity recorded by recorder.

FTIR Spectrometer

- **Use Michelson interferometer to produce the interference signals of the sample source light, with two perpendicularly arranged mirrors, one movable, one fixed.**
- **The source light is split into two half beams and reflected back by each mirror. As there is phase-lags caused by the movable mirror, an interference pattern is produced after combination of two beams, which composed of all frequency signals of sample in time-domain. This is Fourier-transformed into frequency-domain, giving the FTIR spectrum.**

FTIR Instruments

- Light source: similar to dispersive spectrometer, but employs pyroelectric bolometer as detector, having fast response time required by the fast scan. DTGS (deuterated triglycine sulfate) is an example of pyroelectric material.
- Beam splitter uses germanium coated KBr plate.

Sampling Methods

- Window materials: NaCl, KCl, KBr, CsI, etc. (Note for IR transmission limit for each matrial).
- Liquids: hold between NaCl, KBr discs.
- Solutions: put in cells (NaCl, KBr) or IR cards.
- Solids: pressed into nujol mulls or KBr pellets.
- Solvents: CS_2, CCl_4, etc, watch for regions where solvent has absorptions.

Zero order calculations

- **Predicting frequencies of simple functional groups:**

$$\nu = \frac{1}{2\pi}\sqrt{\frac{\kappa}{\mu}}, \qquad \bar{\nu} = \frac{\nu}{c} = \frac{1}{2\pi c}\sqrt{\frac{\kappa}{\mu}}$$

- **Reciprocal mass factor: *G***

$$G = \frac{1}{\mu} \qquad = \frac{1}{2\#}\sqrt{G} \qquad \bar{} = \frac{1}{2\#c}\sqrt{G}$$

k in millidyne/Å = 10^5 dyne cm^{-1}
μ in a.m.u.

Simplified Equation

- **Changing μ into g/moles =** $\frac{\mu(amu)}{N_0}$
- **then the constant is**
- $$\frac{1}{2\pi c}\sqrt{N_0 \bullet 10^5} = 1303$$
- **Simplified equation:**

$$\bar{\nu} = 1303\sqrt{\frac{\kappa}{\mu}} = 1303\sqrt{\kappa G}\,(cm^{-1})$$

Simple Functional Groups

- For C-C bonds: μ = (12x12)/(12+12)= 6 amu, G = 0.17 amu^{-1}.

$$\bar{\nu} = 1303\sqrt{4.25 \times 0.17} = 1100 cm^{-1}$$

- Frequencies proportional to square root of *k*

Bond Type	k	$\bar{\nu}$	μ	G
C—C	4.25	1100	6	0.17
C=C	9.6	1650	6	0.17
C≡C	16	2100	6	0.17

Stretching Frequencies

- Frequency decreases with increasing atomic weight.
- Frequency increases with increasing bond energy.

Bond	Bond Energy [kcal (kJ)]	Stretching Frequency (cm^{-1})
	Frequency dependence on atomic masses	
C—H (heavier atoms ↓)	100 (420)	3000
C—D	100 (420)	2100 ($\bar{\nu}$ decreases ↓)
C—C	83 (350)	1200
	Frequency dependence on bond energies	
C—C	83 (350) (stronger bond ↓)	1200
C=C	146 (611)	1660 ($\bar{\nu}$ increases ↓)
C≡C	200 (840)	2200

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Simple X-H, X=Y, X=Y bonds

Bond Type	k	μ	$\bar{\nu}$
O-H	7	0.94	3600
N-H	6	0.93	3300
C-H	5	0.92	3000
C-C	4.25	6.00	1100
C=C	9.6	6.00	1650
C=O	12	6.86	1725
C≡C	16	6.00	2100
C≡N	21	6.46	2350

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Approximate Frequency Ranges

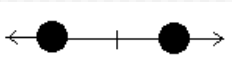
Bond Type	$\bar{\nu}$	Range
H—X	3000	2600-3600
X≡Y	2200	2000-2400
X=Y	1600	1500-1800
X—Y	1000	800-1200

Motion of Polyatomic System

- Molecular motions: described by translational, rotational, and vibrational motions.
- Internal degree of freedoms (i.d.f.): exclude translational and rotational motions.
- For a molecule of *N*-atoms:
- Total d.f. = 3 x *N* , rotational d.f. = Vibrational d.f. = 3
- Total i.d.f. = 3 x *N* – 6
- For linear molecule: Rotational d.f. =2, thus total i.d.f. = 3 x *N* -5

Normal Mode of Vibration

- $3N - 6$ ($3N - 5$) internal degree of freedoms correspond to equal number of vibrational energy transitions.
- Each vibrational transition can be described by normal mode of vibration, in which each connected atoms moving in phase with same frequency with respect to the center of gravity (or moving in synchronization in phase and frequency). The center of gravity does not change its position.



Equation for Normal Mode of Motion

- Each normal mode of motion is considered as a harmonic oscillation, and a wave equation set up for such a system,
- Solution of this equation leads to a potential energy curve (P.E.) with several energy levels and corresponding quantum numbers.
- The transition between these levels is governed by the selection rule, which is the condition imposed by the solution of the wave equation.

Energy Levels and Selection Rule

- For a polyatomic molecule of *N* atoms, its energy state can be described by 3*N* - 6 normal modes with corresponding frequencies: ν_1, ν_2, ν_3 ...ν_N
- and corresponding quantum #'s: υ_1, υ_2, υ_3 ...υ_N

Energy levels:

$$E(\upsilon_1,\upsilon_2,\upsilon_3.....)=\sum_{i=1}^{3N-6}\left(\upsilon_i+\frac{1}{2}\right)h\nu_i$$

Interpretation

- Looking for presence/absence of functional groups
- A polar bond is usually IR active
- A nonpolar bond in a symmetrical molecule will absorb weakly or not at all, but is Raman active

Energy levels and Selection rule

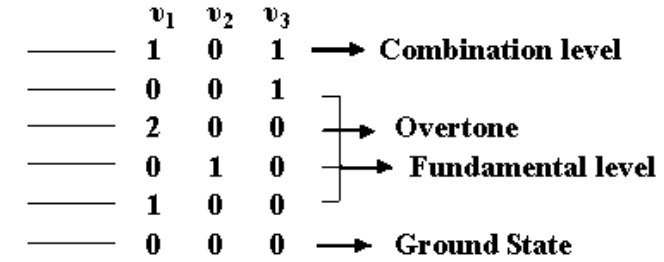
- The quantum #'s are limited to integers:

$$\nu_1, \nu_2, \nu_3 \ldots = 0,1,2\ldots$$

- Transitions among these levels are controlled by the selection rule: $\Delta\upsilon = \pm 1$
- If a transition occurs in accord with this rule then it is called an allowed transition, and if it goes against this rule then it is a forbidden transition.

Normal Mode of Vibration and Selection Rules

- An example of a 3 atoms system: have 3 x 3 – 6 = 3 normal modes or frequencies.



Selection Rules

- **There are two types of transitions: governed by selection rules.**
  - **Allowed Transitions**: transitions from GS to fundamental state are allowed because $\Delta\upsilon = \pm 1$
  - **Forbidden Transitions**: are transitions with Δu > 1 or Δu < -1, such as overtones and combination lines.

Fermi Resonance

- **If two vibrational energy levels have nearly the same energy level in magnitudes and also similar in symmetry, then accidental degeneracy occurs that causes Fermi resonance interaction to give additional vibrational bands.**
- **Giving spectrum of combination lines.**

Basic Modes of Vibration

- **Two basic modes of vibrations are observed in IR spectra:**
  - Stretching vibration: change in bond length.
  - Bending vibration: change in bond angles, including motions like wagging, twisting, rocking etc.

Modes of Vibration in CO_2

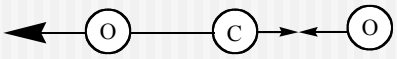
- **CO_2 : a linear molecule with 3 x 3 – 5 = 4 normal modes of vibration.**
- **Symmetric stretching $\bar{\nu}_1$ = 1340 cm^{-1}, this mode is a symmetry forbidden transition in IR due to zero change in dipole moment in stretching motion, i.e.**

$$\left(\frac{d\mu}{dq}\right)_0 = 0$$

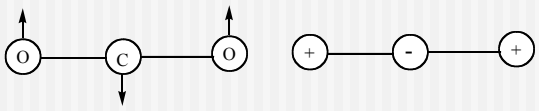
- **As a result this absorption is IR inactive but active in Raman.**

Modes of Vibration in CO_2

- Asymmetric stretching : $\bar{\nu}_2$ = 2349 cm^{-1}, IR active transition, with higher energy than $\bar{\nu}_1$



- Bending vibrations : $\bar{\nu}_3$ = 667 cm^{-1}, with two modes of vibrations having same quantum number and symmetry, and equal in energy level. This is so called two-fold degeneracy.

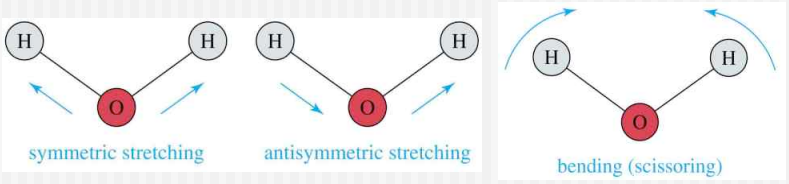


The IR Region

- Just below red in the visible region
- Wavelengths usually 2.5-25 μm
- More common units are wavenumbers, or cm^{-1}, the reciprocal of the wavelength in centimeters (4000-400 cm^{-1})
- Wavenumbers are proportional to frequency and energy

Molecular Vibrations

- **Light is absorbed when radiation frequency = frequency of vibration in molecule**
- **Covalent bonds vibrate at only certain allowable frequencies**
  - Associated with types of bonds and movement of atoms
- **Vibrations include stretching and bending**



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Carbon-Carbon Bond Stretching

- **Stronger bonds absorb at higher frequencies:**
  - 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}

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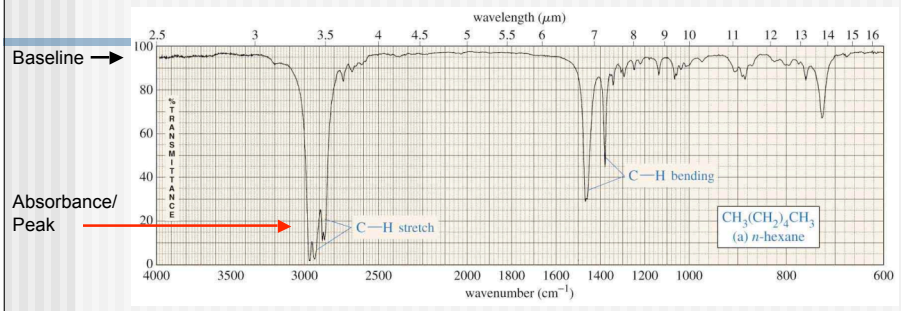
Carbon-Hydrogen Stretching

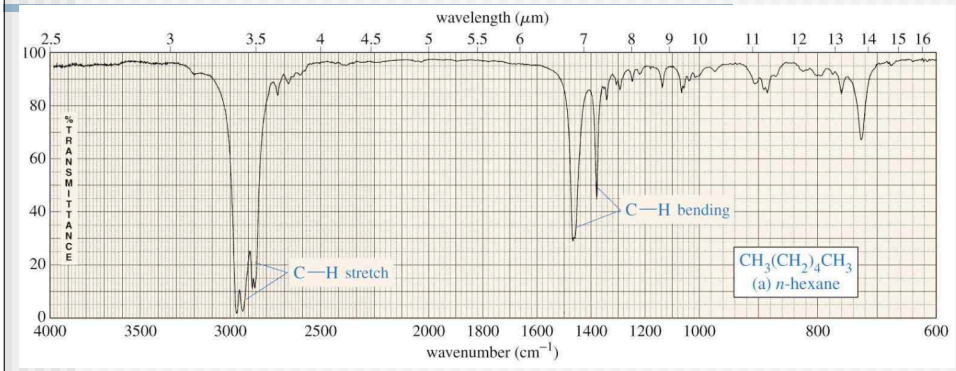
- **Bonds with more *s* character absorb at a higher frequency**
  - sp^3 C-H, just below 3000 cm^{-1} (to the right)
  - sp^2 C-H, just above 3000 cm^{-1} (to the left)
  - *sp* C-H, at 3300 cm^{-1}

IR Spectrum

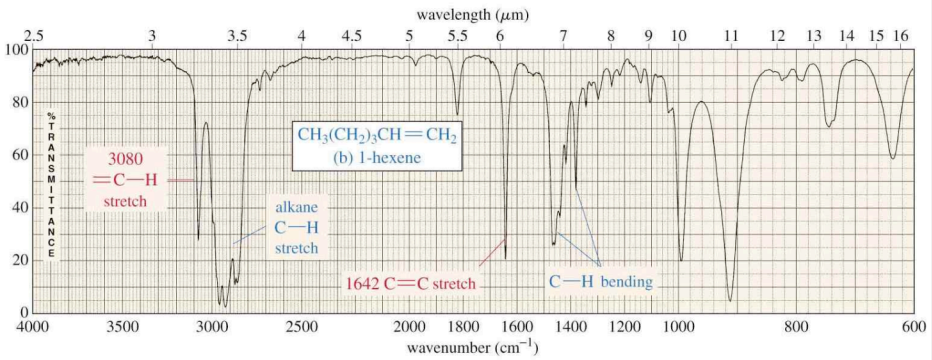


- **No two molecules will give exactly the same IR spectrum (except enantiomers)**
- **Simple stretching: 1600-3500 cm^{-1}**
- **Complex vibrations: 400-1400 cm^{-1}, called the "fingerprint region"**

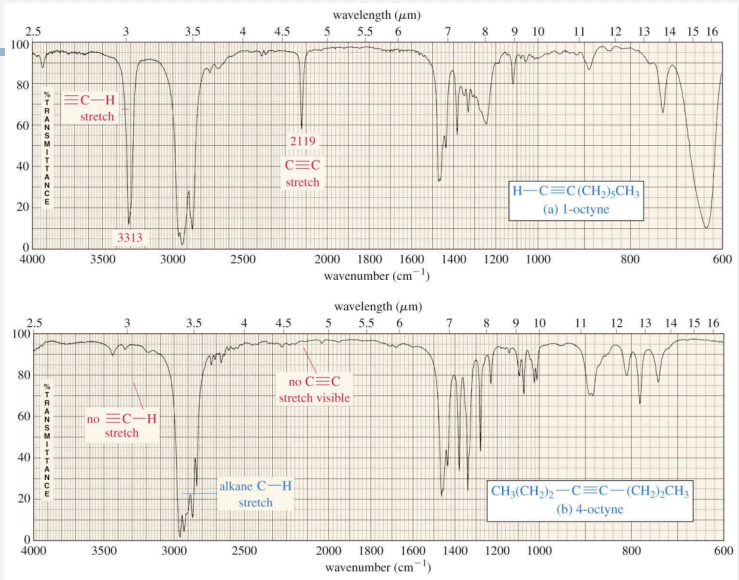
An Alkane IR Spectrum



An Alkene IR Spectrum



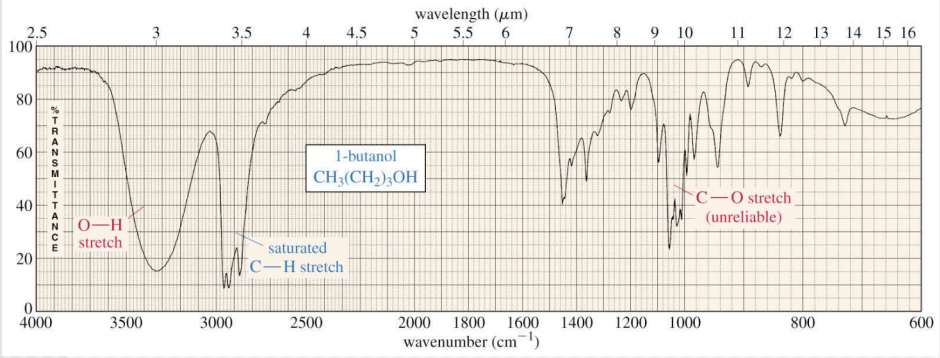
An Alkyne IR Spectrum



O-H and N-H Stretching

- **Both of these occur around 3300 cm^{-1}, but they look different**
  - Alcohol O-H, broad with rounded tip
  - Secondary amine (R_2NH), broad with one sharp spike
  - Primary amine (RNH_2), broad with two sharp spikes
  - No signal for a tertiary amine (R_3N)

An Alcohol IR Spectrum



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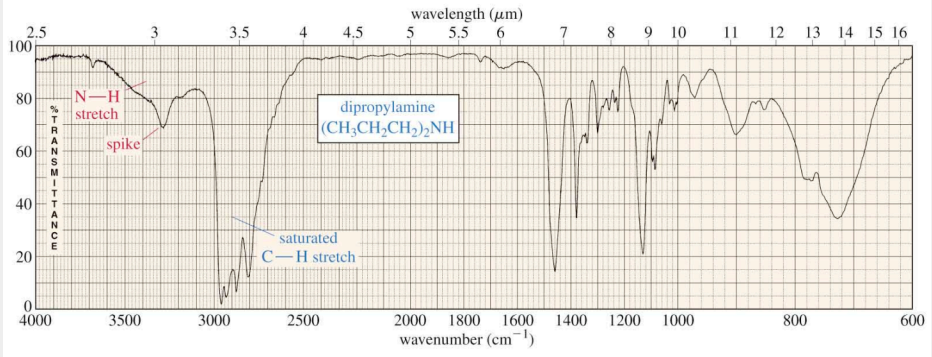
An Amine IR Spectrum



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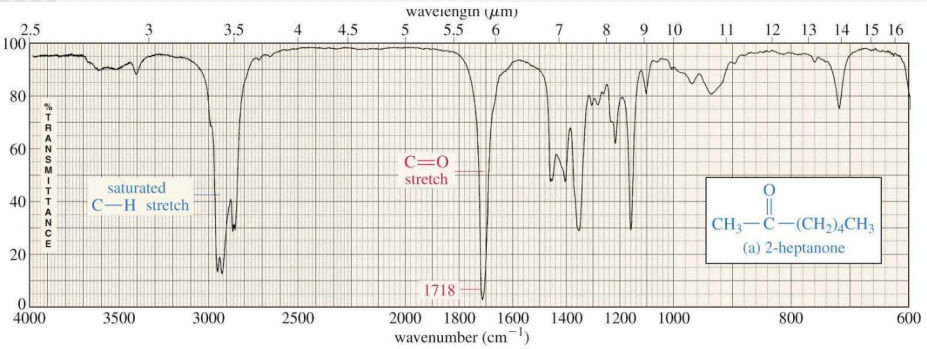
Carbonyl Stretching

- The C=O bond of simple ketones, aldehydes, and carboxylic acids absorb around 1710 cm^{-1}
- Usually, it's the strongest IR signal
- Carboxylic acids will have O-H also
- Aldehydes have two C-H signals around 2700 and 2800 cm^{-1}

A Ketone IR Spectrum



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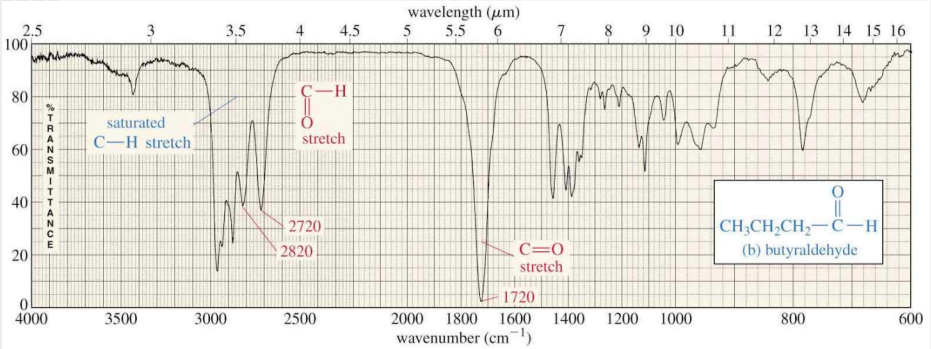
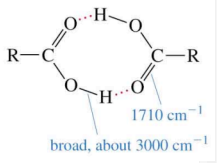
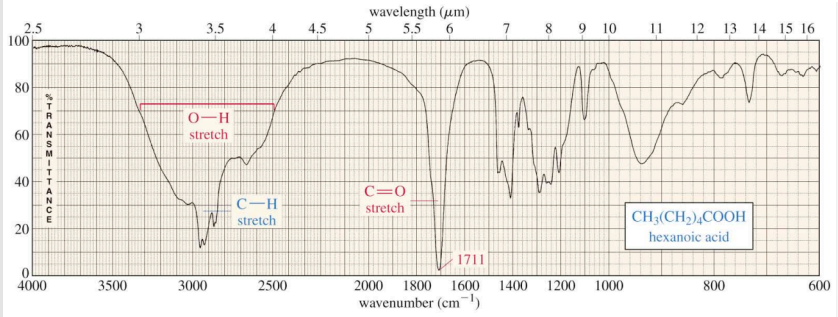
An Aldehyde IR Spectrum



O-H Stretch of a Carboxylic Acid

This O-H absorbs broadly, 2500-3500 cm^{-1}, due to strong hydrogen bonding



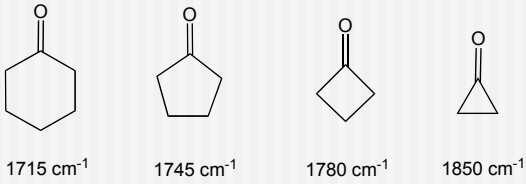


Variations in C=O Absorption

- 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

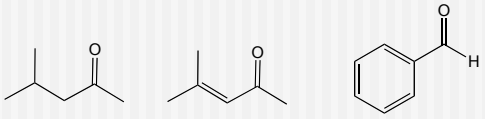
Carbonyl Groups

- The position of C=O stretching vibration is sensitive to its molecular environment
  - as ring size decreases and angle strain increases, absorption shifts to a higher frequency



