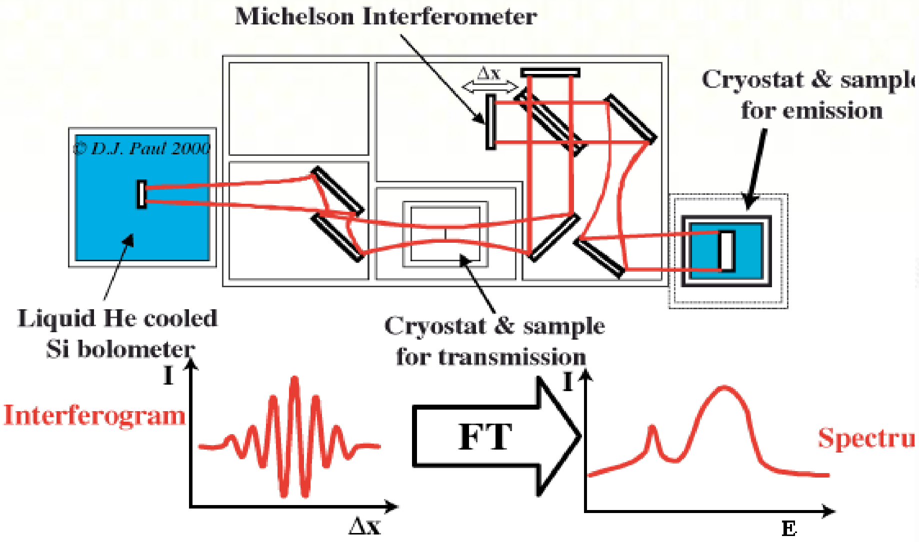
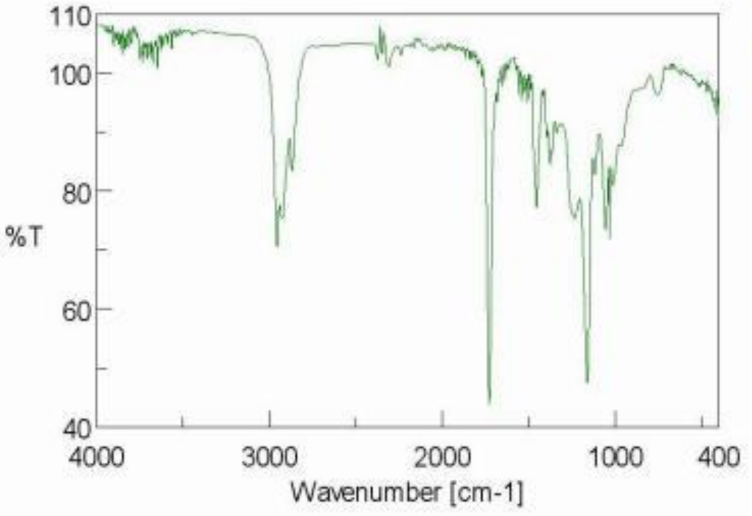
Chapter 5
Fundamentals of FTIR Spectroscopy





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FTIR Usefulness

- ✓ Used for qualitative identification of organic and inorganic compounds
- ✓ Used for checking the presence of functional groups in molecules
- ✓ Can also be used for quantitative measurements of compounds
- ✓ Each compound has its unique IR absorption pattern
- ✓ Wavenumber with units of cm^{-1} is commonly used
- ✓ Wavenumber = number of waves of radiation per centimeter