1715 cm^{-1} 1745 cm^{-1} 1780 cm^{-1} 1850 cm^{-1}

  - conjugation shifts the C=O absorption to lower frequency

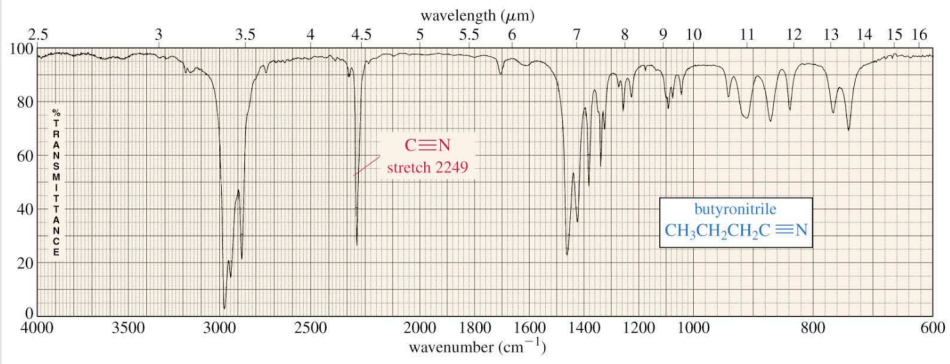


1717 cm^{-1} 1690 cm^{-1} 1700 cm^{-1}

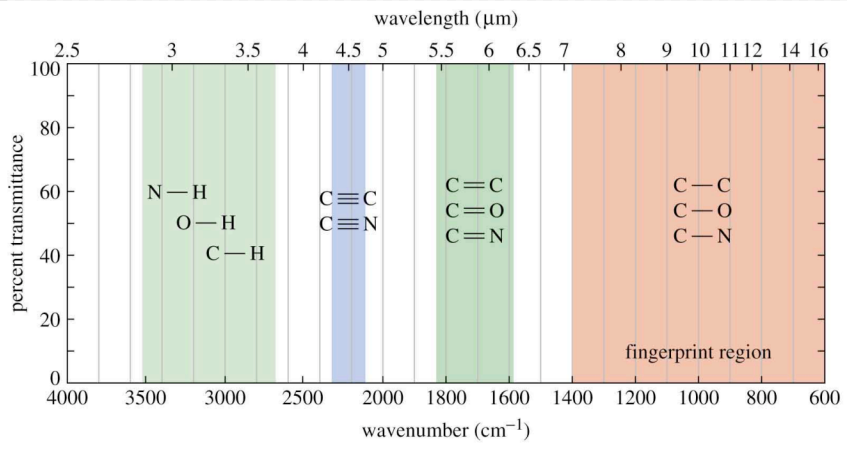
Carbon - Nitrogen Stretching

- 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 ≡ N absorbs strongly just *above* 2200 cm^{-1}. The alkyne C ≡ C signal is much weaker and is just *below* 2200 cm^{-1}

A Nitrile IR Spectrum



Summary of IR Absorptions



Hydrocarbons

Hydro-carbon	Vibration	Frequency (cm^{-1})	Intensity
Alkane			
C-H	Stretching	2850 - 3000	Medium
	Bending	1450-1475	Medium
CH_3	Bending	1375 and 1450	Weak to medium
C-C	(Not useful for interpretation - too many bands		
Alkene			
C-H	Stretching	3000 - 3100	Weak to medium
C=C	Stretching	1600 - 1680	Weak to medium
Alkyne			
C-H	Stretching	3300	Medium to strong
C≡C	Stretching	2100-2250	Weak
Arene			
C-H	Stretching	3030	Weak to medium
C=C	Stretching	1450-1600	Medium
C-H	Bending	690-900	Strong

IR of Molecules with C=O Groups

Carbonyl Group		Vibration	Frequency (cm^{-1})	Intensity
O RCR'	Ketones C=O	Stretching	1630-1820	Strong
O RCH	Aldehydes C=O	Stretching	1630-1820	Strong
	C-H	Stretching	2720	Weak
O RCOH	Carboxylic acids C=O	Stretching	1700-1725	Strong
	O–H	Stretching	2500-3300	Strong (broad)

IR of Molecules with C=O Groups

O $RCNH_2$	Amides C=O	Stretching	1630-1680	Strong
	N–H	Stretching	3200, 3400	Medium
	(1° amides have two N-H stretches) (2° amides have one N-H stretch)			
O RCOR'	Carboxylic esters C=O	Stretching	1735-1800	Strong
	sp^2 C–O	Stretching	1200-1250	Strong
	sp^3 C–O	Stretching	1000-1100	Strong
O O RCOCR	Acid anhydrides C=O	Stretching	1740-1760 and 1800-1850	Strong
	C–O	Stretching	900-1300	Strong
RC≡N	Nitriles C≡N	Stretching	2200-2250	Medium

IR Correlation Table

A. Alkyl			
C—H (stretching)		2853–2962	(m–s)
Isopropyl, $-CH(CH_3)_2$		1380–1385	(s)
	and	1365–1370	(s)
tert-Butyl, $-C(CH_3)_3$		1385–1395	(m)
	and	~1365	(s)
B. Alkenyl			
C—H (stretching)		3010–3095	(m)
C=C (stretching)		1620–1680	(v)
R—CH=CH_2		985–1000	(s)
	and	905–920	(s)
$R_2C=CH_2$	(out-of-plane C—H bendings)	880–900	(s)
cis-RCH=CHR		675–730	(s)
trans-RCH=CHR		960–975	(s)
C. Alkynyl			
≡C—H (stretching)		~3300	(s)
C≡C (stretching)		2100–2260	(v)
D. Aromatic			
Ar—H (stretching)		~3030	(v)
Aromatic substitution type (C—H out-of-plane bendings)			
Monosubstituted		690–710	(very s)
o-Disubstituted	and	730–770	(very s)
m-Disubstituted		735–770	(s)
		680–725	(s)
	and	750–810	(very s)
p-Disubstituted		800–860	(very s)
E. Alcohols, Phenols, and Carboxylic Acids			
O—H (stretching)			
Alcohols, phenols (dilute solutions)		3590–3650	(sharp, v)
Alcohols, phenols (hydrogen bonded)		3200–3550	(broad, s)
Carboxylic acids (hydrogen bonded)		2500–3000	(broad, v)
F. Aldehydes, Ketones, Esters, and Carboxylic Acids			
C=O (stretching)		1630–1780	(s)
Aldehydes		1690–1740	(s)
Ketones		1680–1750	(s)
Esters		1735–1750	(s)
Carboxylic acids		1710–1780	(s)
Amides		1630–1690	(s)

Frequencies of Substituted Alkenes

Structural unit	Frequency, cm^{-1}
Bending vibrations of alkenes	
$RCH=CH_2$	910-990
$R_2C=CH_2$	890
cis-RCH=CHR'	665-730
trans-RCH=CHR'	960-980
$R_2C=CHR'$	790-840

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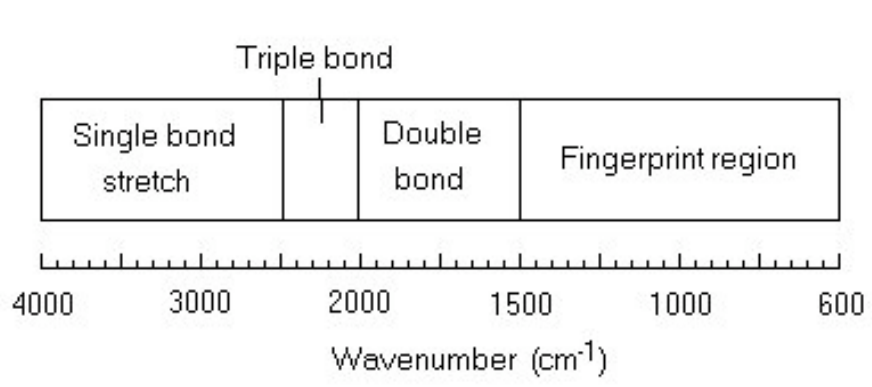
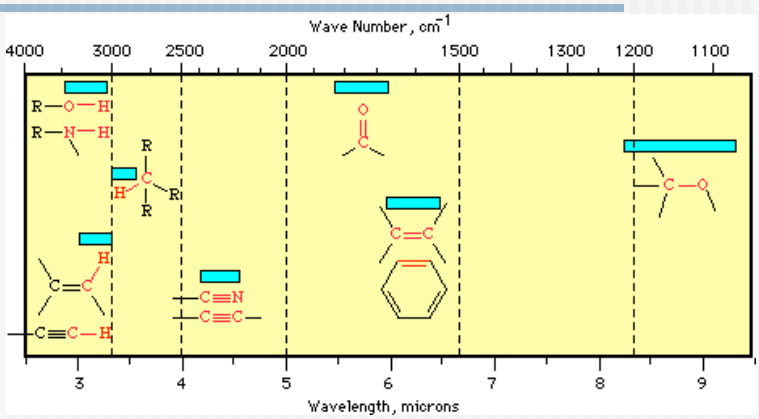
Frequencies of Substituted Benzenes

Structural unit	Frequency, cm^{-1}
Bending vibrations of derivatives of benzene	
Monosubstituted	730-770 and 690-710
Ortho-disubstituted	735-770
Meta-disubstituted	750-810 and 680-730
Para-disubstituted	790-840

Regions of the Infrared Spectrum



Correlation Chart of Common Infrared Bands



http://www.chemguide.co.uk/analysis/IRscopy/PROTOCOL-II/WIN/SPEC/IR/IRF.HTM

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4000 - 2500 cm^{-1} region: C-H stretches

As almost all organic compounds contain C-H stretches in the 3300-2700 cm^{-1} region, these peaks are sometimes not very useful

The C-H peaks in some compounds are diagnostic, when confirmed by other characteristic absorptions:

- Aldehyde C-H stretching normally produces two absorptions in the 2900-2700 cm^{-1} region, and can be confirmed with the C=O stretch at about 1700 cm^{-1}
- Terminal alkynes -C≡H – the C-H stretches appear at about 3300 cm^{-1}

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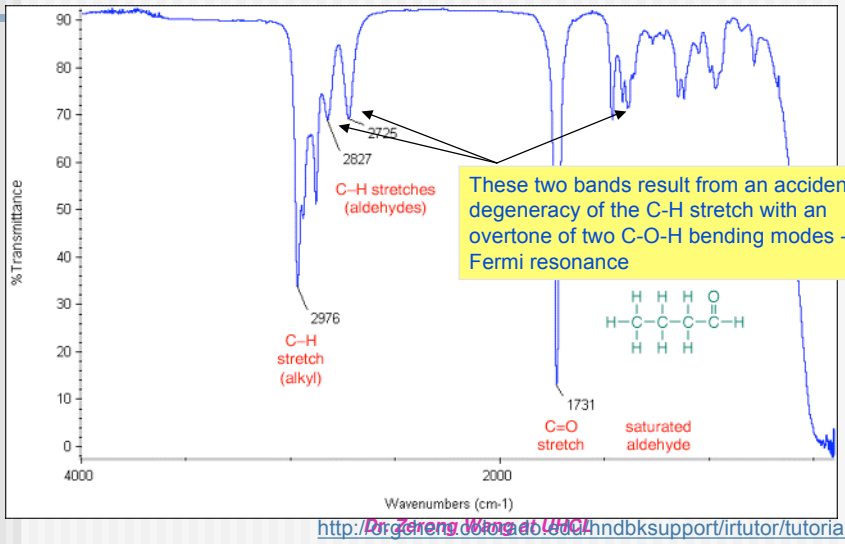
Infrared spectrum of an aldehyde - butyraldehyde



http://orgchem.colorado.edu/hndbksupport/irtutor/tutorial.html

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Parameters for C-H stretches

Bond	≡C—H	=C—H	—C—H
Type	*sp*	sp^2	sp^3
Length	1.08Å	1.10Å	1.12Å
Strength	506 kJ	444 kJ	422 kJ
IR frequency for C-H stretch	3300 cm^{-1}	~3100 cm^{-1}	~2900 cm^{-1}

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Pavia, Lampman & Kriz, p. 34

4000 - 2500 cm^{-1} region: -OH groups

This region is usually dominated by absorptions arising from bonds to hydrogen (X-H):

X = O

-intermolecularly hydrogen-bonded hydroxyl peaks are generally found as broad peaks centered at about 3500 cm^{-1}

-monomeric hydroxyl groups (no hydrogen bonding) have sharp absortions at about 3600 cm^{-1}

-diluting solutions of an alcohol results in a sharpening of the O-H peak and a shift from 3500 to 3600 cm^{-1}

-carboxylic acids give rise to broad peaks due to hydrogen-bonded dimer formation

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4000 - 2500 cm^{-1} region: amines

X = N

Amine N-H can occur in the same location as O-H stretches

N-H absorptions are usually less intense, with one (secondary amines) or two (primary amines) spike superimposed on broad peak

O-H accompanied by:

C-O stretch near 1250 cm^{-1} and/or 1730 cm^{-1} (C=O)

N-H accompanied by:

N-H bending at about 1600 cm^{-1}

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4000 - 2500 cm^{-1} region - amides

Amide N-H stretches also absorb in this region, but can be differentiated from amines by other characteristic bands:

Amide I band: a C=O absorption about 1690 cm^{-1}

Amide II band: a N-H bend in the 1690 - 1520 cm^{-1} range

The positions of these bands depend on how the sample is prepared (solution vs Nujol mull vs KBr disc)

Amide I - 40 cm^{-1} lower in Nujol or KBr, than in solution

Amide II - 30 cm^{-1} higher in Nujol or KBr, than in solution

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2500 - 1900 cm^{-1} region: C≡N stretches

For organic compounds, the only peaks commonly found in this region are due to triple bonds and cumulated double bonds

Alkynes R-C≡C-R' 2200 – 2100 cm^{-1}

Cyano (nitrile) groups R-C≡N 2260 – 2200 cm^{-1}

Cumulated double bonds X=C=Y (X, Y = C, O, N, S)

C=C=C	allenes	1940 cm^{-1}
C=C=O	ketenes	2140 cm^{-1}
N=C=O	isocyanates	2270 cm-1
N=C=S	isothiocyanates	2125 cm^{-1}

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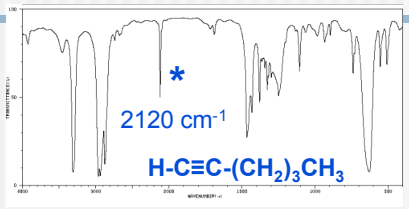
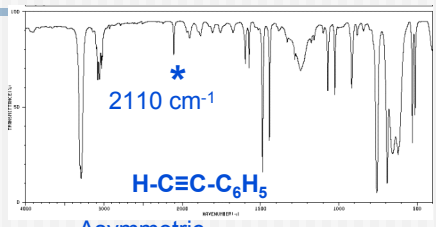
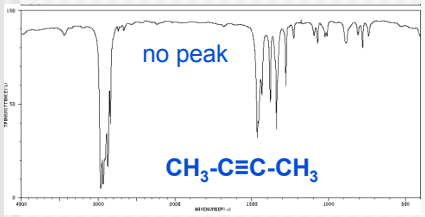
2500 - 1900 cm^{-1} region: C≡C stretches



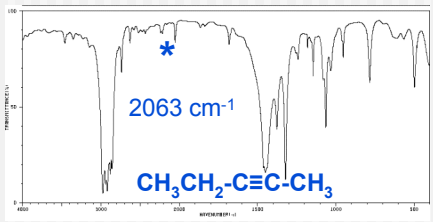
Asymmetric



Asymmetric



Symmetric



Pseudosymmetric

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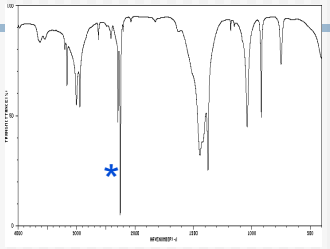
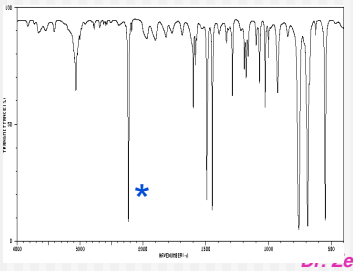
Spectra from the SBDS database

2500 - 1900 cm^{-1} region: -C≡N stretches

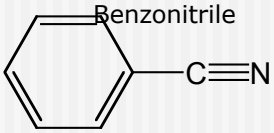


Acetonitrile

$H_3C—C\equiv N$



Benzonitrile



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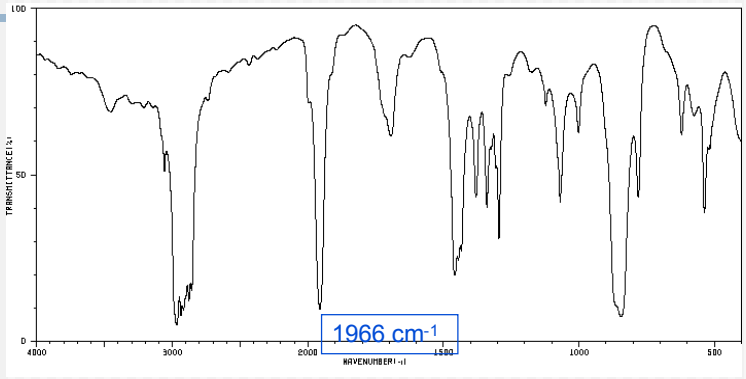
Spectra from the SBDS database

Infrared spectrum of allenes – 1,2-pentadiene



CH_2=C=CH-CH_2CH_3 1,2-pentadiene

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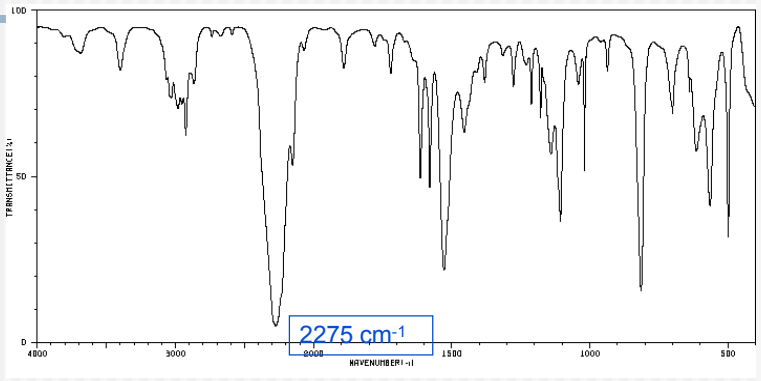
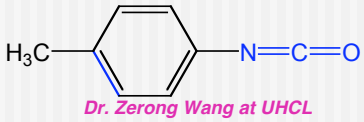
Infrared spectrum of isocyanate – *p*-tolylisocyanate





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1900 - 1500 cm^{-1} region

This region of the spectrum is important for molecules containing C=O (carbonyl) and C=C (alkene) groups

C=O - because of the large dipole moment in the C=O bond, the stretching vibration results in a very strong peak

- carboxylic acids (-COOH) give the strongest absorptions, followed by ketones, aldehydes, and amides (these can be quite variable in intensity)

- carbonyl groups absorb around 1800-1700 cm^{-1}, with the exact position being diagnostic of the type of carbonyl group present in the molecule

anhydrides > acid chlorides > esters > aldehyde > ketone > carboxylic acid > amide

1810 1800 1735 1725 1715 1710 1690 cm^{-1}

← Increase in electronegativity of X in –RCOX group ←

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1900 - 1500 cm^{-1} region

C=C The other prominent type of vibrational mode that appears in this region is the C=C stretch found in alkenes and aromatic rings

- alkene double bonds have absorptions in the 1680 – 1500 cm^{-1} region, with the intensity depending on the symmetry of the substituents. The C=C stretch symmetrically substituted alkenes are very weak (if present), due to the lack of a dipole moment

-conjugation with a carbonyl group intensifies the C=C stretching band

-aromatic rings show two or three bands in the 1600 – 1500 cm-1 range

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1500 - 600 cm^{-1} region (Fingerprint region)

The so-called "fingerprint" region is usually very complicated with a large number of peaks, and it is rarely possible to assign many of them.

- it is called the fingerprint region, because it is useful for direct comparison of your sample with peaks in this region from known samples
- there are some very useful peaks in the region
  - C-H out-of-plane bending for substituted alkenes and benzenes can give an indication of the pattern of substitution
  - X-O single bond stretches (X = C, N, S, Cl, etc.)

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Infrared Correlation Table – X-H Stretches

Group	Frequency Range (cm^{-1})
OH stretching vibrations	
Free OH	**3610-3645 (sharp)**
Intramolecular H bonds	**3450-3600 (sharp)**
Intermolecular H Bonds	**3200-3550 (broad)**
Chelate Compounds	**2500-3200 (very broad)**
NH Stretching vibrations	
Free NH	**3300-3500**
H bonded NH	**3070-3350**
CH Stretching vibrations	
=-C-H	**3280-3340**
=C-H	**3000-3100**
C-CH_3	**2862-2882, 2652-2972**
O-CH_3	**2815-2832**
N-CH_3 (aromatic)	**2810-2820**
N-CH_3 (aliphatic)	**2780-2805**
CH_2	**2843-2863,2916-2936**
CH	**2880-2900**
SH Stretching Vibrations	
Free SH	**2550-2600**

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http://infrared.als.lbl.gov/IRbands.html

Infrared Correlation Table – Multiple Bond Stretches

Group	Frequency Range (cm^{-1})
C=-N Stretching Vibrations	
Nonconjugated	**2240-2260**
Conjugated	**2215-2240**
C=-C Stretching Vibrations	
C=-CH (terminal)	**2100-2140**
C-C=-C-C	**2190-2260**
C-C=-C-C=-CH	**2040-2200**
C=O Stretching Vibrations	
Nonconjugated	**1700-1900**
Conjugated	**1590-1750**
Amides	**~1650**
C=C Sretching Vibrations	
Nonconjugated	**1620-1680**
Conjugated	**1585-1625**

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Infrared Correlation Table – Bending vibrations

Group	Frequency Range (cm^{-1})
CH Bending Vibrations	
CH_2	**1405-1465**
CH_3	**1355-1395, 1430-1470**
C-O-C Vibrations in Esters	
Formates	**~1175**
Acetates	**~1240, 1010-1040**
Benzoates	**~1275**
C-OH Stretching Vibrations	
Secondary Cyclic Alcohols	**990-1060**
CH out-of-plane bending vibrations in substituted ethylenic systems	
-CH=CH_2	**905-915, 985-995**
-CH=CH-(cis)	**650-750**
-CH=CH-(trans)	**960-970**
C=CH_2	**885-895**

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Alkanes

Alkanes have relatively few bands in the infrared, primarily C-H stretches near 3000 cm^{-1} and CH_2 and CH_3 bends between 1475 and 1365 cm^{-1}

C-H stretches: sp^3 C-H stretches between 3000 and 2840 cm^{-1}

CH_2 bend: methylene bend at about 1465 cm^{-1}

CH_2 bend: rocking motion at about 720 cm^{-1} is characteristic of a long-chain (greater than 4 $-CH_2-$ groups) hydrocarbon, but not seen in cyclic hydrocarbons

CH_3 bend: methyl bend at about 1375 cm^{-1}

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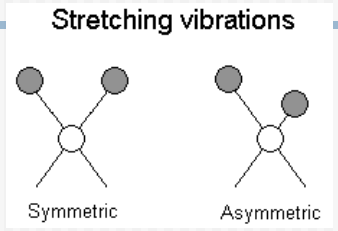
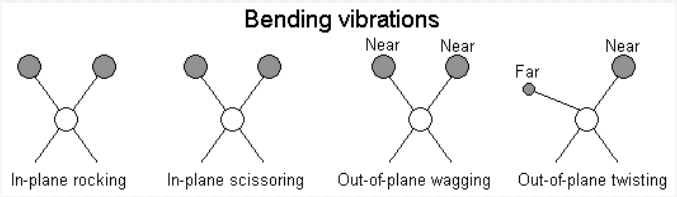
Stretching and Bending Vibrations – CH_2 group





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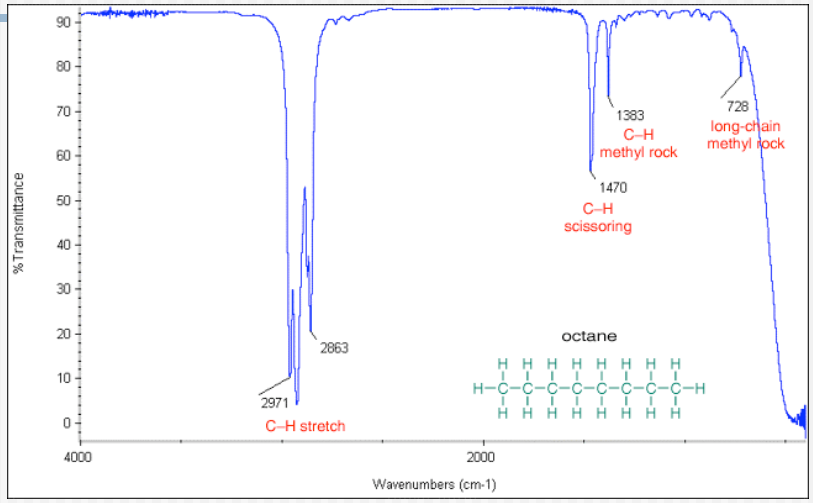
http://www.shu.ac.uk/schools/sci/chem/tutorials/molspec/irspec1.htm

Alkane infrared spectrum - Octane



http://orgchem.colorado.edu/hndbksupport/irtutor/tutorial.html

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Alkenes

Alkenes display more peaks than alkanes.

C-H In addition to sp^3 C-H stretches below 3000 cm^{-1}, the sp^2 C-H stretches appear above 3000 cm^{-1} (generally in the 3010 – 3095 cm^{-1} range).

Alkenes also show out-of-plane bending modes in the range of 1000-650 cm^{-1}, which are characteristic of the degree and symmetry of substitution

C=C For unsymmetrical alkenes, the C=C stretching peak occurs near 1650 cm^{-1}. Symmetically tetrasubstituted C=C bonds are absent, while symmetrically disubstituted C=C bonds are weak (*cis* > *trans*).

The C=C stretching band moves to lower frequency, with an increase in intensity when conjugated to other multiple bonds

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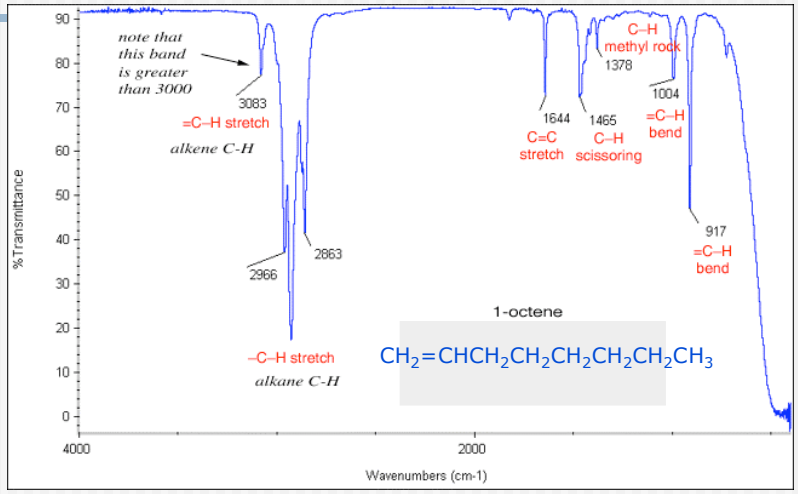
Alkene infrared spectrum - Octene



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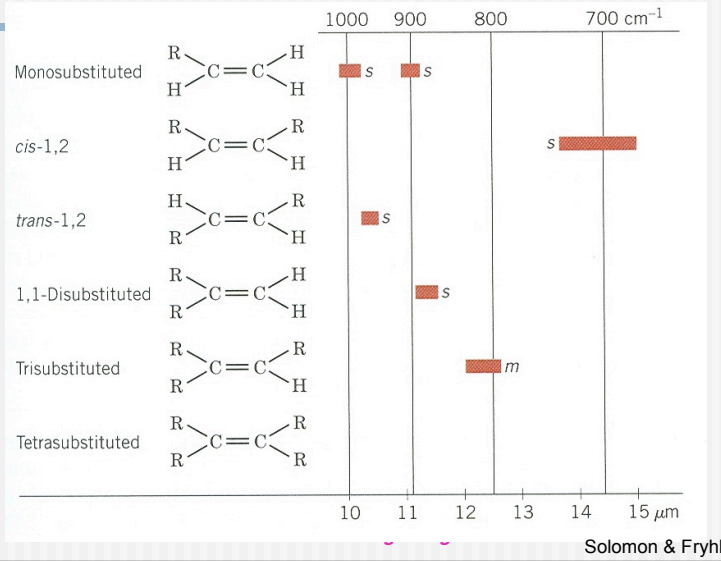
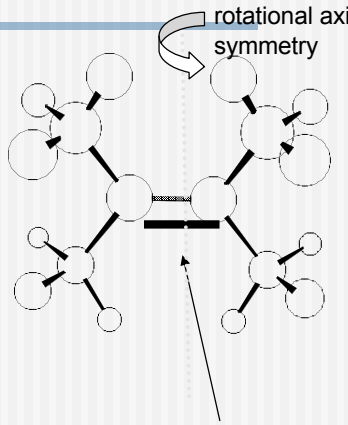
Out-of-plane bending of substituted ethylenes



Solomon & Fryhle, p. 85

2,3-dimethyl-2-butene

No change in the dipole moment with a symmetrical C=C stretch or an out-of-plane bend



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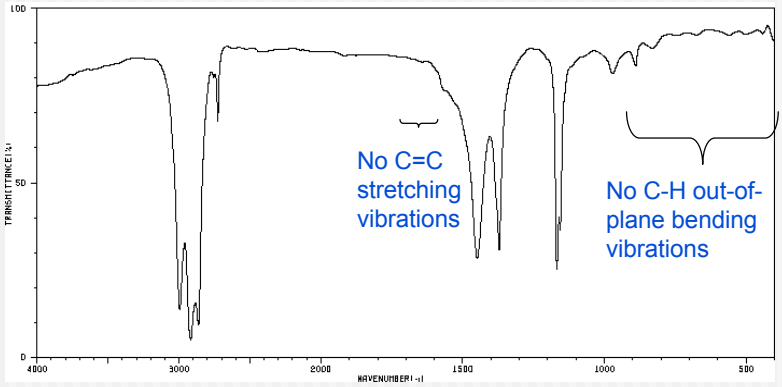
Infrared Spectrum of 2,3-dimethyl-2-butene



4000 3000 2000 1500 1000 500 cm^{-1}

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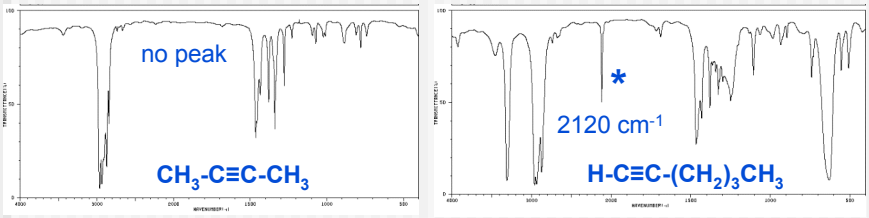
Alkynes

For terminal alkynes, R-C≡CH, a strong sharp band is seen at about 3300 cm^{-1}, while the C≡C stretching vibration is found at about 2150 cm^{-1}. Conjugation of the triple bond to other multiple bonds lowers the energy of the band. The intensity of the C≡C band depends on the symmetry of the substitution of the triple bond, as discussed previously.



Symmetric

Asymmetric

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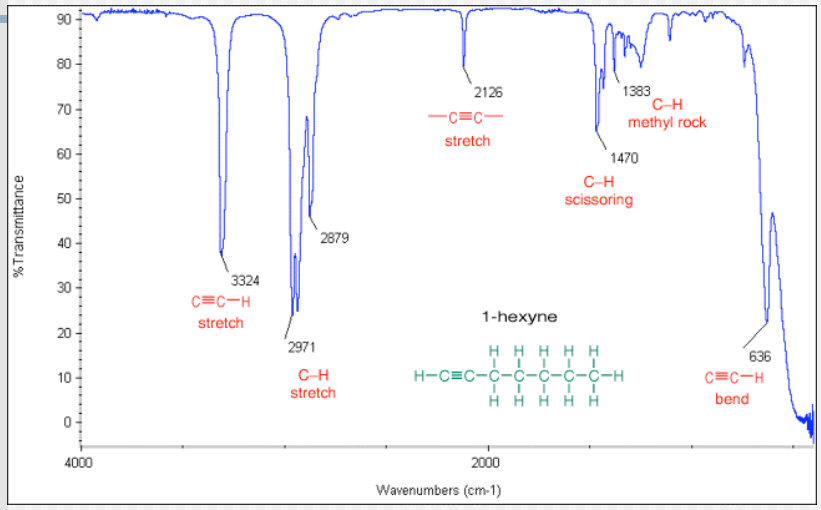
Infrared spectrum of alkynes - Hexyne



http://orgchem.colorado.edu/hndbksupport/irtutor/tutorial.html

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Alcohols and Phenols

The appearance of the –OH stretching band of alcohols and phenols depends on the concentration of the compound.

- In very dilute solutions, a “free” –OH band appears as a weak, but sharp band in the 3650 – 3600 cm^{-1} range

- In more concentrated solutions a “hydrogen-bonded” –OH peak is also found as a strong, broad band in the 3400 – 3300 cm^{-1} band. As a pure, “neat” liquid, this is the only band seen in this region

The C-O-H bending mode is located in the 1440 – 1220 cm^{-1} range, but is broad and weak and often obscured by CH_3 bending modes (~1375)

The C-O stretching vibration usually occurs in the 1260 – 1000 cm^{-1} region, and can be helpful in distinguishing between primary, secondary, tertiary, and aromatic (phenol) alcohols

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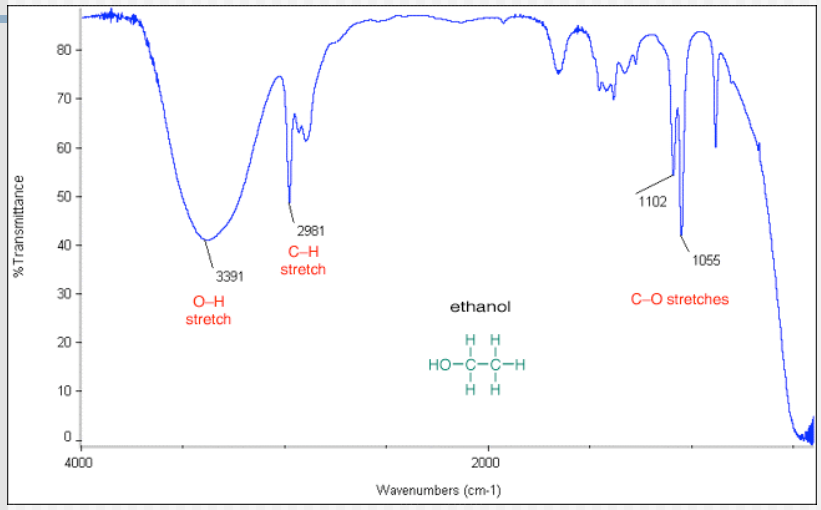
Infrared spectrum of an alcohol - ethanol



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Alcohols and Phenols

The C-O stretching band, and to a lesser extent the free O-H band, positions can be used to establish whether the alcohol is primary (RH_2COH), secondary (R_2HCOH), or tertiary (R_3COH), or an aromatic phenol

Compound	C-O stretch (cm^{-1})	O-H stretch (cm^{-1})
Phenol	1220	3610
3° (tertiary)	1150	3620
2° (secondary)	1100	3630
1° (primary)	1050	3640

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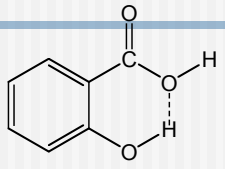
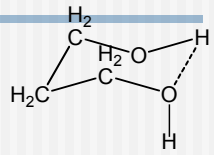
Intramolecular and intermolecular hydrogen bonding

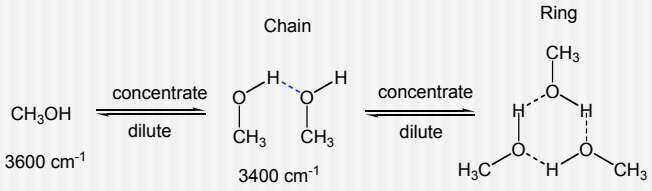


Salocylic Acid



1,3-Propanediol

Intramolecular Hydrogen Bonding



Intermolecular Hydrogen Bonding

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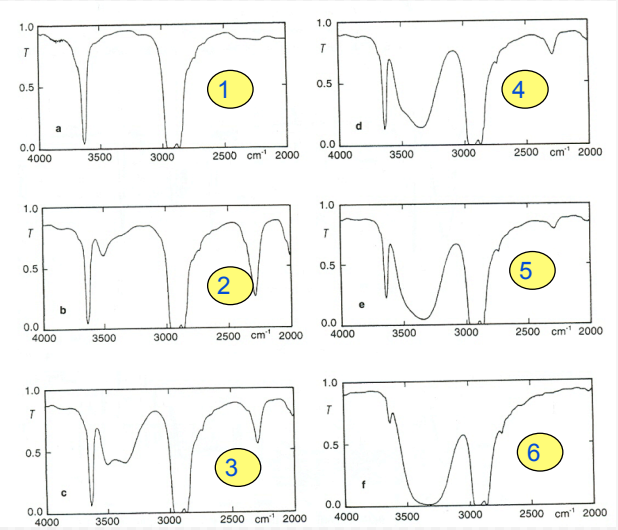
Effect of concentration on O-H stretching peaks

As the concentration of *n*-butanol (in CCl_4) is increased from spectrum 1 to 6, the sharp peak for the "free" O-H stretch at 3650 cm^{-1} decreases in intensity, while the broad "hydrogen-bonded" O-H stretching band at ~3300 cm-1 increases in intensity.



Gunzler and Gremlich, *IR Spectroscopy*, p. 206

Ethers

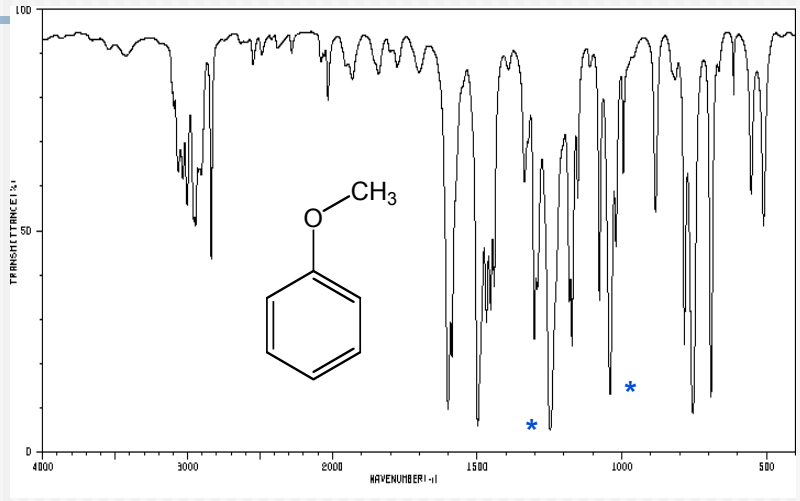
Ethers exhibit at least one C-O absorbance band in the 1300 – 1000 cm^{-1} region

To rule out an ester {(-C(=O)OR} C-O stretch or an alcohol C-OH stretch, you need to look for an absence of the C=O and O-H stretches, respectively.

Aliphatic ethers: one strong band at about 1120 cm^{-1}

Aromatic ethers: two strong bands at about 1250 and 1120 cm^{-1}

Infrared spectrum of an ether - anisole



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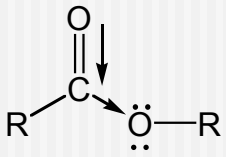
from SDBS database

Carbonyl Compounds

As mentioned above, the C=O stretch is a very strong band because of the large dipole moment, and the frequency of the band depends on the type of carbonyl group present.

The range of values is due to electron-withdrawing effects, resonance effects, and hydrogen bonding present in the various carbonyl functional groups.



Electron-withdrawing effect raises the C=O frequency of esters

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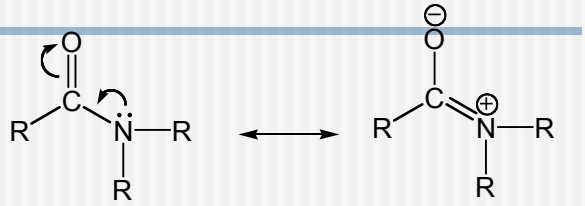
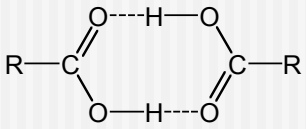
Carbonyl Compounds



Resonance effect lowers C=O frequency of amides



Carboxylic acids in the pure liquid or solid states exist as hydrogen-bonded dimers, weakening the C=O bond

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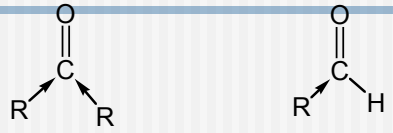
Carbonyl Compounds



Ketones have a lower C=O frequency than aldehydes because the additional electron-donating R group weakens the C=O bond

anhydrides > acid chlorides > esters > aldehyde > ketone > carboxylic acid > amide
1810 1800 1735 1725 1715 1710 1690 cm-1

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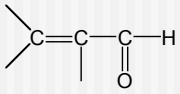
Aldehydes

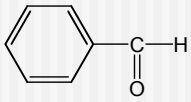
Aldehydes exhibit a very strong absorption band for the carbonyl group (C=O) in the range of 1740-1725 cm^{-1} for normal aliphatic aldehydes R-CH(=O)

Conjugation of the carbonyl group moves the C=O stretch to lower frequencies:



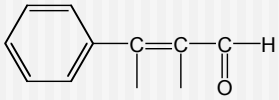
1700 - 1680 cm^{-1} for C=O

1640 cm^{-1} for C=C



1700 - 1660 cm^{-1} for C=O

1640 cm^{-1} for ring



1680 cm^{-1} for C=O

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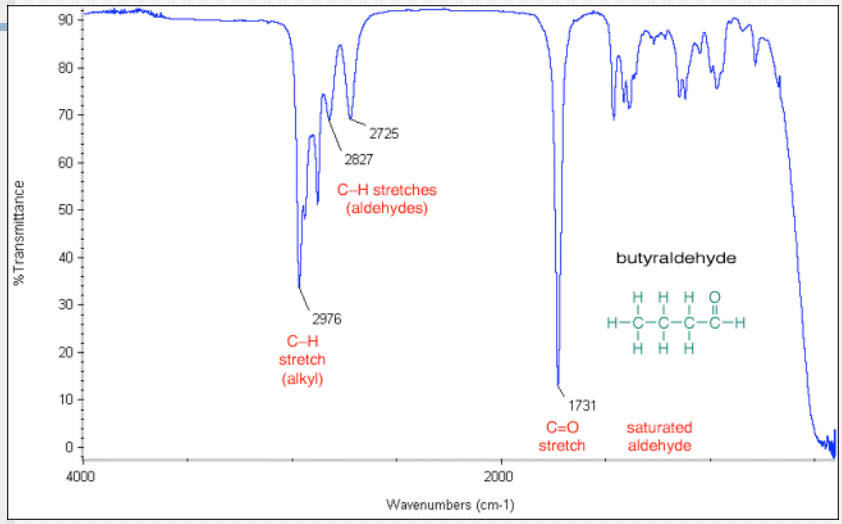
Infrared spectrum of an aldehyde - butyraldehyde



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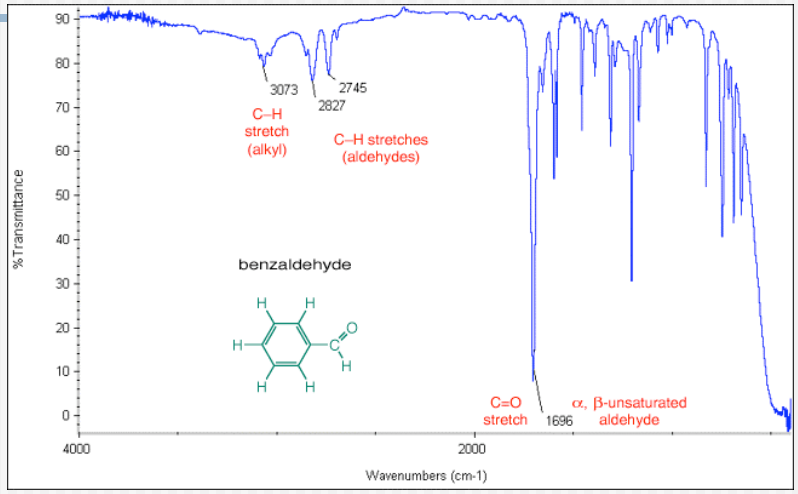
Benzaldehyde



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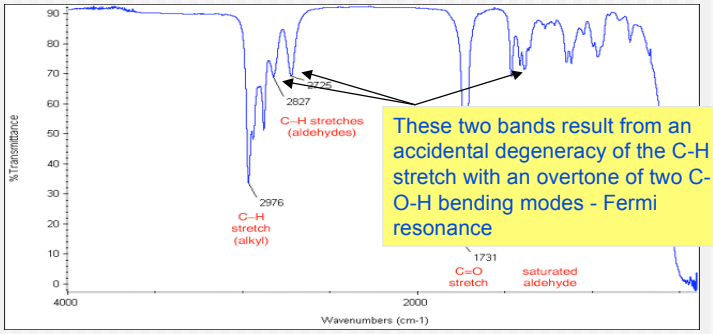
Aldehydes

The C-H stretch of the aldehyde hydrogen –CH(=O) appear as a characteristic pair of weak bands at 2860-2800 cm^{-1} (sometimes obscured by aliphatic C-H bands) and 2760-2700 cm^{-1} (easier to see).



These two bands result from an accidental degeneracy of the C-H stretch with an overtone of two C-O-H bending modes - Fermi resonance

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Ketones

For ketones, R-CR(=O), the C=O stretch appears in the 1720 – 1708 cm^{-1} range for aliphatic ketones.