FTIR Domain: IR Region & Wavelength

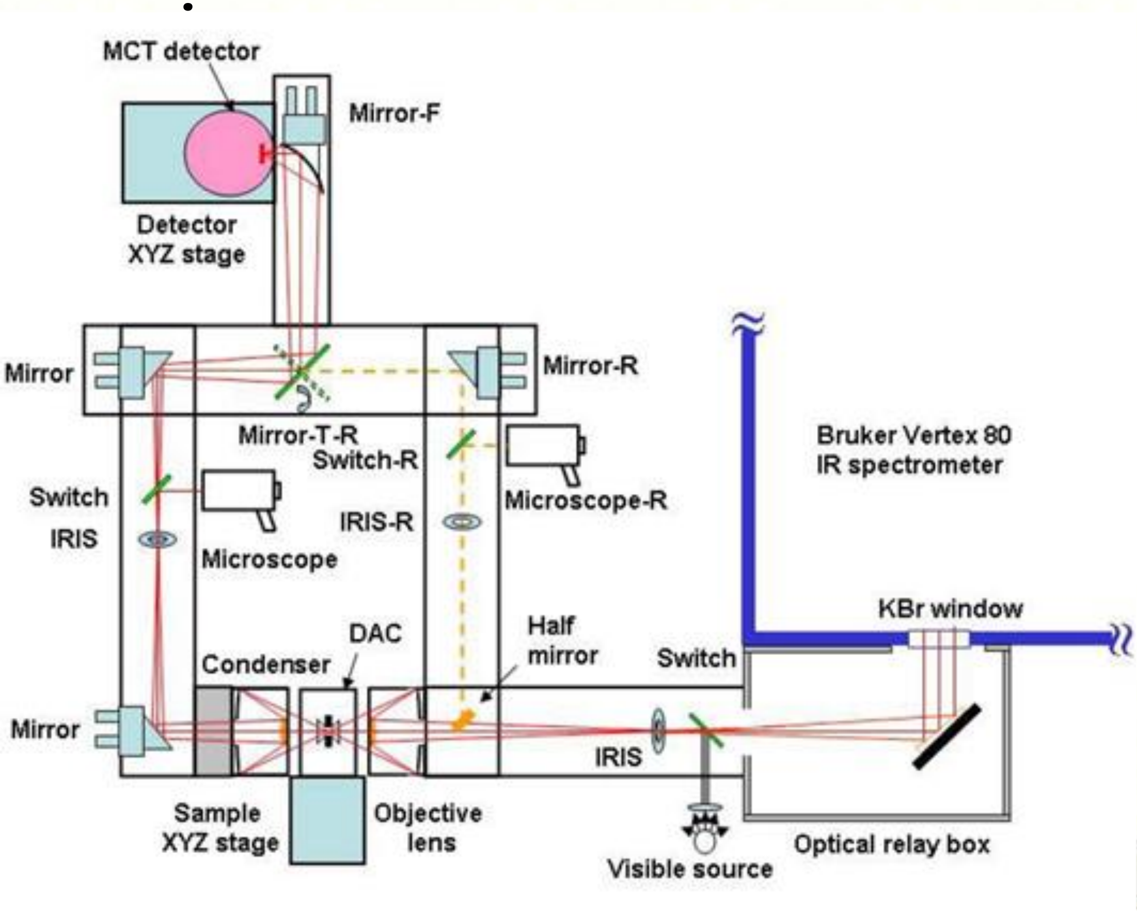
- ✓ The IR region has lower energy than visible radiation and higher energy th

The IR region is divid

Near-IR (NIR): 750 nr

Mid-IR: 2500 nm – 20

Far-IR: 20000 nm – 4



IR Absorption by Molecules

- ✓ Molecules with covalent bonds absorb IR radiation
- ✓ Absorption is quantized
- ✓ Molecules move to a higher energy state (Rotational & Vibrational)
- ✓ IR radiation is sufficient enough to cause rotation and vibration
- ✓ Radiation between 1 and 100 μm will cause excitation to higher vibrational states
- ✓ Radiation higher than 100 μm will cause excitation to higher rotational states

IR Absorption by Molecules

- ✓ Absorption spectrum is composed of broad vibrational absorption bands

- ✓ Molecules absorb radiation when a bond in the molecule vibrates at the same frequency as the incident radiant energy

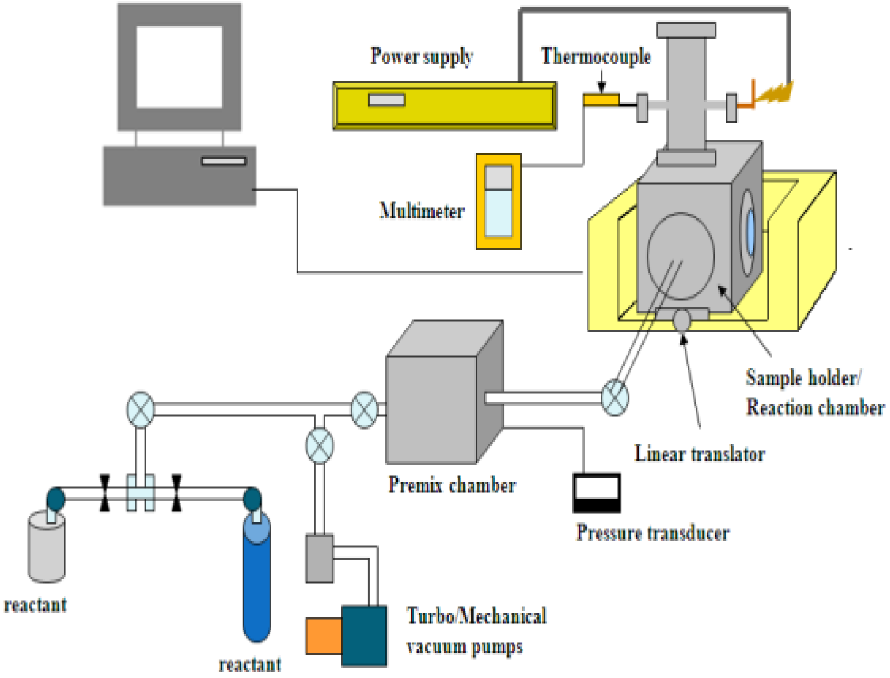
- ✓ Molecules vibrate at higher amplitude after absorption

- ✓ A molecule must have a **change** in **dipole moment** during vibration in order to absorb IR radiation

IR Absorption by Molecules

Absorption frequency depends on

- ✓ Masses of atoms in the bonds
- ✓ Geometry of the molecule
- ✓ Strength of bond
- ✓ Other contributing factors



Dipole Moment (μ)

$$\mu = Q \times r$$

Q = charge and r = distance between charges

- ✓ Asymmetrical distribution of electrons in a bond renders the bond polar
- ✓ A result of electro-negativity difference
- ✓ μ changes upon vibration due to changes in r
- ✓ Change in μ with time is necessary for a molecule to absorb IR radiation

Dipole Moment (μ)

- ✓ The repetitive changes in μ makes it possible for polar molecules to absorb IR radiation
- ✓ Symmetrical molecules do not absorb IR radiation since they do not have dipole moment (O_2, F_2, H_2, Cl_2)
- ✓ Diatomic molecules with dipole moment are IR-active (HCl, HF, CO, HI)
- ✓ Molecules with more than two atoms may or may not be IR active depending on whether they have permanent net dipole moment

Principal Modes of Vibration

Stretching

- ✓ Change in bond length resulting from change in Inter-atomic distance (r)

Two stretching modes

- ✓ Symmetrical and asymmetrical stretching
- ✓ Symmetrical stretching is IR-inactive (no change in μ)

Principal Modes of Vibration

Bending

- ✓ Change in bond angle or change in the position of a group of atoms with respect to the rest of the molecule

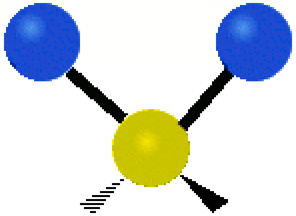
Bending Modes

- ✓ Scissoring and Rocking
- ✓ In-plane bending modes (atoms remain in the same plane)
- ✓ Wagging and Twisting
- ✓ Out-of-plane (oop) bending modes (atoms move out of plane)

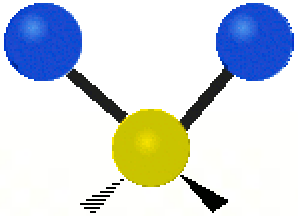
Modes of Vibration

Radiation in the Mid IR region will cause *stretching and bending vibrations of the bonds* in most covalent molecules.

1- Stretching Vibrations



Symmetric stretching

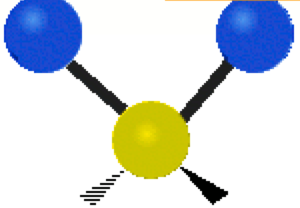


Asymmetric stretching

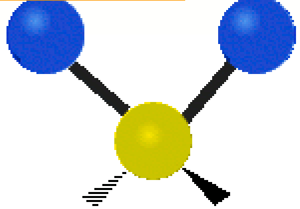
$\bar{\nu}\text{Asym} > \bar{\nu}\text{Sym} >> \bar{\nu}\text{Bending}$