Conjugation with:

C=C-C=O	C=O at 1700 – 1675 cm^{-1}; C=C at 1644 – 1617 cm^{-1}
Phenyl	C=O at 1700 – 1600 cm^{-1}; 1600 – 1450 cm^{-1} for ring
Two phenyls	C=O at 1670 – 1600 cm^{-1}

The C-C(=O)-C bending gives rise to a medium intensity band in the 1300-1100 cm^{-1} range

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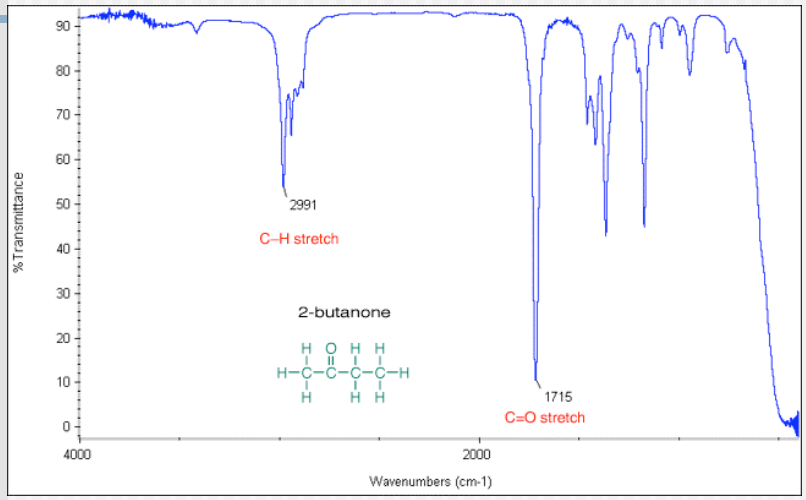
Infrared spectrum of a ketone - 2-butanone



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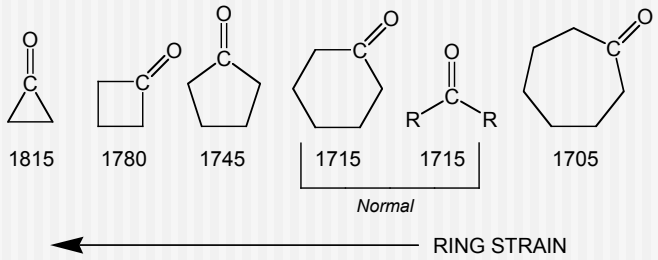
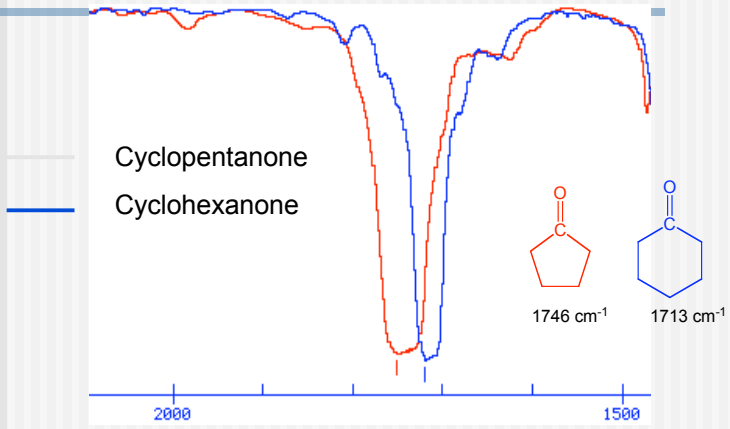
Cyclic Ketones

For cyclic ketones, the C=O frequency increases with decreasing ring size, as the π character of the C=O group increases



Dr. Zerong Wang at UHCL Pavia, Lampman & Kriz, p. 59

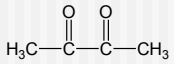
Infrared Spectra of cyclic ketones – ring size



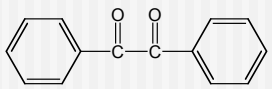
Dr. Zerong Wang at UHCL http://www.chemistry.uhcl.edu/cgi-bin/webspectra.cgi/rp1/l/rp2/l?nolinks=1

α- and β-diketones

α–diketones (1,2-diketones)

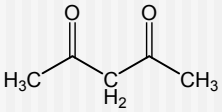


1716 cm^{-1}



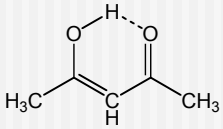
1680 cm^{-1}

β–diketones (1,3-diketones) often experience tautomerism, an equilibrium between enol and keto tautomers



Keto tautomer

C=O doublet
1723 cm^{-1} (symmetric stretch)
1706 cm^{-1} (asymmetric stretch)



Enol tautomer

C=O (hydrogen-bonded), 1622 cm^{-1}
O-H (hydrogen-bonded), 3200-2400 cm^{-1}

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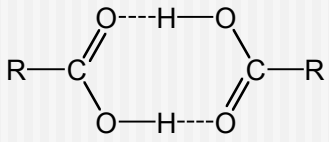
Carboxylic Acids

A strong C=O stretching band is observed at 1730-1700 cm^{-1} for simple aliphatic carboxylic acids in the dimeric, hydrogen-bonded form in the pure liquid or solid states, with a very broad O-H stretch at 3400-3200 cm^{-1} (overlapping with C-H stretches)



In dilute solution, the C=O band is found at 1760 cm^{-1}. Conjugation of the C=O to C=C or phenyl groups moves the band lower frequencies.

The C-O single bond stretch is found in the 1320-1210 cm^{-1} as a medium intensity band.

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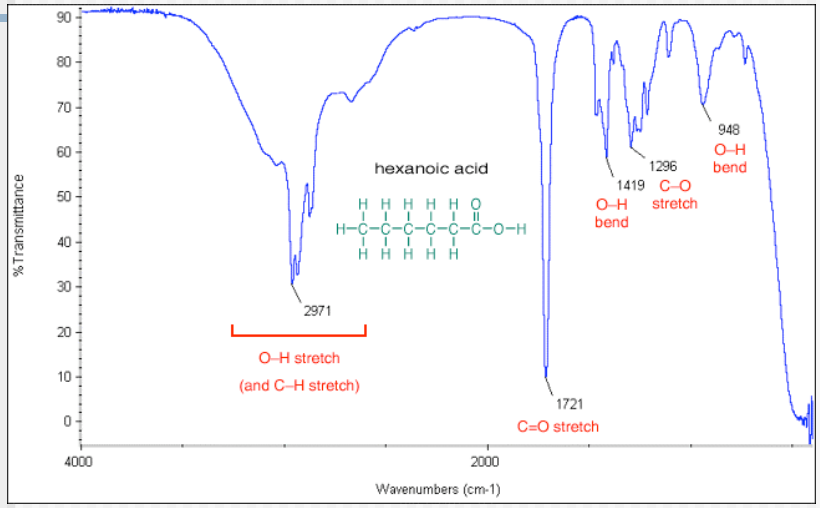
Hexanoic acid



http://orgchem.colorado.edu/hndbksupport/irtutor/tutorial.html

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Esters

The C=O stretch for an aliphatic ester appears as a strong band in the 1750 – 1735 cm^{-1} range.

Conjugation:

C=C-C(=O)-OR	1740–1715 cm^{-1} for C=O; 1640-1625 cm^{-1} for C=C (sometimes two bands)
with phenyl	1740-1715 cm^{-1} for C=O;1600-1450 cm^{-1} for ring
RC(=O)-O-C=C	conjugation of single bonded O atom with C=C or phenyl moves C=O to 1765-1762 cm^{-1} due to resonance effects

The C-O stretch appears as two or more bands of unequal intensity and width in the 1300-1000 cm^{-1} range.

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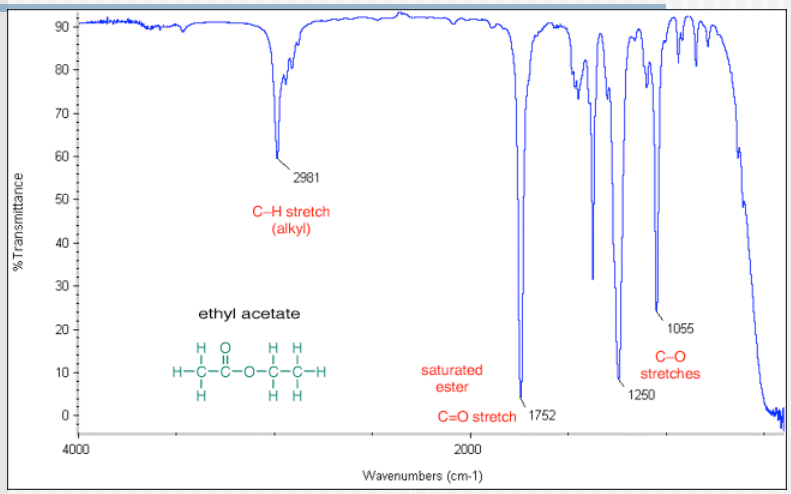
Infrared spectrum of an ester - Ethylacetate



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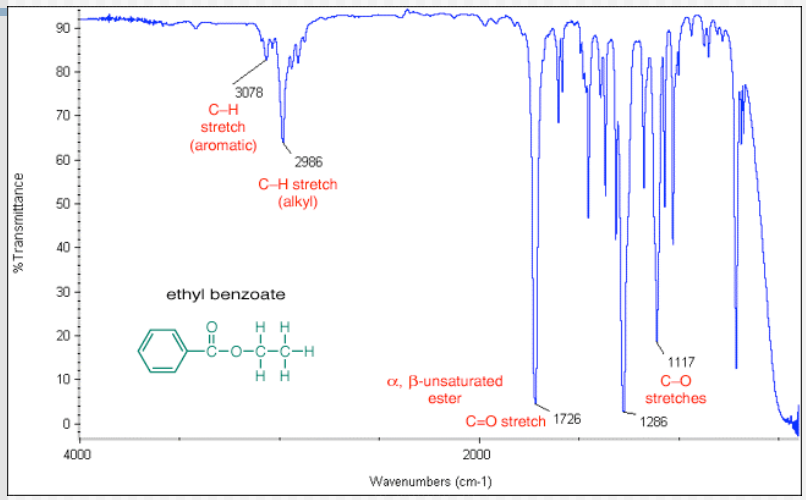
Ethylbenzoate



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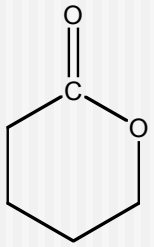
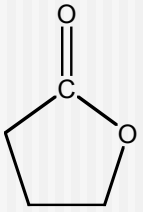
Cyclic Esters - Lactones

Cyclic esters are called lactones, and the C=O vibrations shift to higher frequencies with decreasing ring size



δ-valerolactone
1735 cm^{-1}

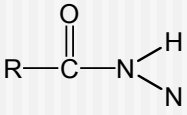


γ-butyrolactone
1770 cm^{-1}

Amides

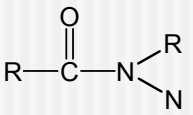
All amides have a broad C=O stretch in the 1680-1630 cm^{-1} range when measured as solids (due to hydrogen bonding). The N-H bending mode occurs in the 1640-1620 cm^{-1} which can make the C=O band appear as a doublet. In dilute solution, where hydrogen bonding is minimized, the C=O band moves to 1690 cm^{-1}. Tertiary amides, with no N-H groups, are unaffected by the physical state of the sample.

N-H stretches



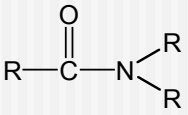
Primary amides

N-H at 3350 and 3180 cm^{-1}



Secondary amides

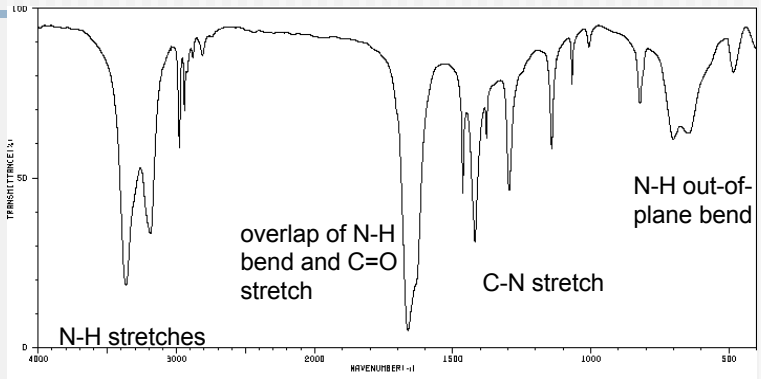
N-H at 3300 cm^{-1}



Tertiary amides

No N-H stretch

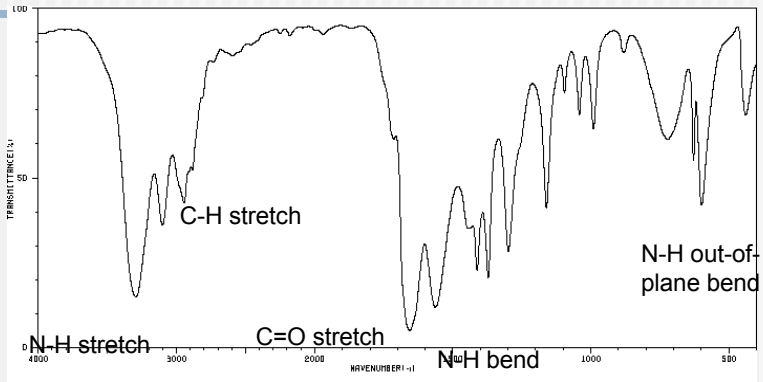
Infrared spectrum of an amide – propionamide



$CH_3CH_2CH_2C(=O)NH_2$

Dr. Zerong Wang at UHCL Spectrum from SDBS database

Infrared spectrum of an amide – N-methylacetamide

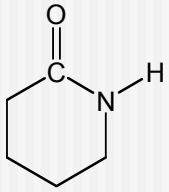


$CH_3C(=O)NH(CH_3)$

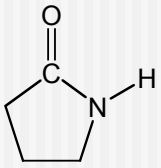
Dr. Zerong Wang at UHCL Spectrum from SDBS database

Cyclic Amides - Lactams

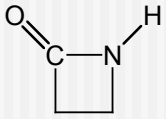
Cyclic amides are called lactams. The C=O stretching frequency increases with decreasing ring size, as we have seen before for cyclic ketones (lactones)



~ 1660 cm^{-1}



~ 1705 cm^{-1}



~ 1745 cm^{-1}

Amines

Aliphatic amine N-H stretches are found in the 3500-3300 cm^{-1} range:

Primary amines, RNH_2, show two N-H stretches

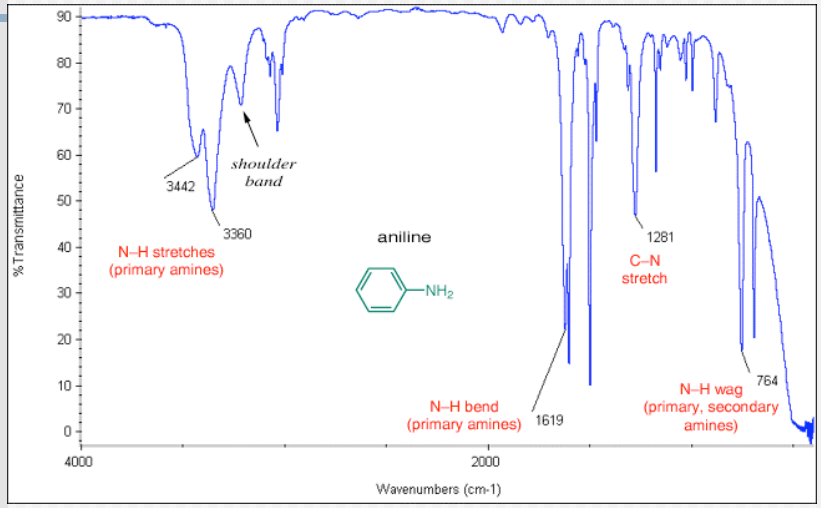
Secondary amines, R_2NH, have only one band

Tertiary amines, R_3N, have no bands in this region

The N-H bend is a broad band at 1640–1560 cm^{-1} for primary amines and about 1500 cm^{-1} for secondary amines. Out-of-plane bending modes are sometimes seen near 800 cm^{-1}

The C-N stretch occurs in the range of 1350-1000 cm^{-1}

Aniline



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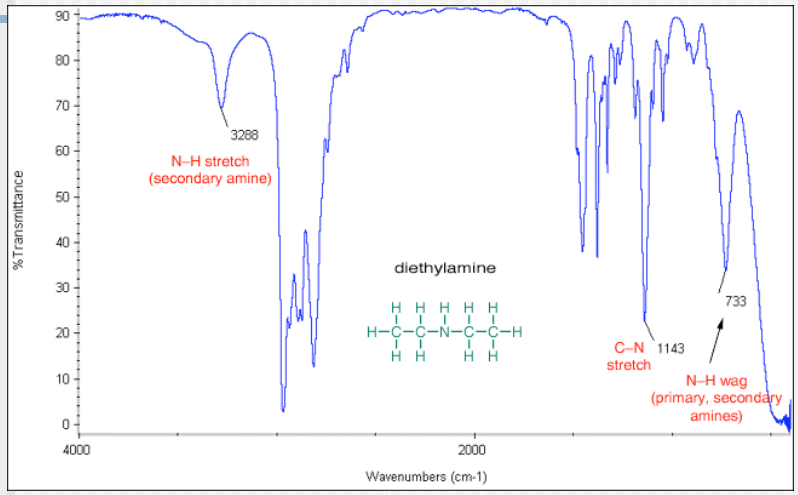
Diethylamine



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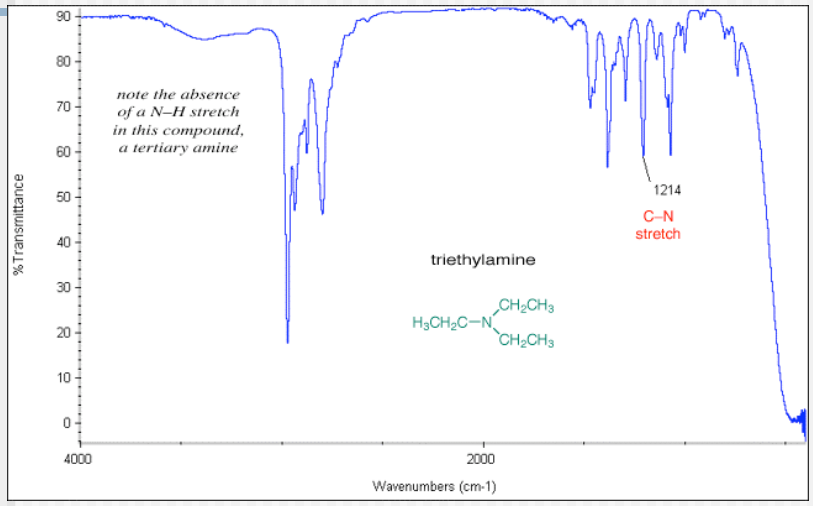
Triethylamine



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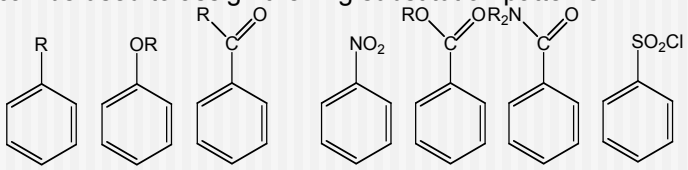
Aromatic rings

The =C-H stretches for aromatic rings are found at frequencies greater than 3000 cm^{-1} (3050-3010 cm^{-1})

The =C-H out-of-plane bending modes are observed at 900-600 cm^{-1} and can be used to assign the ring substitution patterns.



Reliable Interpretation Unreliable Interpretation

The C=C ring stretching absorptions are often seen in pairs at 1600 cm^{-1} and 1475 cm^{-1}

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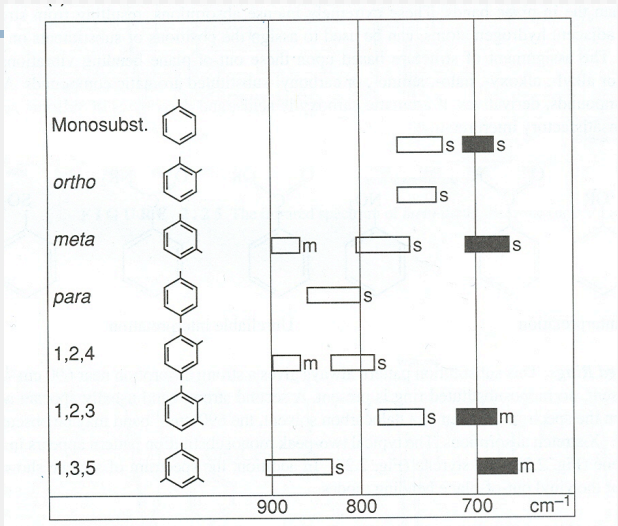
C-H out-of-plane bending for substituted benzenes

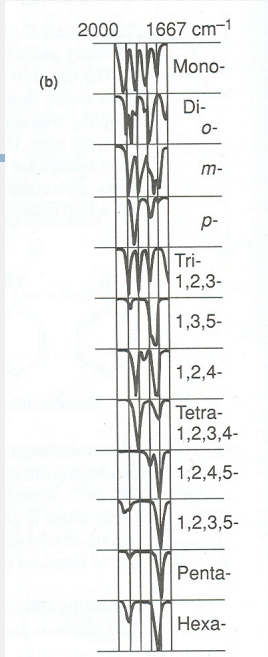


Pavia, Lampman & Kriz, p. 44

Aromatic Rings

Overtone/combination bands which appear between 2000 and 1660 cm^{-1} are weak absorptions which can also be used to assign the ring substitution pattern.

Compounds need to be run as neat liquids or concentrated solutions to see these weak bands and if the compound contains a carbonyl group, then these overtone bands are often obscured.