2- Bending Vibrations

A- In-plane bending

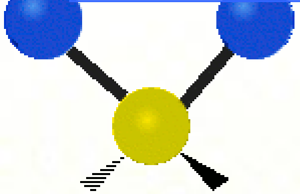


Scissoring

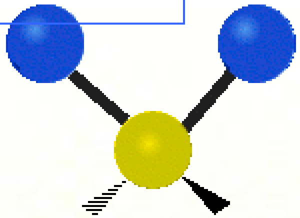


Rocking

B- Out-of-plane bending



Twisting



Wagging

Principal Modes of Vibration

3N-6 possible normal modes of vibration

N = number of atoms in a molecule

Degrees of freedom = 3N

H_2O for example

- ✓ 3 atoms
- ✓ Degrees of freedom = 3 x 3 = 9
- ✓ Normal modes of vibration = 9-6 = 3

Principal Modes of Vibration

Linear Molecules

✓ Cannot rotate about the bond axis

✓ Only 2 degrees of freedom describe rotation

✓ 3N-5 possible normal modes of vibration

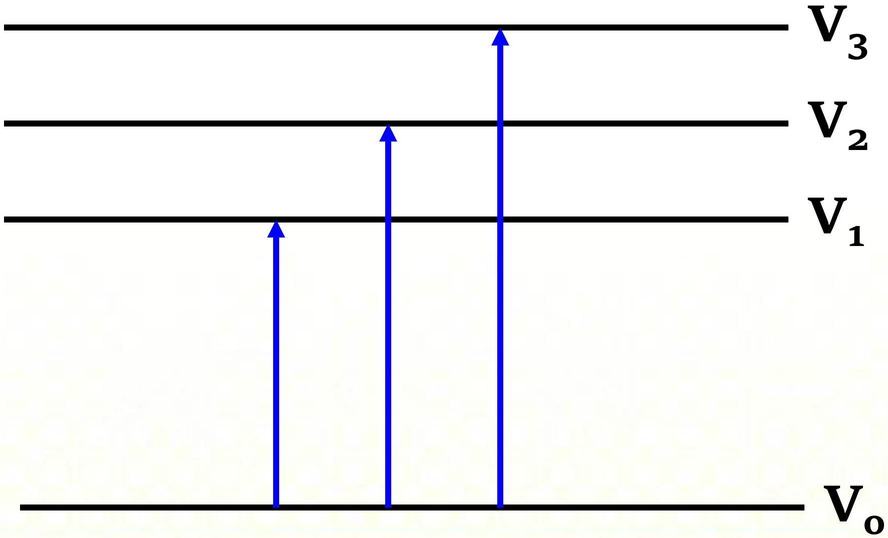
CO_2 for example

- 3 atoms
- Normal modes of vibration = 9-5 = 4

Transitions

Fundamental

- ✓ Excitation from the ground state V_o to the first excited state V_1
- ✓ The most likely transition and have strong absorption bands



Fundamental Transitions

Overtone

- ✓ Excitation from ground state to higher energy states V_2, V_3, ...
- ✓ Result in overtone bands that are weaker than fundamental
- ✓ Frequencies are integral multiples of fundamental absorption
- ✓ Fewer peaks are seen than predicted on spectra due to IR-inactive vibrations, degenerate vibrations, weak vibrations
- ✓ Additional peaks may be seen due to overtones

Vibrational Motion

- ✓ Consider a bond as a spring $\tilde{\nu} = \frac{1}{2\pi c}\sqrt{\frac{f}{\mu}}$

c = speed of light (cm/s)

f = force constant (dyne/cm; proportional to bond strength)

f for a double bond = 2f for a single bond

f for a triple bond = 3f for a single bond

$$\mu = \text{Reduced mass (in gm)} = \frac{M_1 M_2}{M_1 + M_2}$$

- ✓ M_1 and M_2 are masses of vibrating atoms connecting the bond

Instrumentation

Components

- ✓ Radiation source
- ✓ Sample holder
- ✓ Monochromator
- ✓ Detector
- ✓ Computer

Monochromators

- ✓ Salt prisms and metal gratings are used as dispersion devices

- ✓ Mirrors made of metal with polished front surface

- ✓ Spectrum is recorded by moving prism or grating such that different radiation frequencies pass through the exit slit to the detector

- ✓ Spectrum obtained is %T verses wave-number (or frequency)

FT Spectrometers

- ✓ Based on Michelson interferometer
- ✓ Employs constructive and destructive interferences
- ✓ Destructive interference is a maximum when two beams are 180° out of phase
- ✓ An FT is used to convert the time-domain spectrum obtained into a frequency-domain spectrum
- ✓ The system is called FTIR