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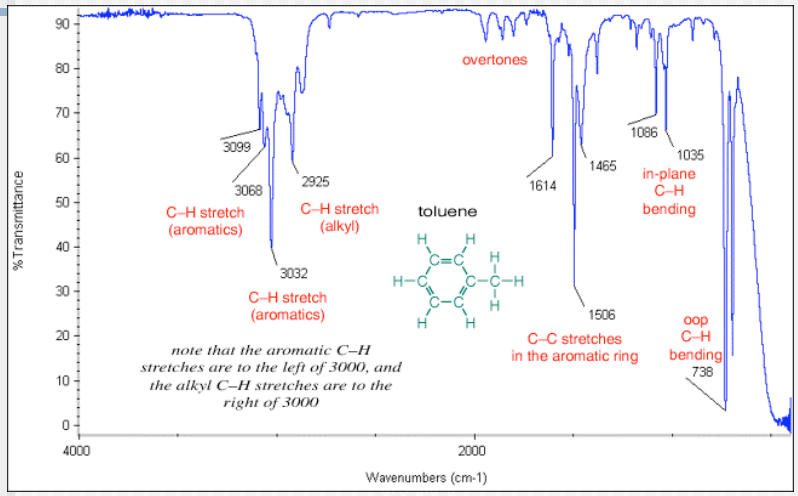
Pavia, Lampman & Kriz, p. 44

Toluene



http://orgchem.colorado.edu/hndbksupport/irtutor/tutorial.html

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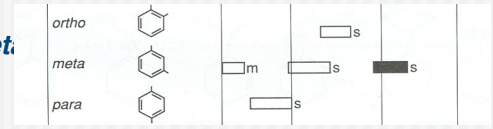
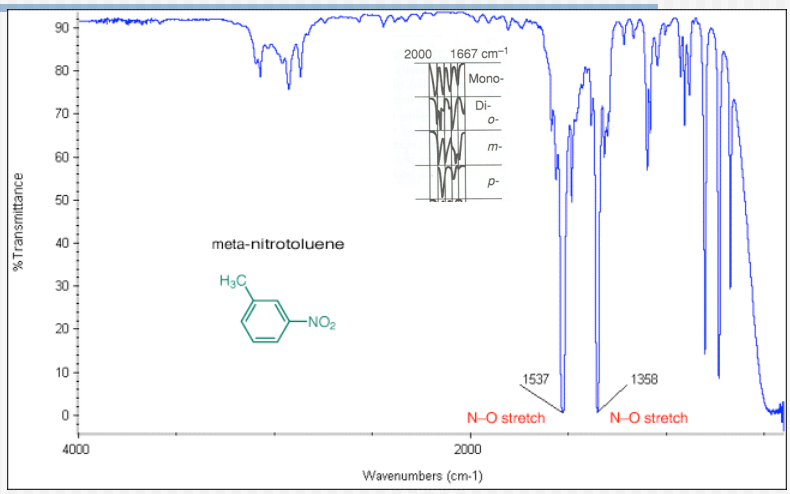
Meta





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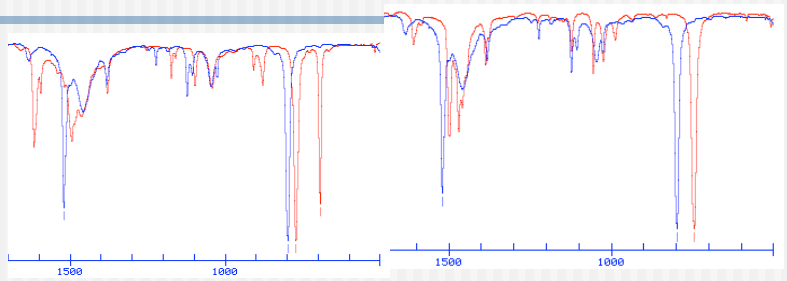
Disubtituted Dimethylbenzenes (xylenes)



meta-xylene

para-xylene

ortho-xylene

para-xylene

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Nitro compounds, -NO_2

Aliphatic nitro compounds:

Asymmetric stretch (strong) 1600-1530 cm^{-1}

Symmetric stretch (medium) 1390-1300 cm^{-1}

Aromatic nitro compounds:

Asymmetic stretch (strong) 1550-1490 cm^{-1}

Symmetric stretch (strong) 1355-1315 cm^{-1}

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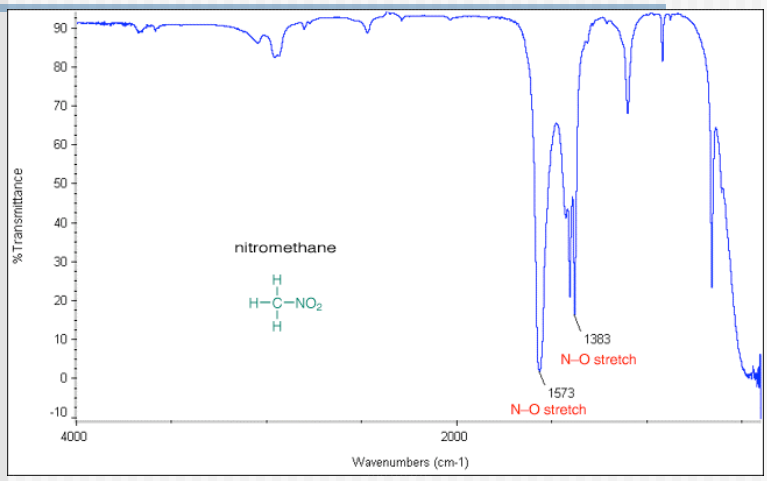
Nitromethane



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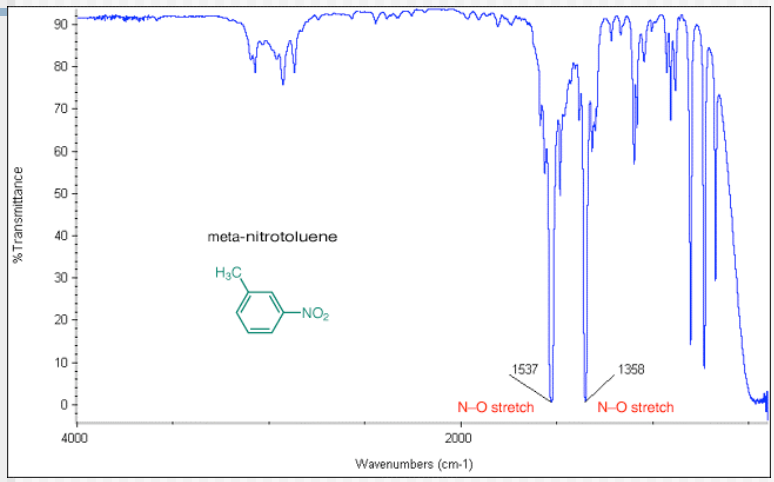
Meta-nitrotoluene



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Alkyl and Aryl halides

The C-X stretching frequencies occur at very low frequencies in the fingerprint region (C-F > C-Cl > C-Br > C-I, primarily due to the effects of the reduced mass) and thus the presence of a halide is often difficult to confirm by means of the infrared spectrum. In addition, commonly used solvents for solution IR, such as $CHCl_3$ and CCl_4, also absorb in this regions. Also, for pure liquids, the NaCl plates have an absorbance cut-off below 600 cm^{-1}, so acquisition of the spectrum of a solid as a KBr disk is the preferred method.

C-F Strong stretch in the 1400-1000 cm^{-1}, with aryl fluorides between 1250 cm^{-1} and 1100 cm^{-1}. Monofluoralkanes absorb at the high end of the range, with polyfluoroalkanes exhibiting strong bands in the 1350-1100 cm^{-1} range.

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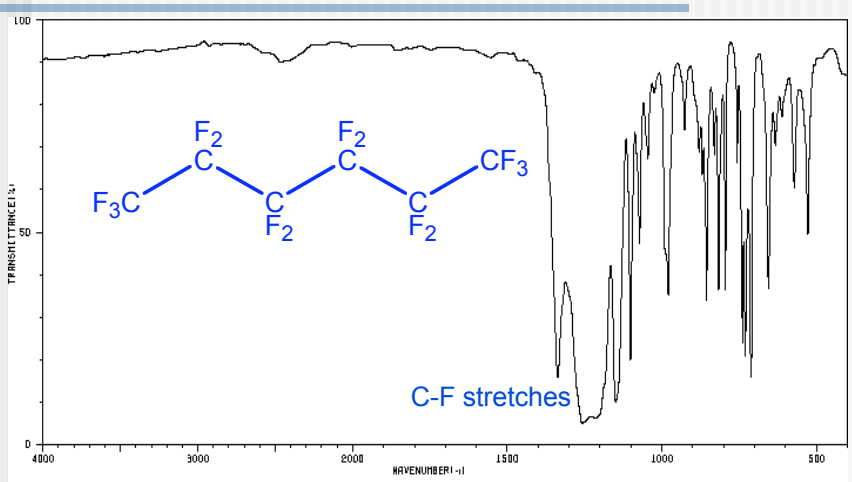
Infrared Spectrum of Perfluorohexane



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Spectrum from SDBS database

Alkyl and Aryl halides

C-Cl The C-Cl stretch of aliphatic chlorides occurs as a strong band in the 785-540 cm^{-1} region (primary > secondary > tertiary), while aromatic C-Cl stretches are found at 1100-1035 cm^{-1}

CH_2Cl_2	739 cm^{-1}
$CHCl_3$	759 cm^{-1}
CCl_4	785 cm^{-1}

C-Br Aliphatic C-Br at 650-510 cm^{-1}; Aryl C-Br at 1075-1030 cm^{-1}

C-I Aliphatic C-I at 600-485 cm^{-1} (out of range for NaCl plates)

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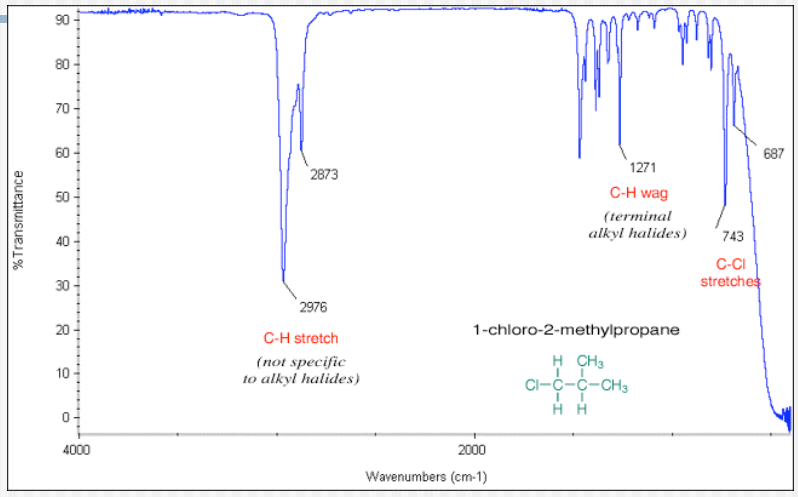
1-chloro-2-methylpropane



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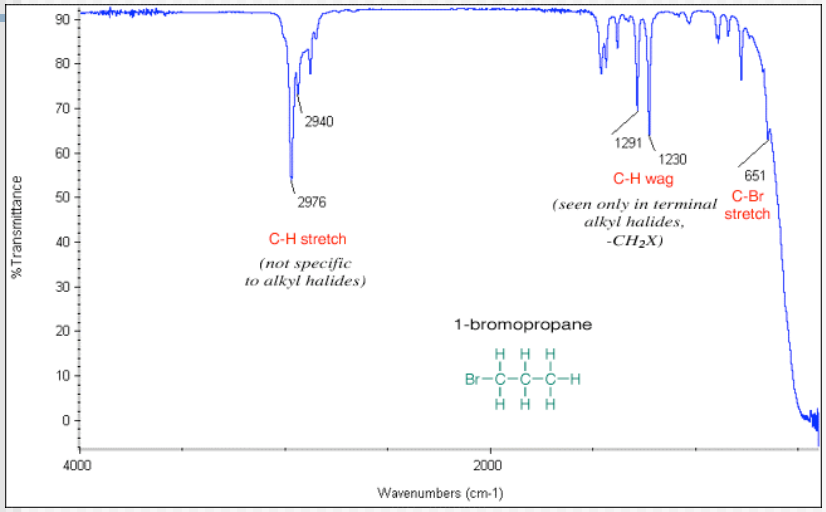
1-Bromopropane



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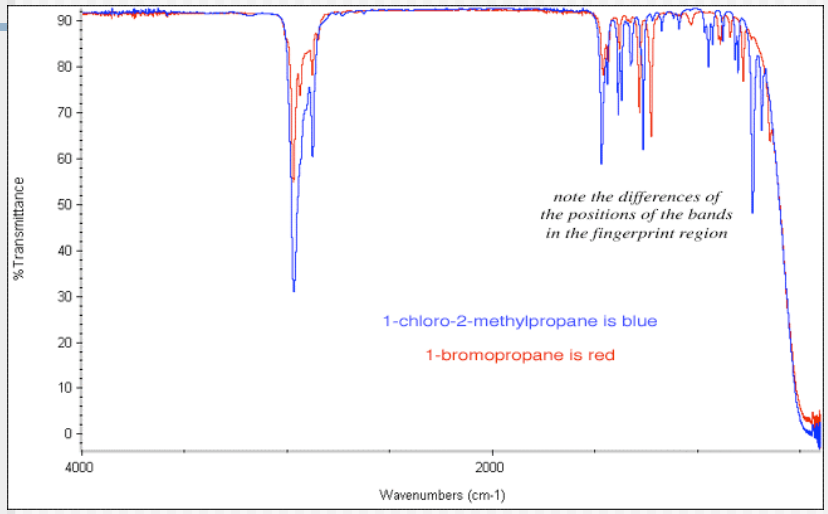
Comparison of chloro/bromo groups



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Strategies for Analyzing an Infrared Spectrum

1. Look first for a carbonyl C=O band in the 1820-1660 cm^{-1} range. It will usually be the most intensive band (medium width) in the spectrum. If you see a carbonyl band, look for other bands associated with carbonyl functional groups, by going to step 2. If there is no C=O stretch present, check for alcohols by going to step 3.
2. If a C=O stretch is present, you can determine the nature of the carbonyl group by looking its position and by examining other characteristic bands:

   Carboxylic acid: An O-H stretch should be present as a broad band near 3300 cm^{-1}, which may overlap with C-H stretches. There will also be a C-O stretch in the 1300-1000 cm^{-1} region.

   Ester: Look for the C-O stretch as a medium intensity band in the 1300-1000 cm^{-1} region, and the absence of an O-H stretching band.

Strategies for Analyzing an Infrared Spectrum

Aldehyde: The aldehydes have a characteristic pair of C-H peaks near 2850 and 2750 cm^{-1}, usually of equal intensity.

Ketone: These will have a C=O stretch in the same region as an aldehyde, but the aldehyde C-H bands will be absent.

3. If no carbonyl C=O band is present, look for an alcohol O-H band near 3600-3300 cm^{-1} and a C-O band in the 1300-1000 cm^{-1} range.
4. If no C=O or O-H bands are present in the spectrum, look for the C=C stretches of an alkene or an aromatic ring, or a C≡C of an acetylene or a C≡N of a nitrile.

   Alkene: Look for a relatively weak C=C band near 1650 cm^{-1} and a C-H stretch, just above 3000 cm^{-1}

   Aromatic: The aromatic (benzene) C=C stretches appear as medium to strong absorptions in the 1650-1450 cm^{-1} region and a weak C-H band may be found at about 3100 cm^{-1}

Strategies for Analyzing an Infrared Spectrum

Acetylene: The C≡C stretch is found in the 2150 cm^{-1} region, with a terminal ≡C-H stretch at 3300 cm^{-1}

Nitrile: The C≡N stretch is a strong band at about 2250-2200 cm^{-1}.

5. If none of the above groups appear to be present, the compound may be an alkane. The main absorptions will be C-H stretches below 3000 cm^{-1} and a C-H bending band near 1450 cm^{-1}.

6. An alkyl halide might be present if bands near 785-540 cm^{-1} (chloride) or 650-510 cm^{-1} (bromide) are observed

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Important infrared frequencies

Base values for bond stretching absorption frequencies

bond	frequency	bond	frequency
O-H	3400 cm^{-1}	C≡C	2150 cm^{-1}
N-H	3400 cm^{-1}	C=O	1715 cm^{-1}
C-H	3000 cm^{-1}	C=C	1650 cm^{-1}
C≡N	2250 cm^{-1}	C-O	1100 cm^{-1}

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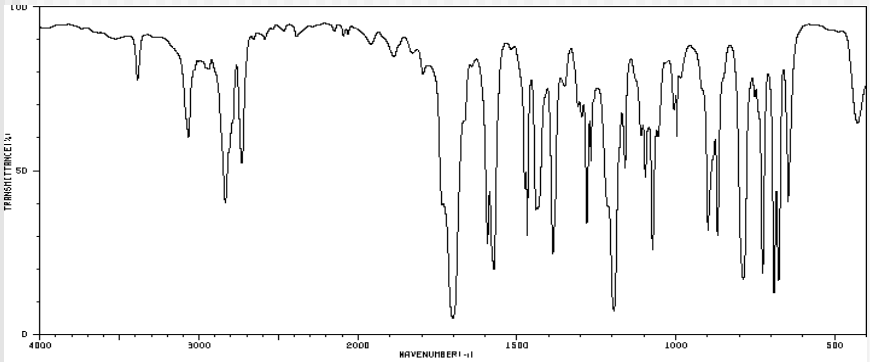
Pavia, Lampman & Kriz, p. 27

Infrared of ????

liquid film

cm^{-1}	%T								
3387	74	1673	19	1308	66	1096	46	788	16
3067	58	1476	42	1297	64	1074	24	752	70
2940	77	1468	29	1281	32	1056	58	727	17
2834	38	1440	36	1268	60	1006	66	691	12
2731	50	1434	36	1195	7	997	58	677	15
1702	4	1387	25	1160	49	899	30	647	36
1693	26	1351	72	1109	68	869	28	429	62



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liquid film

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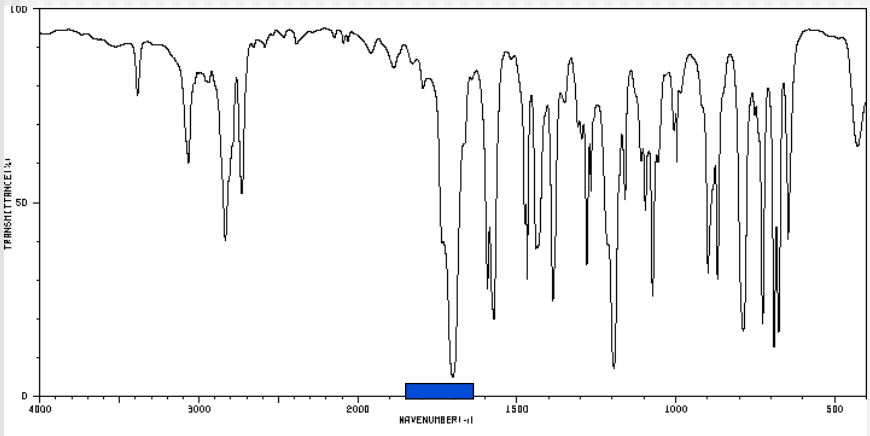

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Analysis of an Infrared Spectrum

Step 1. Look for carbonyl C=O bands

- carbonyl stretch found at 1702 cm^{-1}
- could be a ketone, aldehyde, carboxylic acid
- therefore need to look for other bands characteristic of these particular carbonyl functional groups
- aldehyde – two "C-H" bands at about 2750 and 2850 cm^{-1}
- carboxylic acid – very broad O-H stretch at 3400-2400 cm^{-1} region

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Infrared of ????

liquid film

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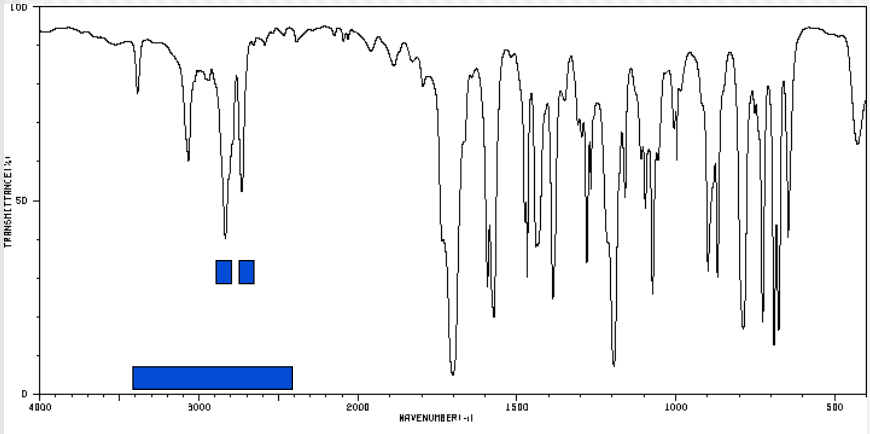

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Analysis of an Infrared Spectrum

Step 1. Look for carbonyl C=O bands

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- could be a ketone, aldehyde, carboxylic acid

- therefore need to look for other bands characteristic of these particular carbonyl functional groups

- aldehyde – two "C-H" bands at about 2750 and 2850 cm^{-1}

- carboxylic acid – very broad O-H stretch at 3400-2400 cm^{-1} region

-there are two bands at 2834 and 2731 cm^{-1} - suggests an aldehyde

-no broad O-H bands – tends to rule out a carboxylic acid

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Analysis of an Infrared Spectrum

-there are two bands at 2834 and 2731 cm^{-1} - suggests an aldehyde

No need to consider Step 3 for alcohol as we saw no broad O-H stretch when looking for carboxylic acid peaks

Step 4. Look for evidence of C=C (alkenes or aromatics) or triple bonds C≡C or C≡N.

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Infrared of ????

liquid film

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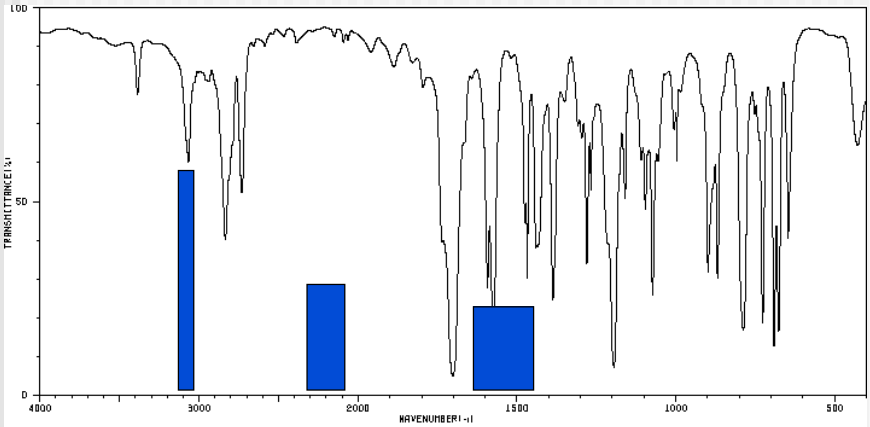

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Analysis of an Infrared Spectrum

-there are two bands at 2834 and 2731 cm^{-1} - suggests an aldehyde

No need to consider Step 3 for alcohol as we saw no broad O-H stretch when looking for carboxylic acid peaks

Step 4. Look for evidence of C=C (alkenes or aromatics) or triple bonds C≡C or C≡N.

- no bands in the triple bond region
- there is a band at 3067 cm^{-1} indicative of a C-H stretch on an aromatic ring or possible an alkene
- there are several bands in the 1500-1400 cm^{-1}, consistent with an aromatic C=C stretch

*do we have an aromatic aldehyde?

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Analysis of an Infrared Spectrum

- there is a band at 3067 cm^{-1} indicative of a C-H stretch on an aromatic ring or possible an alkene

- there are several bands in the 1500-1400 cm^{-1}, consistent with an aromatic C=C stretch

*do we have an aromatic aldehyde?

Look for bands in the fingerprint region consistent with a particular substitution pattern

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Infrared of ????

liquid film

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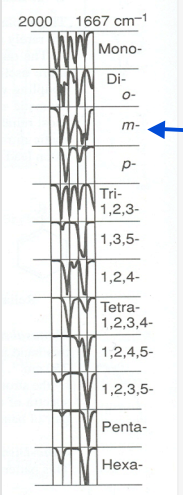

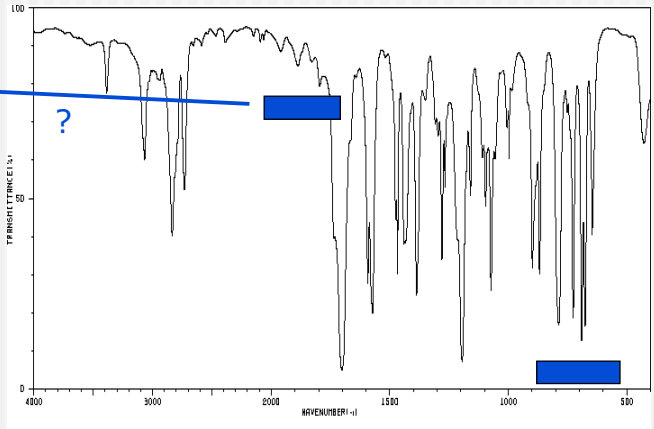

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Infrared of ????

liquid film

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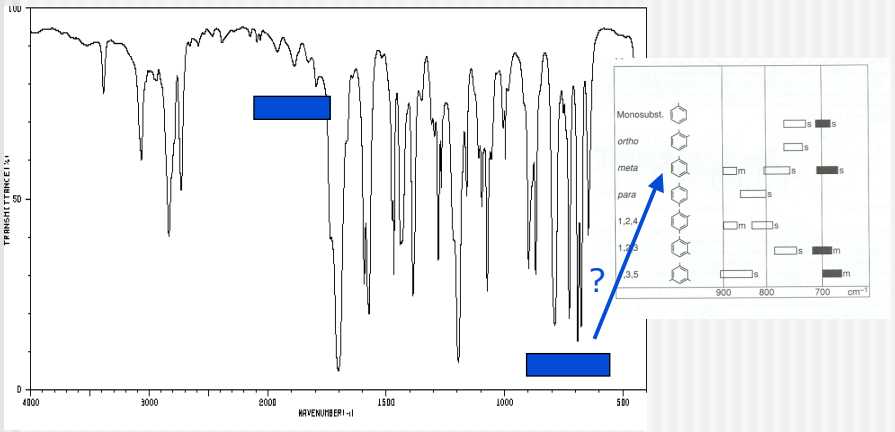

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Analysis of an Infrared Spectrum

- there is a band at 3067 cm^{-1} indicative of a C-H stretch on an aromatic ring or possible an alkene

- there are several bands in the 1500-1400 cm^{-1}, consistent with an aromatic C=C stretch

*do we have an aromatic aldehyde?