Sample

- ✓ Sample holder must be transparent to IR- salts
- ✓ Liquids
  - ✓ Salt Plates
  - ✓ Neat, 1 drop
  - ✓ Samples dissolved in volatile solvents- 0.1-10%

- ✓ Solids
  - ✓ KBr pellets
  - ✓ Mulling (dispersions)

- ✓ Quantitative analysis-sealed cell with NaCl/NaBr/KBr windows

Advantages of FT Spectrometers

- ✓ Has higher signal-to-noise ratio
- ✓ More accurate and precise than dispersive monochromators (Conne’s advantage)
- ✓ Much greater radiation intensity falls on the detector due to the absence of slits (throughput or Jacquinot’s advantage)

Selectivity

- ✓ Offers much more selectivity than UV-vis spectroscopy
- ✓ Absorption peaks are narrow in comparison and the energies of the absorption bands are unique for sets of functional groups
- ✓ Thus, qualitative information is readily obtained from IR spectra
- ✓ Correlation charts and compilations of IR spectra for unknown matching
- ✓ But IR spectra do not have the specificity that NMR spectra or electron impact mass spectra tend to exhibit

Sensitivity

- ✓ This is perhaps the major shortcoming of this technique when compared to fluorescence, or especially mass spectrometry
- ✓ However, Beer's law type analysis are possible and fairly routine using FT-IR
- ✓ Detection limits are in the ppm range (mM)

Near-IR (NIR) Spectroscopy

- ✓ Region covers 750 nm – 2500 nm (13000 cm^{-1} – 4000 cm^{-1})
- ✓ Long wavelength end of IR region
- ✓ Bands occurring in this region are due to OH, NH, and CH bonds
- ✓ Bands are primarily overtone and combination bands
- ✓ Light source is tungsten-halogen lamp
- ✓ Detector is lead sulfide photo-detector
- ✓ Quartz or fused silica sample cells with long path lengths are used

Near-IR (NIR) Spectroscopy

Primary absorption bands seen in NIR

C–H Bands

2100 – 2450 nm and 1600 – 1800 nm

N–H Bands

1450 – 1550 nm and 2800 – 3000 nm

O–H Bands

1390 – 1450 nm and 2700 – 2900 nm

Near-IR (NIR) Spectroscopy

- ✓ Used for quantitative analysis of solid and liquid samples containing OH, NH, CH bonds
- ✓ For quantitative characterization of polymers, food, proteins, agricultural products
- ✓ Pharmaceutical tablets can be analyzed nondestructively
- ✓ Forensic analysis of unknown wrapped powders believed to be rugs are analyzed without destroying the wrappers

Applications of IR Spectroscopy

Quantitative

- ✓ Extent of absorption and Beer’s law can be used to determine concentration of unknown analytes in sample
- ✓ Absorption band unique to the analyte molecule should be used for measurements
- ✓ Generally performed with samples in solutions
- ✓ Light scattering may occur with pellets which deviates from Beer’s law

Applications of IR Spectroscopy

Quantitative

- ✓ Measure absorption intensities of standard solutions and unknown at exactly the same wavenumber
- ✓ All measurements must be made from the same baseline
- ✓ Plot a calibration curve
- ✓ Use the relationship obtained to determine the concentration of unknown
- ✓ Not as accurate as using UV-VIS spectroscopy

Applications of IR Spectroscopy

Quantitative

- ✓ Determination of impurities in raw materials (quality control)
- ✓ Analysis of contaminations from oil or grease
- ✓ Determination of reaction rates of slow reactions

Applications of IR Spectroscopy

Qualitative

- ✓ Identification of unknown samples by matching the absorption spectra with that of known compounds
- ✓ Identification of functional groups present in a sample (classification of unknowns)

Predicting Unknown Structure

- ✓ Identify the major functional groups from the strong absorption peaks
- ✓ Identify the compound as aromatic or aliphatic
- ✓ Subtract the FW of all functional groups identified from the given molecular weight of the compound
- ✓ Look for C≡C and C=C stretching bands
- ✓ Look for other unique CH bands (e.g. aldehyde)
- ✓ Use the difference obtained to deduce the structure

Interpretation of IR Spectra

Functional Group Region

✓ Strong absorptions due to stretching from hydroxyl, amine, carbonyl, CH_x

4000 – 1300 cm^{-1}

Fingerprint Region

✓ Result of interactions between vibrations

1300 – 910 cm^{-1}

Interpretation of IR Spectra

Hydrocarbons

- ✓ Absorption bands are due to the stretching or bending of C–H and C–C bonds
- ✓ C–C stretching vibrations are distributed across the fingerprint region (not useful for identification)
- ✓ C–C bending vibrations occur below 500 cm^{-1}(not useful for identification)
- ✓ Observed bands are due to C–H stretching or bending