Look for bands in the fingerprint region consistent with a particular substitution pattern

- the patterns in the 2000-1670 cm^{-1} region (weak) and the 900–650 cm^{-1} region (strong) are consistent with meta disubstitution

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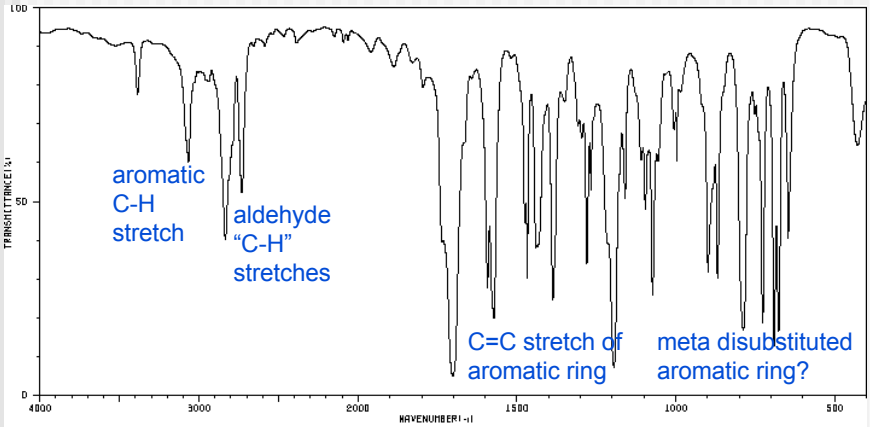
Infrared of ????

liquid film

3387	74	1673	19	1308	66	1096	45	788	16
3067	58	1476	42	1297	64	1074	24	752	70
2940	77	1468	29	1281	32	1056	58	727	17
2834	38	1440	36	1268	60	1006	66	691	12
2731	50	1434	36	1195	7	997	58	677	15
1702	4	1387	25	1160	49	899	30	647	36
1593	26	1361	72	1109	68	869	28	429	62



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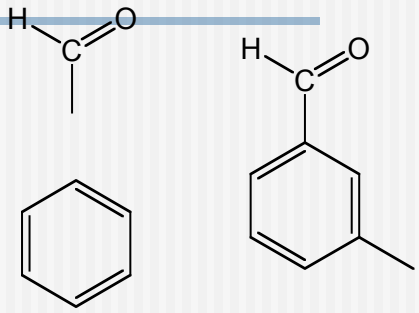
Analysis of an Infrared Spectrum

What do we have?

aldehyde

aromatic ring

meta-disubstituted?



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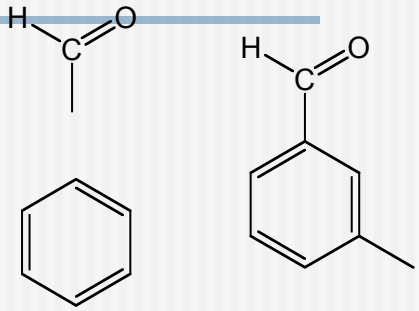
Analysis of an Infrared Spectrum

What do we have?

aldehyde

aromatic ring

meta-disubstituted?



Cl

C_7H_5O + ?

Additional information needed, such as the molecular formula:

C_7H_5ClO degree of unsaturation is 7 - ½(6) + 1 = 5

The degree of unsaturation is accounted for and the extra atom is Cl

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Infrared of ????

liquid film

3387	74	1673	19	1308	66	1096	46	788	16
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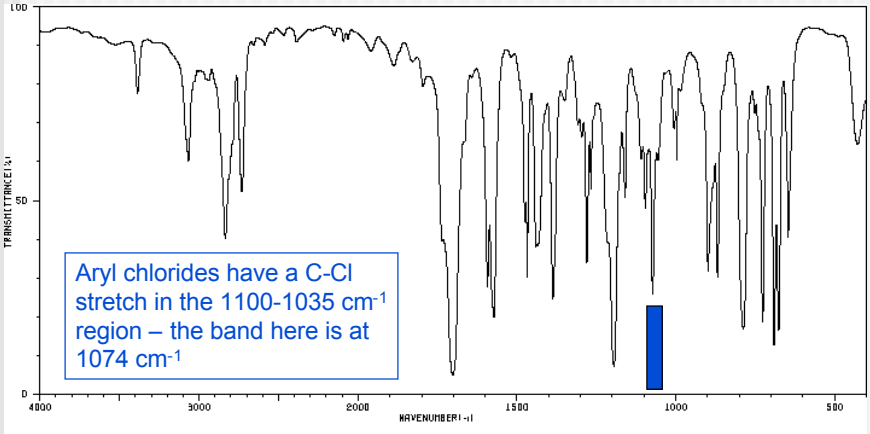

Aryl chlorides have a C-Cl stretch in the 1100-1035 cm^{-1} region – the band here is at 1074 cm^{-1}

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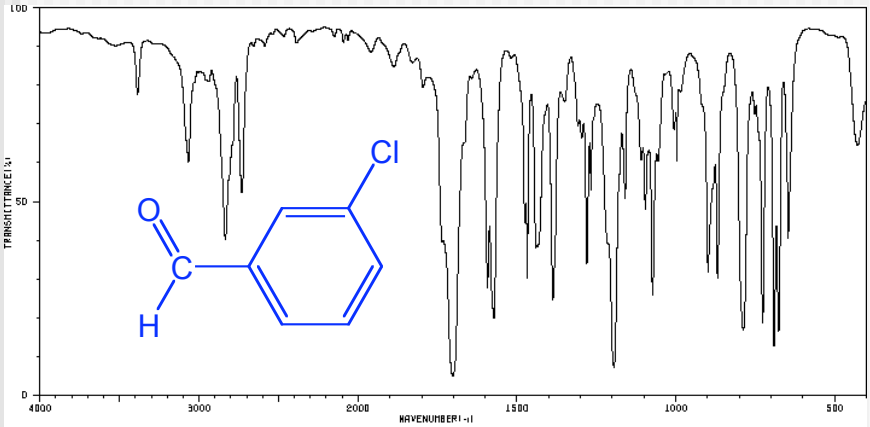
Infrared spectrum of *meta*-chlorobenzaldehyde

liquid film



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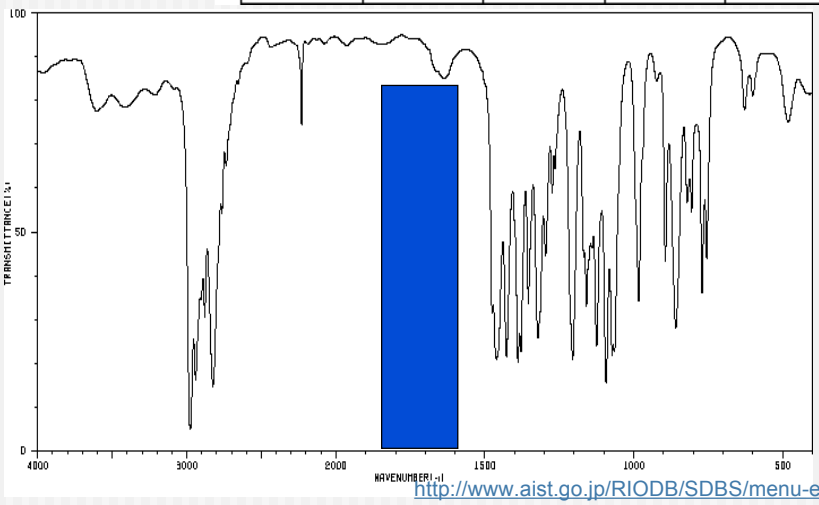
KBr disk

3600	74	2736	62	1364	32	1169	32	869	26
3413	74	2231	72	1322	24	1125	23	821	55
2977	4	1478	30	1296	42	1093	14	806	52
2941	15	1461	20	1275	67	1073	21	771	34
2879	29	1428	20	1265	62	1065	21	755	42
2825	13	1389	19	1206	20	984	39	629	74
2765	62	1380	21	1168	42	895	41	483	72



http://www.aist.go.jp/RIODB/SDBS/menu-e.html

Analysis of an Infrared Spectrum

Step 1. Look for carbonyl C=O bands

- no C=O bands observed – not a carbonyl group

go to Step 3. Look for O-H stretches of an alcohol

- no O-H stretches – not an alcohol

go to Step 4. Look for C=C stretches, C≡C stretches, or C≡N stretches

- no C=C stretches around 1650 cm^{-1} or C-H stretches above 3000 cm^{-1} – no alkene group

- aromatic C=C stretches in the 1650-1450 cm^{-1} region? perhaps – but no C-H stretch around 3100 cm^{-1} – probably not an aromatic group

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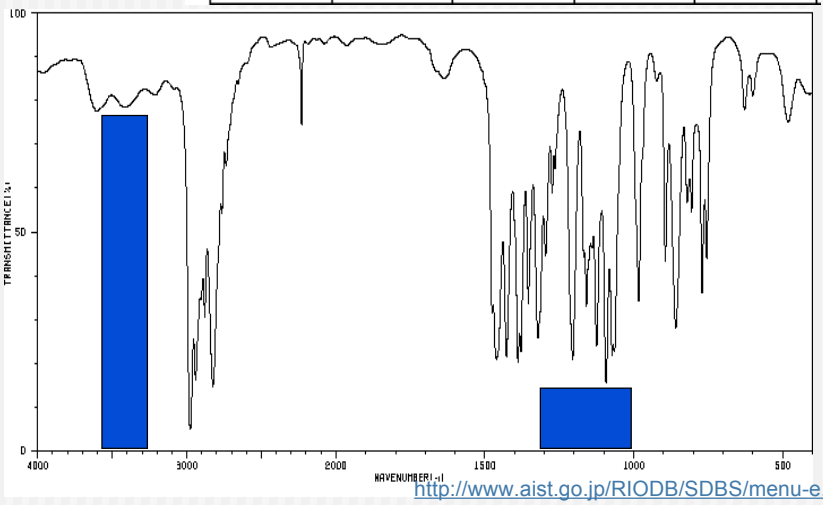
3600	74	2736	62	1364	32	1169	32	869	26
3413	74	2231	72	1322	24	1125	23	821	55
2977	4	1478	30	1296	42	1093	14	806	52
2941	15	1461	20	1275	67	1073	21	771	34
2879	29	1428	20	1265	62	1065	21	755	42
2825	13	1389	19	1206	20	984	35	629	74
2766	52	1380	21	1168	42	896	41	483	72



http://www.aist.go.jp/RIODB/SDBS/menu-e.html

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Dr. Zerong Wang at UHCL

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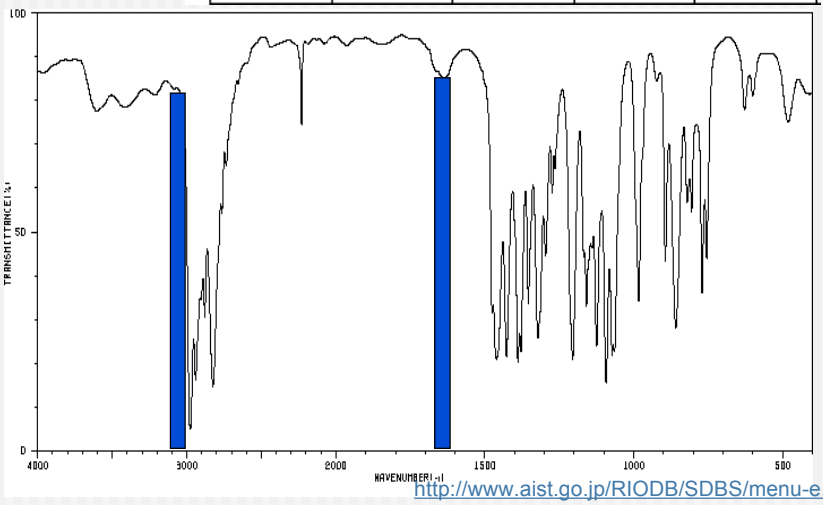

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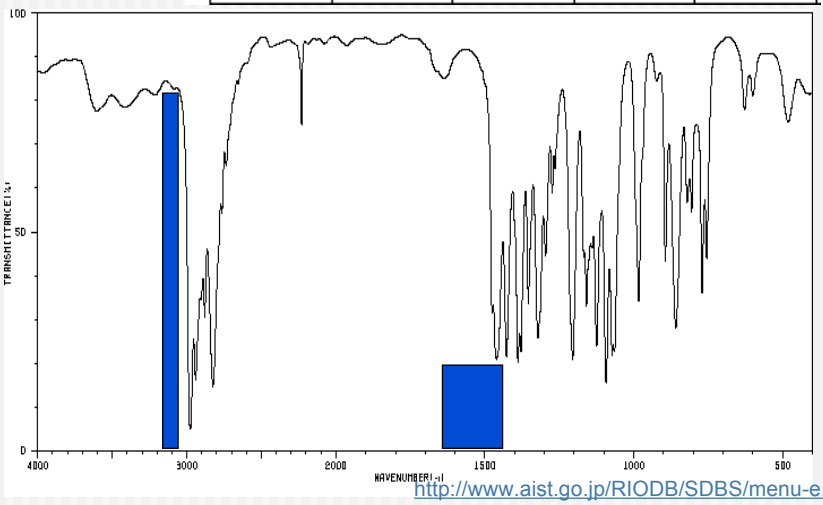

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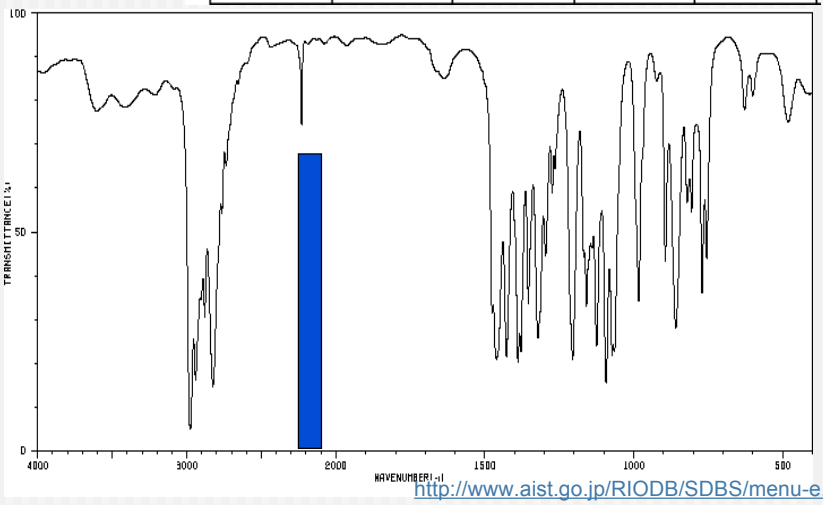

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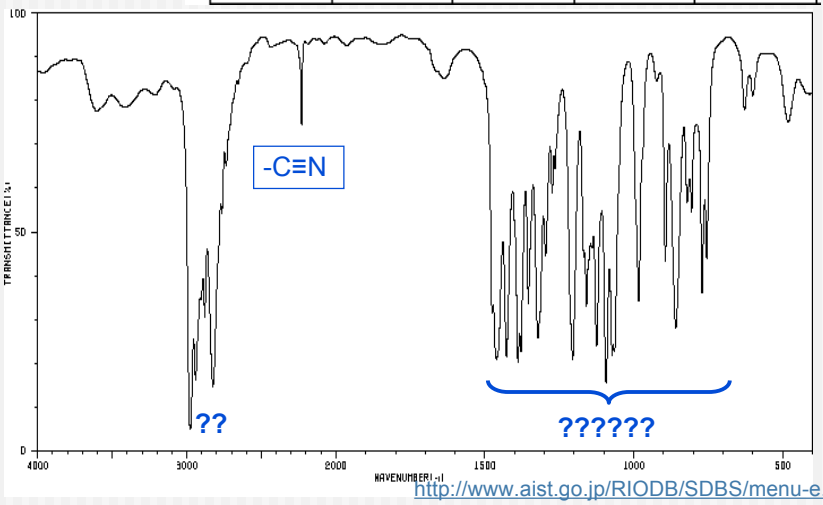

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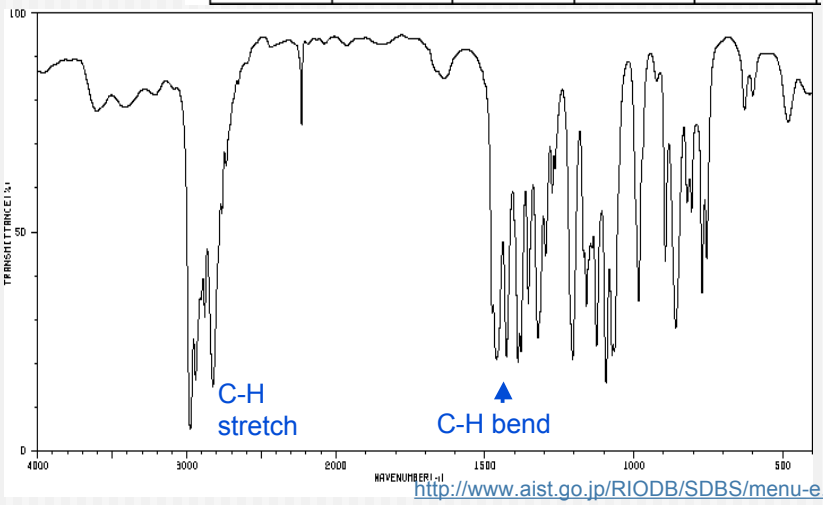

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Analysis of an Infrared Spectrum

what next?

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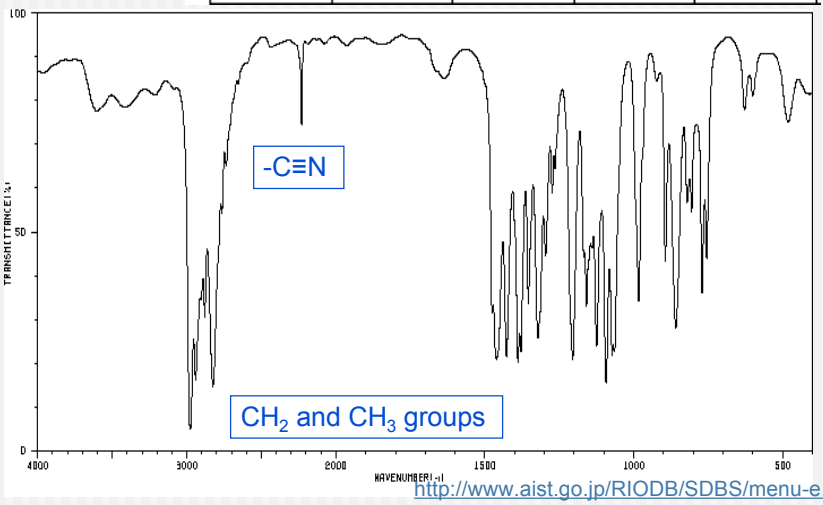

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The remainer of the strong bands are found in the fingerprint region, so it is difficult to make any additional assignments without further information about the compound.

Molecular formula = $C_6H_{12}N_2$

*confirms that there are no carbonyl or alcohol groups, because there are no oxygen atoms

Dr. Zerong Wang at UHCL

Analysis of an Infrared Spectrum

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*degree of unsaturation = 6 - ½(10) + 1 = 2

The degree of unsaturation of 2 is already accounted for in our nitrile C≡N group

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Analysis of an Infrared Spectrum

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Dr. Zerong Wang at UHCL

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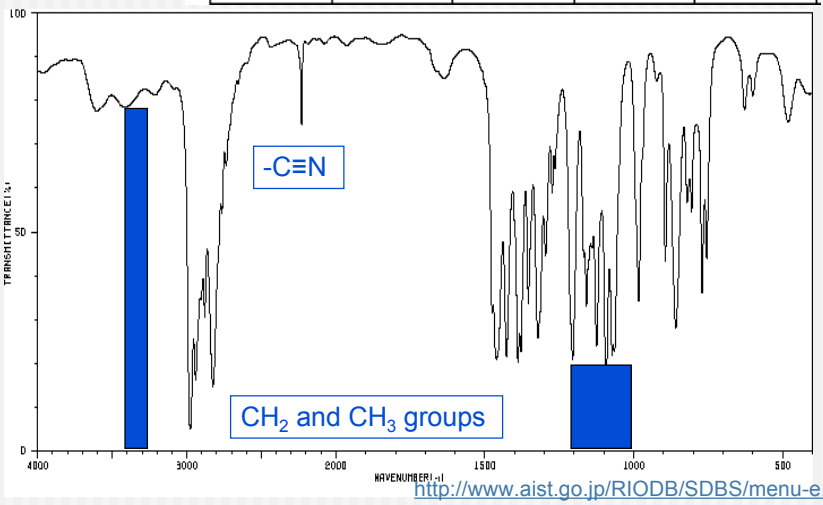

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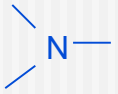

$-C\equiv N$ $-CH_2-$ $-CH_3$

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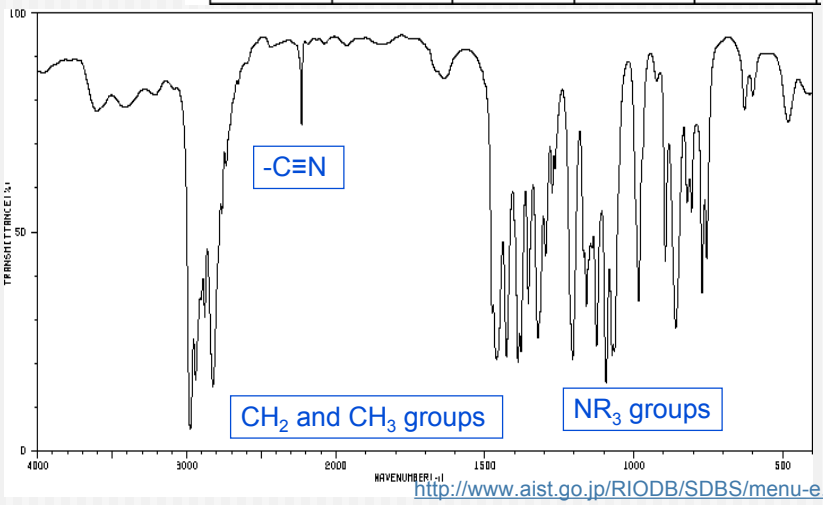

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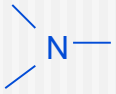