Interpretation of IR Spectra

Cyclic Alkanes

- ✓ No peak around 1375 cm^{-1} due to absence of methyl groups

- ✓ Two peaks at ~ 900 cm^{-1} and 860 cm^{-1} due to ring deformation

Alkenes

- ✓ Contain many more peaks than alkanes

- ✓ Peaks of interest are due to stretching and bending of C–H and C=C bonds

- ✓ C=C band will not appear if there is symmetrical substitution about the C=C bond

Interpretation of IR Spectra

Alkynes

- ✓ C≡C peak appears around 2100 – 2200 cm^{-1}
- ✓ Terminal alkyne ≡C–H stretch occurs near 3300 cm^{-1}

Aromatic Hydrocarbons

- ✓ C→H absorption occurs above 3000 cm^{-1}
- ✓ Aromatic C=C ring stretching absorption around 1400 – 1600 cm^{-1} appears as doublet
- ✓ Aromatic C↓H oop band around 690 – 900 cm^{-1}
- ✓ Overtones around 1660 – 2000 cm^{-1}

Interpretation of IR Spectra

Alcohols

- ✓ OH band in neat aliphatic alcohols is a broad band centered at ~ 3300 cm^{-1} due to hydrogen bonding (3100 – 3600 cm^{-1})
- ✓ OH band in dilute solutions of aliphatic alcohols is a sharp peak ~ 3600 cm^{-1}
- ✓ C–C–O stretch ~ 1048 cm^{-1} for primary alcohols
- ✓ Decreasing frequency by 10 cm^{-1} in the order $1^o > 2^o > 3^o$
- ✓ Methyl bending vibrations at ~ 1200 – 1500 cm^{-1}

Interpretation of IR Spectra

Phenol

- ✓ CO→H stretch is broad band
- ✓ C→H stretch ~ 3050 cm^{-1}
- ✓ C–C→O band ~ 1225 cm^{-1}
- ✓ C –O–H bend ~ 1350 cm^{-1}
- ✓ Aromatic ring C stretching between 1450 – 1600 cm^{-1}
- ✓ Monosubstituted bands ~ 745 – 895 cm^{-1} and 1650 – 2000 cm^{-1}

Interpretation of IR Spectra

Aliphatic Acids

- ✓ Broad OH band around 2900 cm^{-1}
- ✓ C–H stretching bands from CH_3 and CH_2 stick out at the bottom of the broad OH band
- ✓ C=O stretch ~ 1710 cm^{-1}
- ✓ In-plane C –O–H bend ~ 1410 cm^{-1} and oop C –O–H bend ~ 930 cm^{-1}
- ✓ C –C–O stretch dimer at ~ 1280 cm^{-1}

Interpretation of IR Spectra

Carboxylic Acids, Esters, Ketones, Aldehydes

- ✓ Characterized by very strong carbonyl (C=O) stretching band between 1650 cm^{-1} and 1850 cm^{-1}

- ✓ Fermi resonance seen in aldehydes(doublet due to resonance with an overtone of the aldehydic C–H bend at 1390 cm^{-1})

Interpretation of IR Spectra

Nitrogen-Containing Compounds

- ✓ 1° amines (NH_2) have scissoring mode and low frequency wagging mode
- ✓ 2° amines (NH) only have wagging mode (cannot scissor)
- ✓ 3° amines have no NH band and are characterized by C–N stretching modes ~ 1000 – 1200 cm^{-1} and 700 – 900 cm^{-1}
- ✓ 1°, 2°, 3° amides are similar to their amine counterparts but have additional C=O stretching band

Interpretation of IR Spectra

Nitrogen-Containing Compounds

- ✓ C=O stretching called amide I in 1° and 2° amides and amide II in 3° amides
- ✓ N–H stretch doublet ~ 3370 – 3291 cm^{-1} for 1° amines
- ✓ 1° N–H bend at ~ 1610 cm^{-1} and 800 cm^{-1}
- ✓ Single N–H stretch ~ 3293 cm^{-1} for 2° but absent in 3° amine
- ✓ C–N stretch weak band ~ 1100 cm^{-1}