$-C\equiv N$ $-CH_2-$ $-CH_3$

actual compound is $(CH_3CH_2)_2NCH_2C\equiv N$

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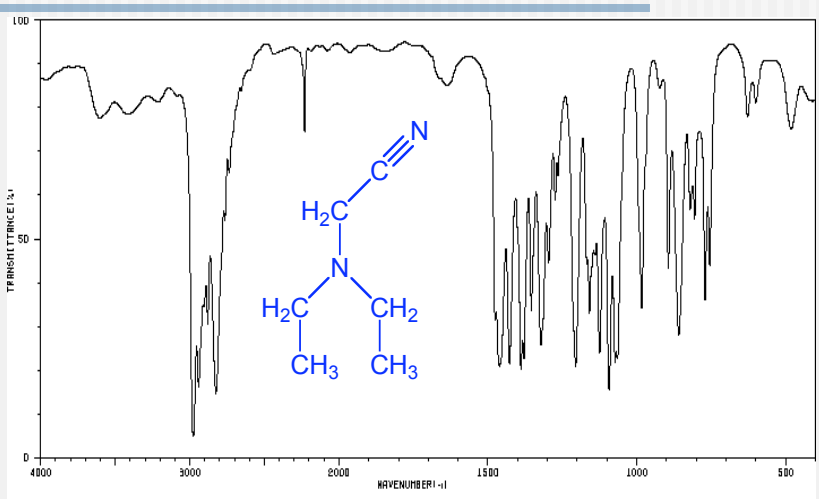
Infrared spectrum of (diethylamino)acetonitrile



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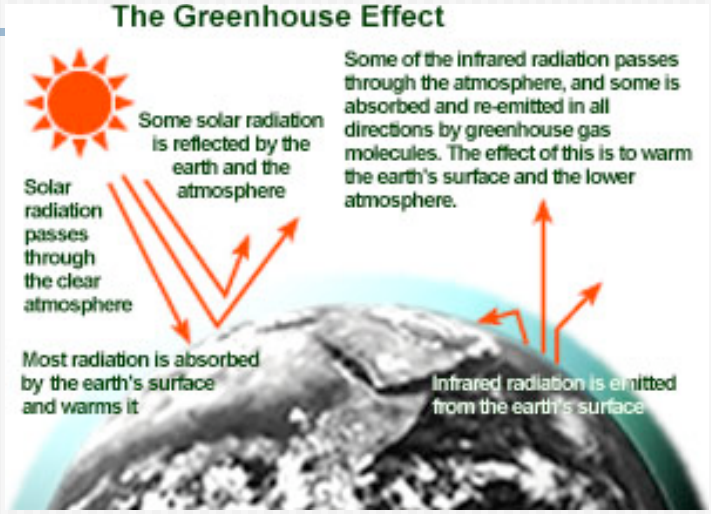
http://www.aist.go.jp/RIODB/SDBS/menu-e.html

The Greenhouse Effect



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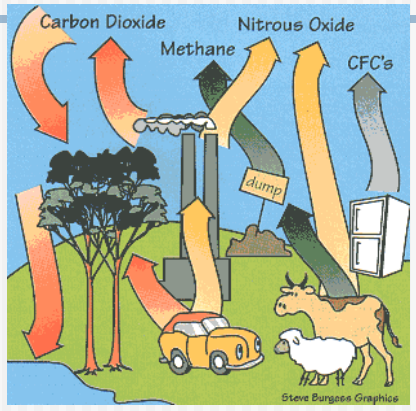
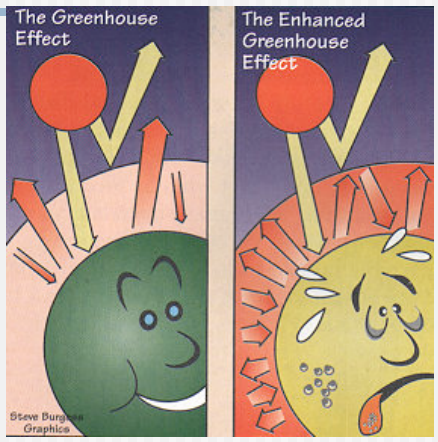
http://climate.volpe.dot.gov/science.html

Greenhouse Effect





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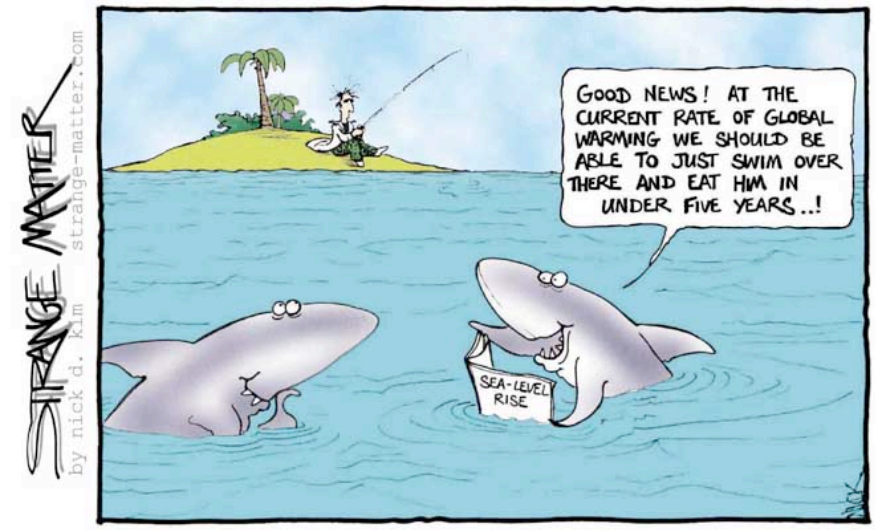
http://www.maf.govt.nz/MAFnet/rural-nz/sustainable-resource-use/climate/impact-on-industries/index.htm

Global Warming



Greenhouse gases

Trace gas	*Chemical formula*	*Atmospheric lifetime* (years)	*Pre-industrial concentration*	*Concentration in 1994*
water vapour	H_2O	week	varies strongly	varies strongly
carbon dioxide	CO_2	50-200	280 ppmv	358 ppmv
methane	CH_4	12	0.7 ppmv	1.72 ppmv
nitrous oxide	N_2O	120	275 ppbv	312 ppbv
perfluorocarbon	CF_4	50000	0	72 pptv
CFC-11	CCl_3F	50	0	268 pptv
CFC-12	CCl_2F_2	102	0	503 pptv
CFC-13	$Cl_3FC{-}CClF_2$	85	0	82 pptv
HCFC-22	$CHClF_2$	12	0	110 pptv

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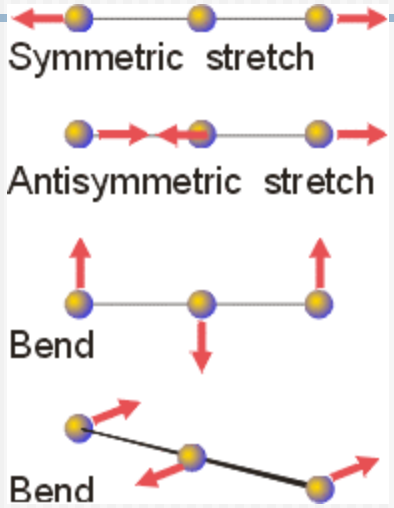
http://www.oun.nl/open/dja/Klimaat/System/greenhouse_gases.htm

Infrared vibrations of CO_2



Infrared inactive

Infrared active

Degenerate bending modes

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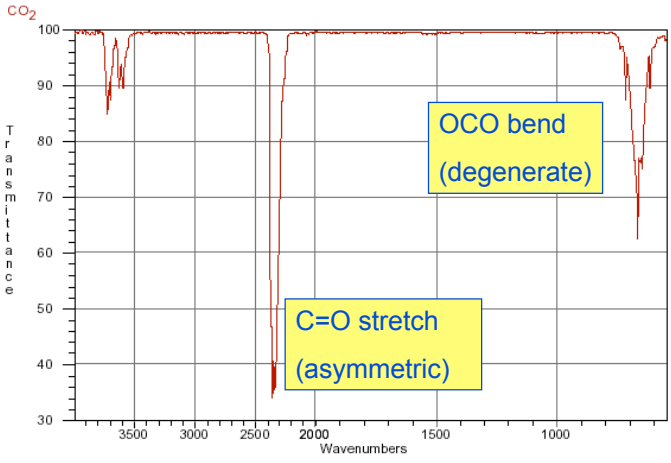
Shriver & Atkins, *Inorganic Chemistry*, p. 134

Infrared Spectrum of CO_2

http://chemistry.beloit.edu/Warming/pages/infrared.html



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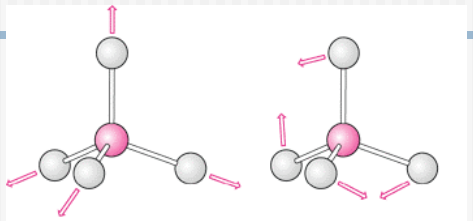
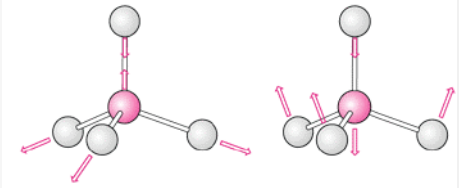
Vibrational modes of methane (CH_4)



Infrared inactive vibrations



Infrared active vibrations

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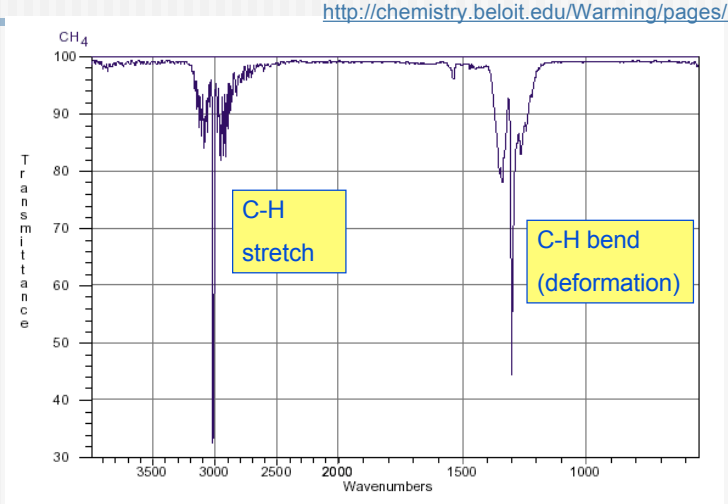
Housecroft and Sharpe, p. 85

Infrared Spectrum of CH_4

http://chemistry.beloit.edu/Warming/pages/infrared.html



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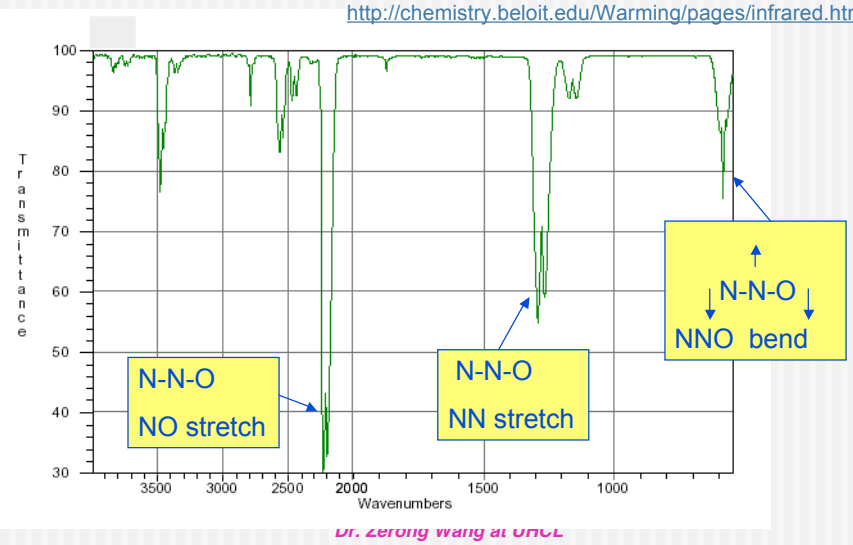
Infrared Spectrum of N_2O

http://chemistry.beloit.edu/Warming/pages/infrared.html



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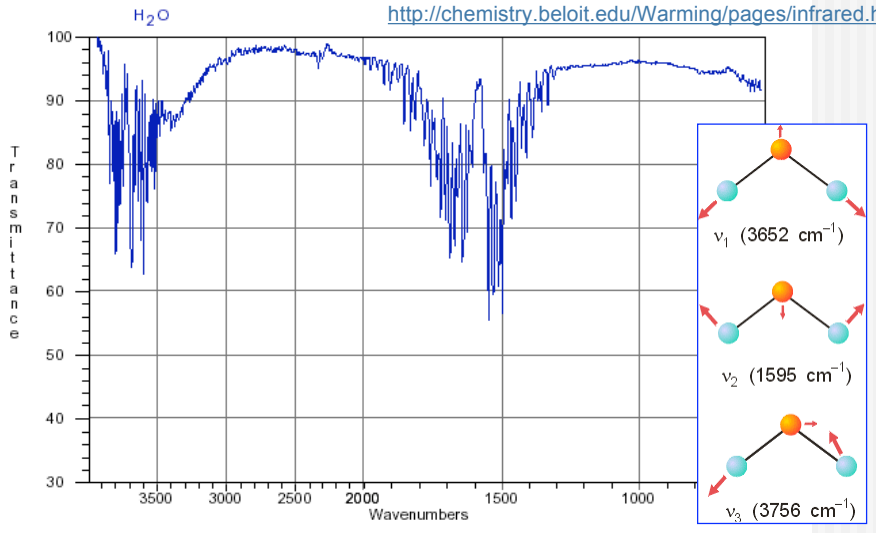
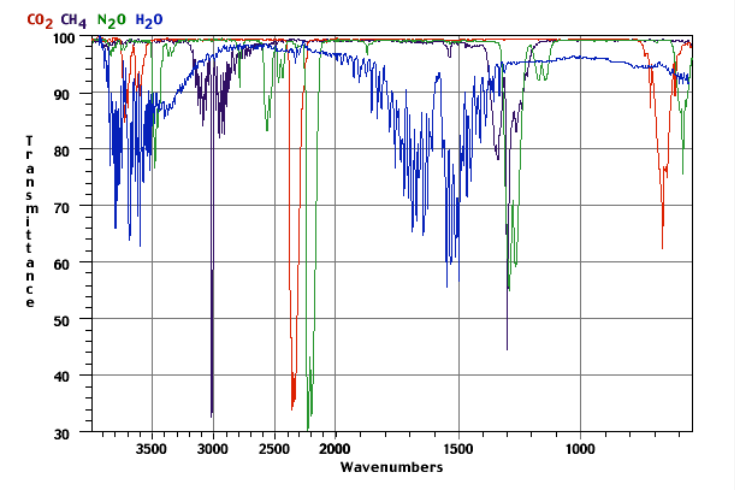
Infrared Spectrum of H_2O

http://chemistry.beloit.edu/Warming/pages/infrared.html



Shriver & Atkins, *Inorganic Chemistry*, p. 133

Infrared Spectra of Greenhouse Gases



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http://chemistry.beloit.edu/Warming/pdf/greenIR.pdf

Recyclable Polymers

1 PETE — Poly(ethylene terephthalate) (PET)

2 HDPE — High Density Poly(ethylene)

3 V — Poly(vinyl chloride)

4 LDPE — Low Density Poly(ethylene)

5 PP — Poly(propylene)

6 PS — Poly(styrene)

7 OTHER — Composites:

eg. PET with Poly(ethylene vinyl alcohol)

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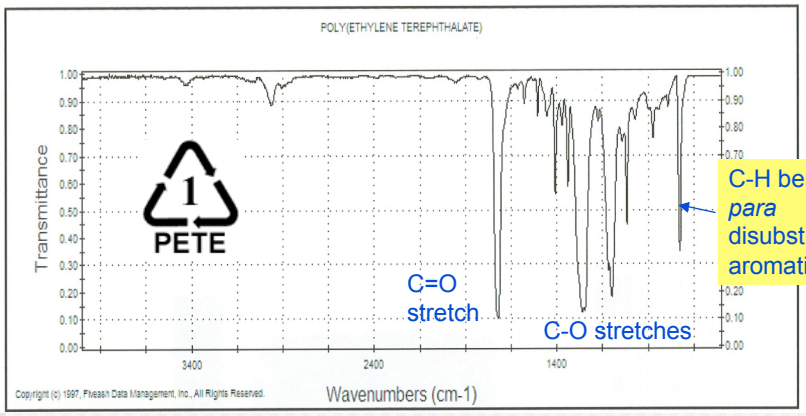
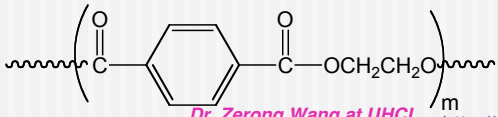
Infrared Spectrum of Poly(ethylene terephthalate)





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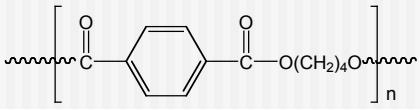
http://www.fdmspectra.com/

PBTE

A freestyle ski area at Sheffield Ski Village, in England, uses Snowflex "virtual snow" for year-round fun. BRITON ENGINEERING PHOTO

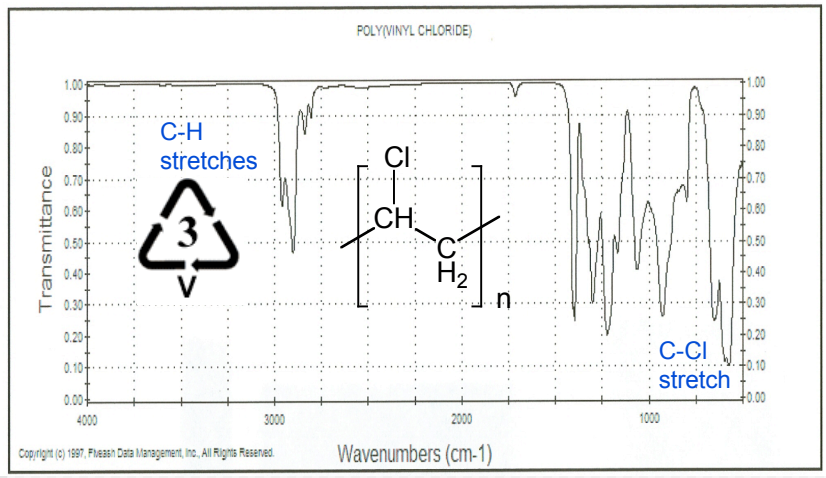
Snowflex, for example, has a slippery polybutylene terephthalate fiber surface layer that sits atop a shock-absorbing pad that has a woven backing. Water piped through the layers exits recessed nozzles and mists the surface, which helps reduce friction even further.



Dr. Zerong Wang at UHCL

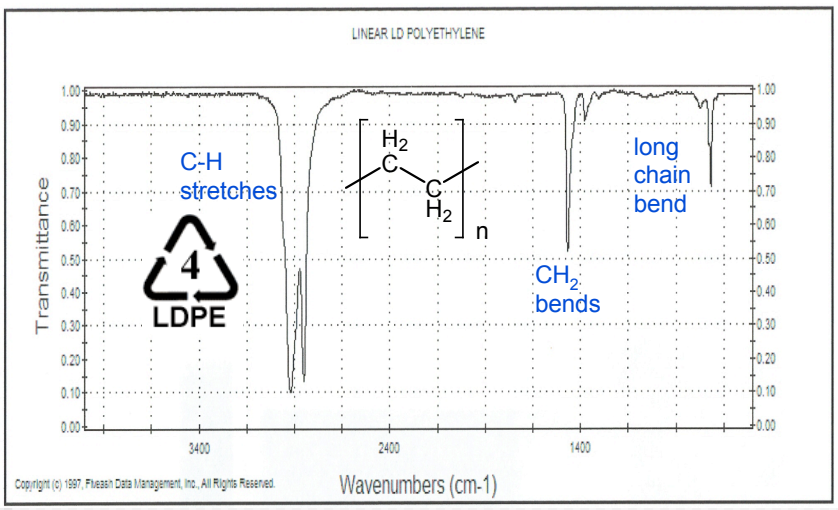
http://pubs.acs.org/cen/whatstuff/stuff/8203snow.html

Infrared Spectrum of Poly(vinyl chloride)



Dr. Zerong Wang at UHCL http://www.fdmspectra.com/

Infrared Spectrum of Low Density Polyethylene



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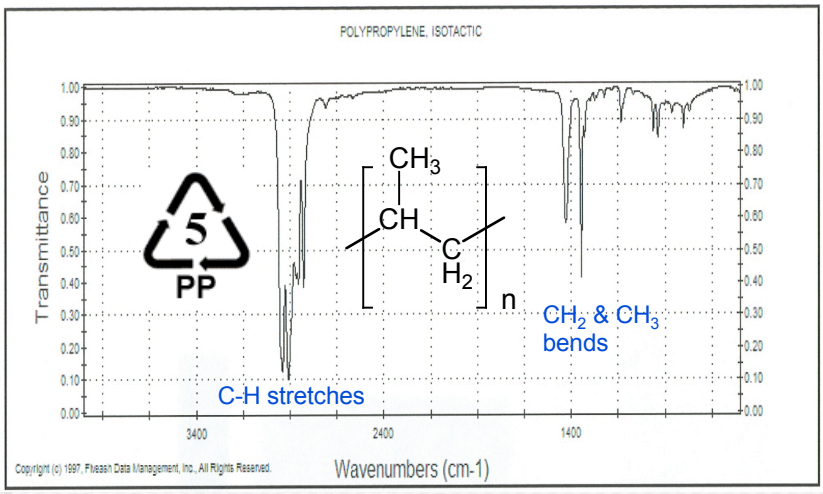
Infrared Spectrum of Polypropylene



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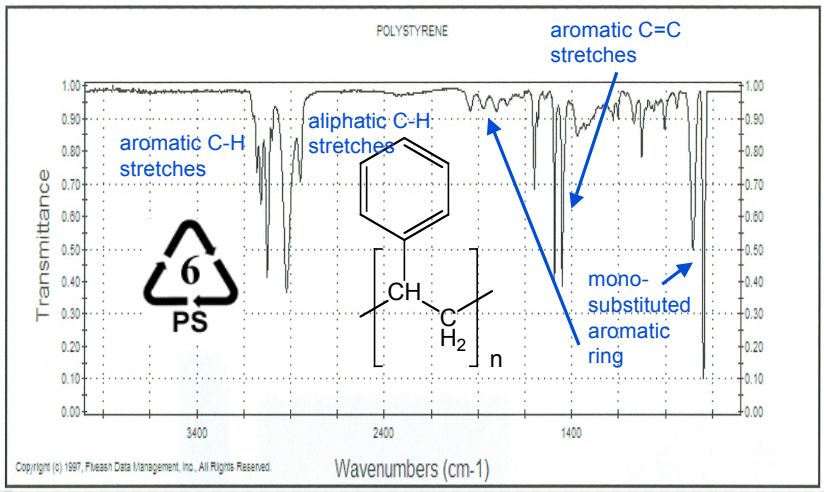
Infrared Spectrum of Polystyrene



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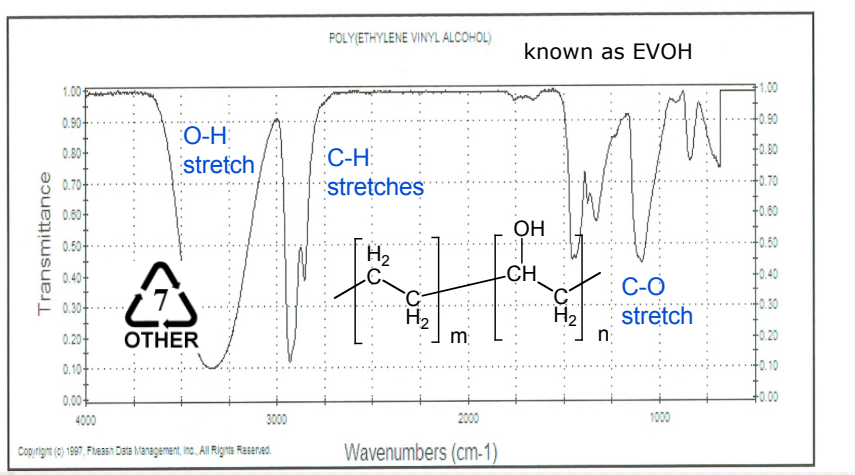
Infrared Spectrum of Poly(ethylene vinyl alcohol)



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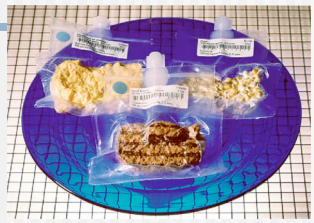
Ethylene-vinyl alcohol copolymer (EVOH)



Wipak Walstrode produces films for packaging freeze-dried astronaut food and other space products for NASA. A layer of EVOH is used for high vacuum properties.

Del Monte has developed an alternative to glass bottles for the packaging of ketchup. Layers of PET and EVOH are co-injected and blown to make the final package.

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http://www.chemicals-technology.com/projects/eval/index.html#eval1

PET Beer Bottles

Plastic beer bottle unveiled
Fri, 04 Oct 2002

WATERLOO, ONTARIO - An Ontario company has produced the country's first plastic bottle for beer.

Brick Brewing of Waterloo, Ont., unveiled its new light-weight alternative: PET or polyethylene terephthalate. The bottle had been in development for more than a year.

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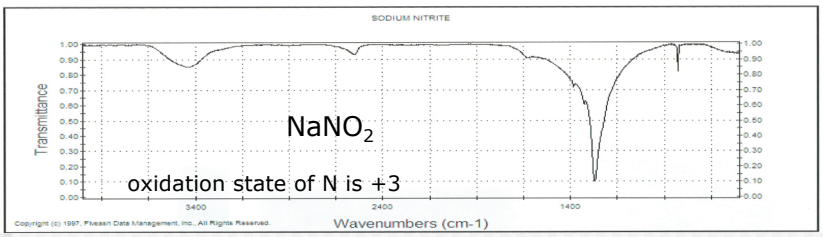
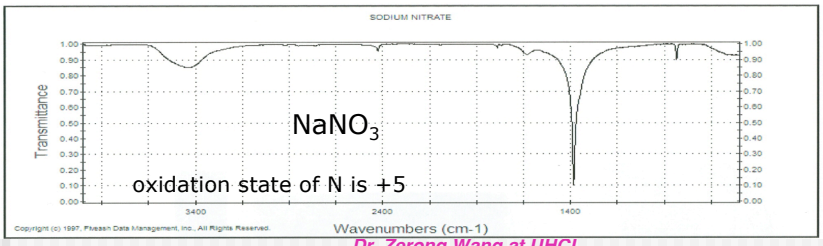
http://www.thekirkwoodgroup.com/beverages/beer/brick/

Infrared Spectrum of Sodium Nitrite/Nitrate





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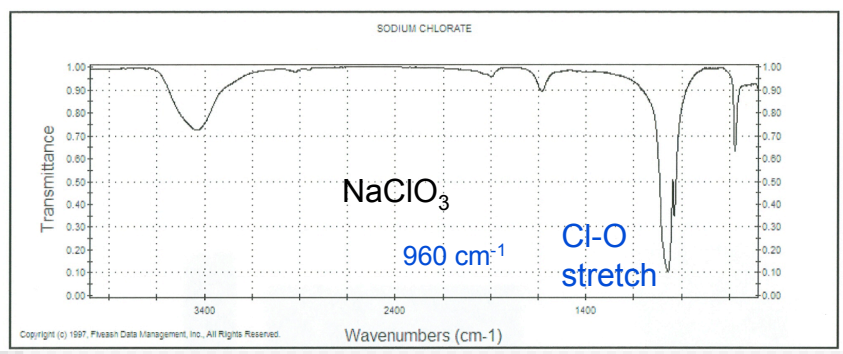
Infrared Spectrum of Sodium Chlorate



Chlorine in the +5 oxidation state

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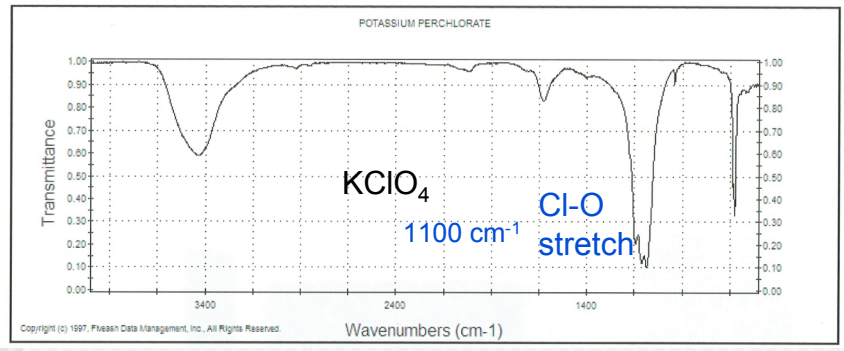
Infrared Spectrum of Potassium Perchlorate



Chlorine in the +7 oxidation state

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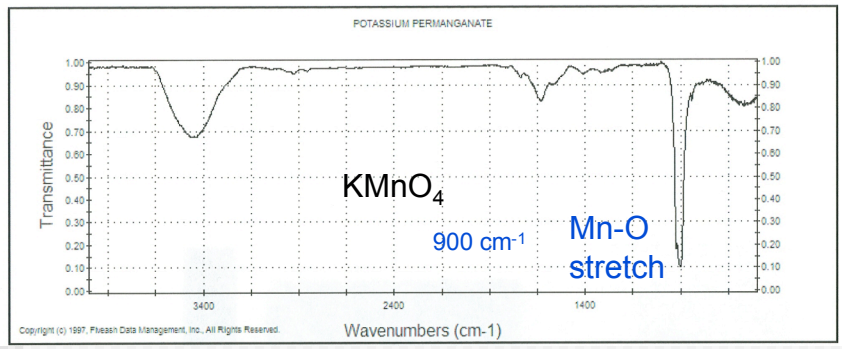
Infrared Spectrum of Potassium Permanganate



Manganese in the +7 oxidation state

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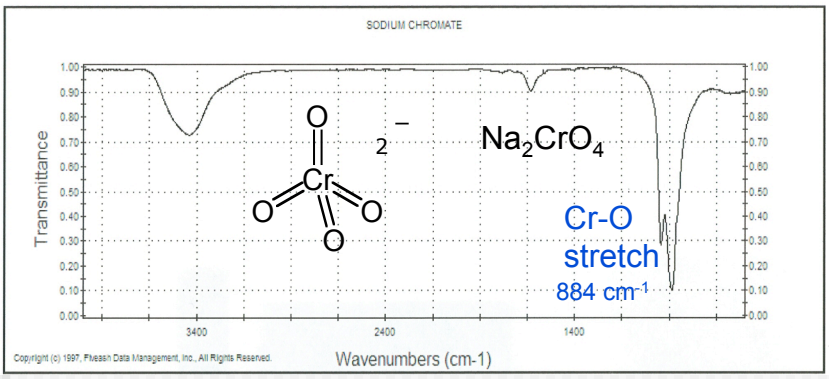
Infrared Spectrum of Sodium Chromate



Chromium in the +6 oxidation state

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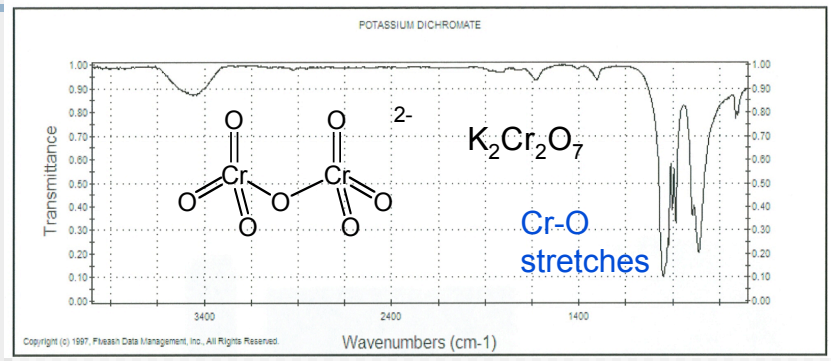
Infrared Spectrum of Potassium Dichromate



Cr-O 1.62 Å terminal Cr-O

Cr-O 1.80 Å bridging Cr-O

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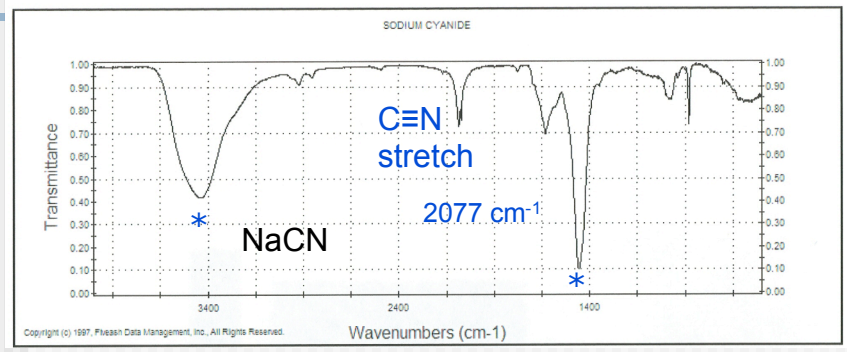
Infrared Spectrum of Sodium Cyanide



*These peaks are due to water in the sample

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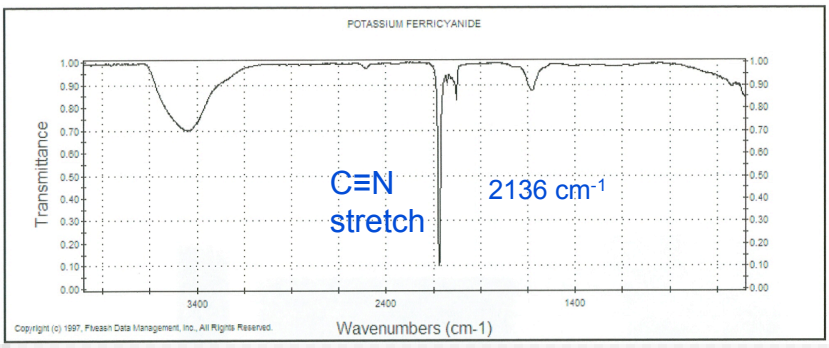
Infrared Spectrum of Potassium Ferricyanide



$K_3[Fe(CN)_6]$ Iron in the +3 oxidation state

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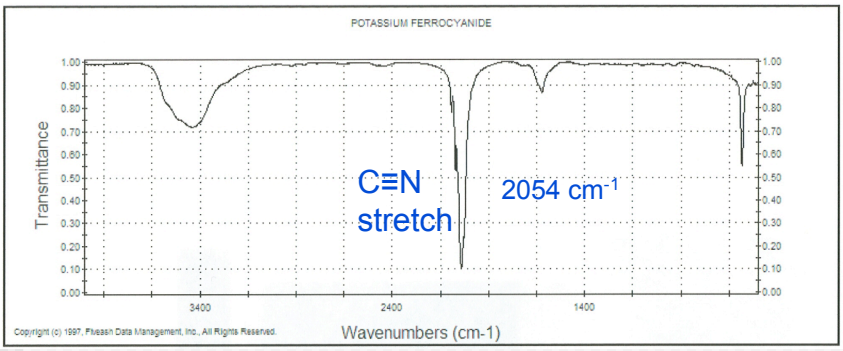
Infrared Spectrum of Potassium Ferrocyanide



$K_4[Fe(CN)_6$ Iron in the +2 oxidation state and electrons flow from the metal into the C≡N π^* orbitals, weakening the bond

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IR stretching frequencies of important ligand groups

Group	Frequency, cm^{-1}
Terminal CN	2200-2000
Terminal CO	2150-1850
Bridging CO	1850-1700
Terminal M-H of *d*-block hydride	1950-1750
M-X in metal halides (Cl, Br, I)	450-150
Metal-metal bond	250-150

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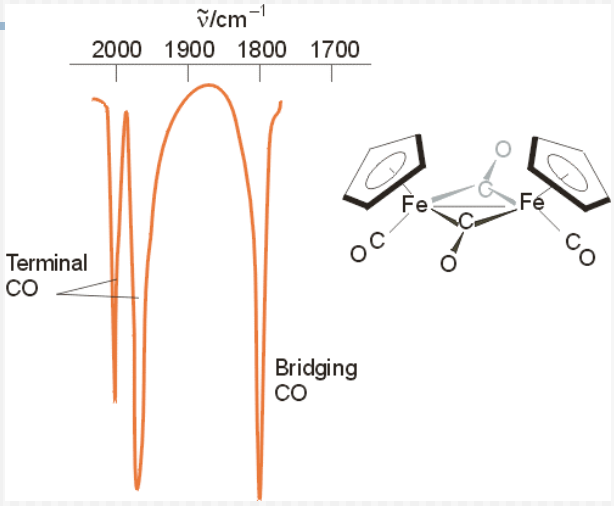
Infrared Spectrum of $Cp(CO)Fe(\mu\text{-}CO)_2Fe(CO)Cp$



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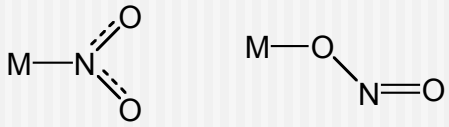
Infrared Spectrum of the Nitrite Ion, NO_2^-

The IR spectrum of the unperturbed (or "ionic") nitrite anion, NO_2^-, consists of three bands at 1335 cm^{-1} (ν_s), 1250 cm^{-1} (ν_{as}), and 830 cm^{-1} (δ). The nitrite ion can function as a ligand, and it is conceivable that coordination of NO_2^- to a metal ion could occur in either of two ways. These are shown below.



nitro ligand nitrito ligand

http://www.wpi.edu/Academics/Depts/Chemistry/Courses/CH2670/infrared.html#inorg

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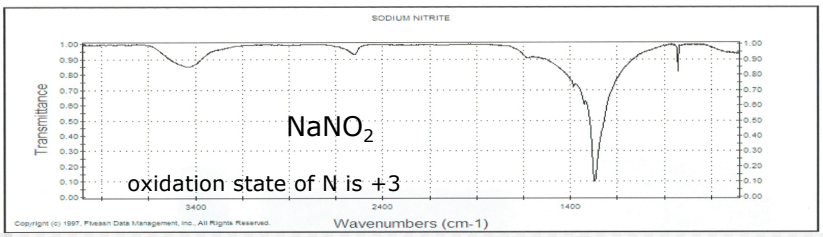
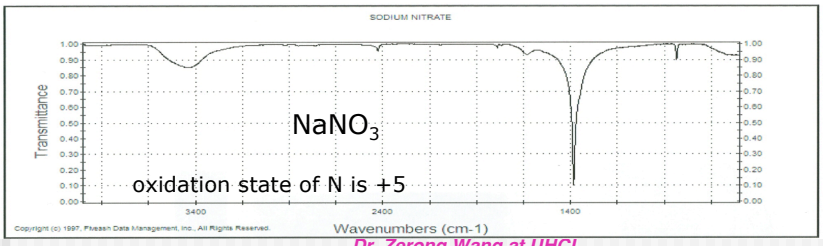
Infrared Spectrum of Sodium Nitrite/Nitrate





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http://www.fdmspectra.com/

Infrared Spectrum of the Nitrite Ion, NO_2^-

How will the coordination of NO_2^- to a metal ion affect its infrared spectrum and can it be used to diagnose the mode of coordination?

When NO_2^- bonds through an oxygen atom, one of the NO bonds is very nearly a double bond, whereas the other is a single bond.

In the free NO_2^- ion and when it binds to the metal via the nitrogen, on the other hand, both NO bonds are intermediate between single and double bonds.

The vibrational frequency of a bond increases as its strength increases, so we would expect the frequencies of the NO bonds in NO_2^- to increase in the order N-single bond-O (in O-bonded) < NO (in N-bonded) < N-double bond-O (in O-bonded).

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http://www.wpi.edu/Academics/Depts/Chemistry/Courses/CH2670/infrared.html#inorg

Infrared Spectrum of the Nitrite Ion, NO_2^-

In agreement with this, it has been found that in complexes in which NO_2^- is bonded through oxygen, the two N-O stretching frequencies lie in the ranges 1500-1400 cm^{-1} for N=O and 1100-1000 cm^{-1} for N-O.

In complexes in which NO_2^- is bonded through nitrogen, the bands occur at similar frequencies which are intermediate between the ranges above; namely, 1340-1300 cm^{-1} and 1430-1360 cm^{-1}.

Thus it is relatively easy to tell on the basis of IR whether a nitrite ion is coordinated, and if so, whether it is coordinated through N or O.

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http://www.wpi.edu/Academics/Depts/Chemistry/Courses/CH2670/infrared.html#inorg

Nitro/Nitrito Coordination Linkage Isomers

$[Co(NH_3)_5(ONO)]^{2+}$ ⇌ $[Co(NH_3)_5(NO_2)]^{2+}$

nitrito isomer — nitro isomer

kinetic isomer — thermodynamic isomer

Compound	ν_{as} (NO_2) (nm)	ν_s (NO_2) (nm)	δ (NO_2) (nm)
$NaNO_2$	1335	1250	830
$[Co(NH_3)_5(NO_2)]^{2+}$ nitro isomer	1428	1310	824
$[Co(NH_3)_5(ONO)]^{2+}$ nitrito isomer	1468	1065	825

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IR active vibrational modes of inorganic compounds

Coordination Number	Geometry	Example	Number of IR active stretches	Number of IR active bends
4	Tetrahedral	$[NiCl_4]^{2-}$	1	1
4	Square planar	$[PtCl_4]^{2-}$	1	2
5	Trigonal bipyramidal	PF_5	2	3
6	Octahedral	ML_6	1	1

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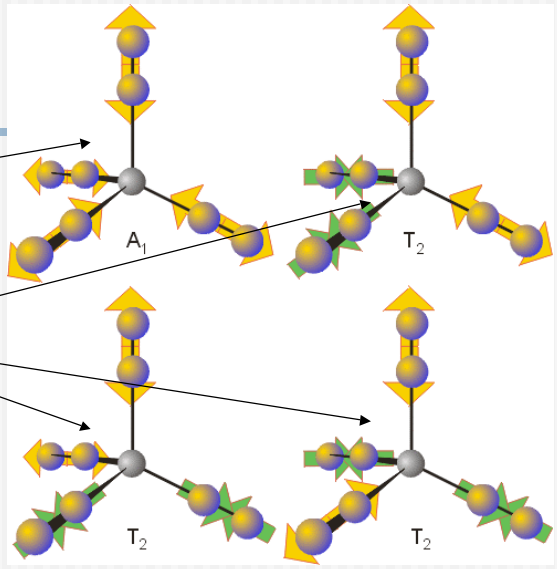
Brisdon, p. 18

Tetrahedral

Infrared inactive

Triply degenerate infrared active

e.g. $Ni(CO)_4$



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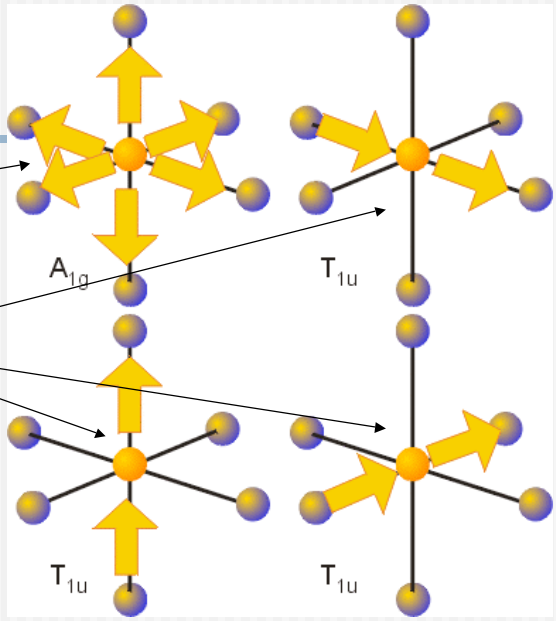
Shriver & Atkins, *Inorganic Chemistry*, p. 139

Infrared inactive

Triply degenerate infrared active

e.g. OsF_6



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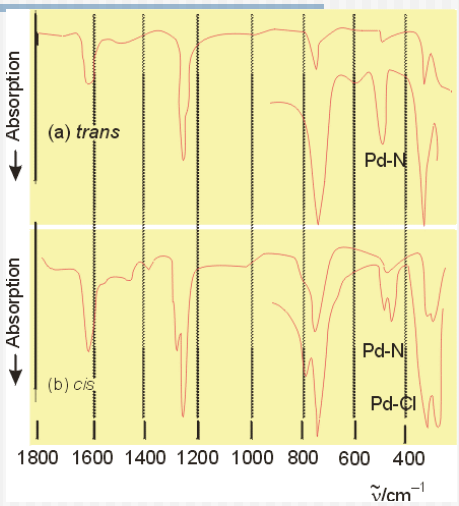
Shriver & Atkins, *Inorganic Chemistry*, p. 139

Cis- and *trans*-$[Pt(NH_3)_2Cl_2]$

inactive anti-cancer drug

active anti-cancer drug

Cisplatin



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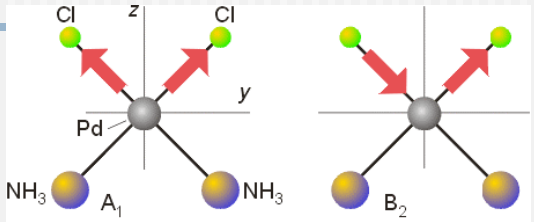
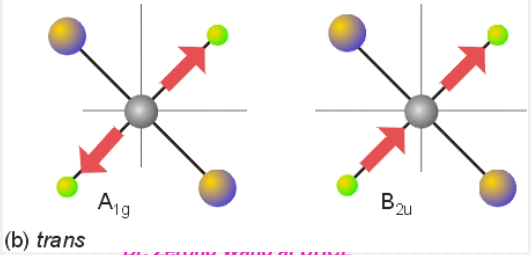
Shriver & Atkins, *Inorganic Chemistry*, p. 138

Cis- and *trans*-$[Pt(NH_3)_2Cl_2]$

both modes are infrared active



one mode is infrared inactive



Shriver & Atkins, *Inorganic Chemistry*, p. 137

Strengths and Limitations

- IR alone cannot determine a structure
- Some signals may be ambiguous
- The functional group is usually indicated
- 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

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