Interpretation of IR Spectra

Amino Acids [$RCH(NH_2)COOH$]

- ✓ IR spectrum is related to salts of amines and salts of acids
- ✓ Broad CH bands that overlap with each other
- ✓ Broad band ~ 2100 cm^{-1}
- ✓ NH band ~ 1500 cm^{-1}
- ✓ Carboxylate ion stretch ~ 1600 cm^{-1}

Interpretation of IR Spectra

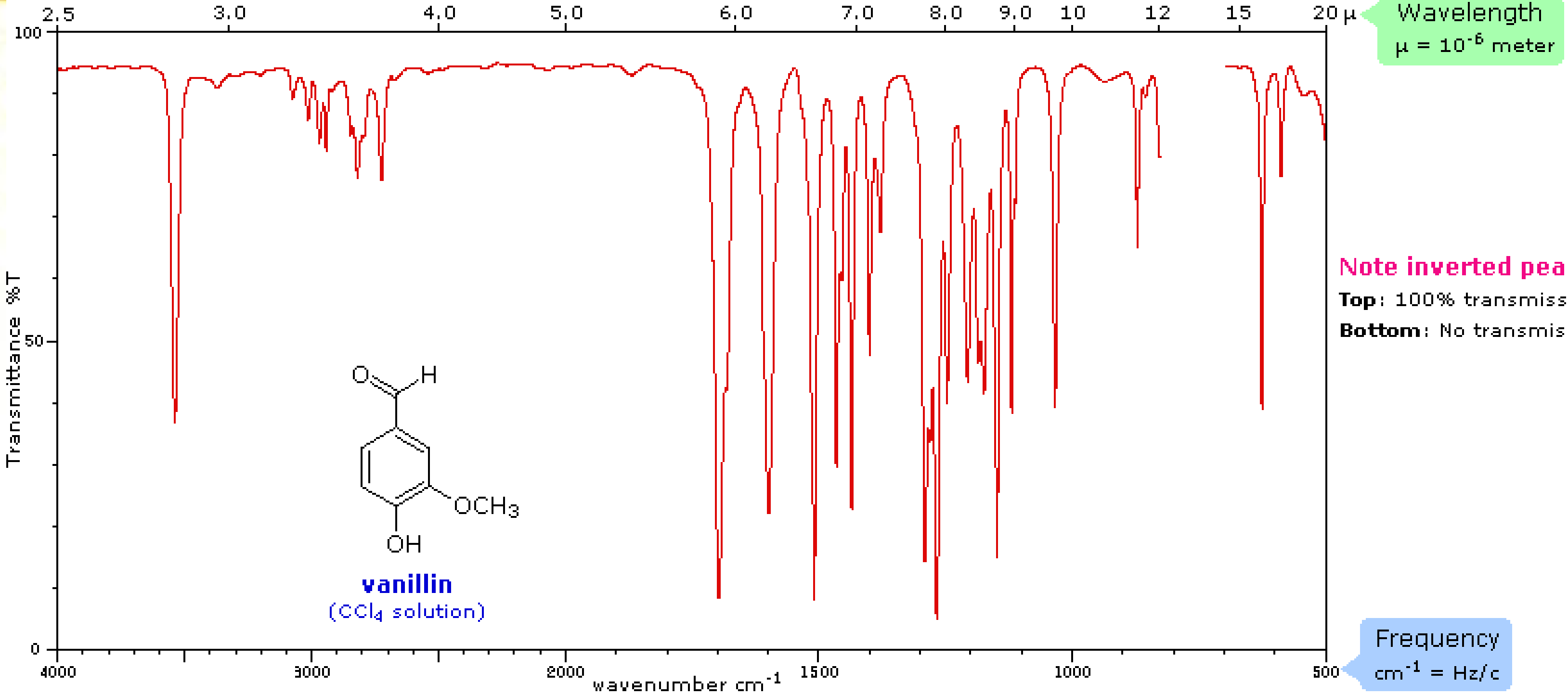
Halogenated Compounds

- ✓ C→X strong absorption bands in the fingerprint and aromatic regions
- ✓ More halogens on the same C results in an increase in intensity and a shift to higher wavenumbers
- ✓ Absorption due to C–Cl and C–Br occurs below 800 cm^{-1}

Limitations of IR Spectroscopy

- ✓ Short path length
- ✓ Path length may vary from sample to sample
- ✓ Sample cells are soluble in water

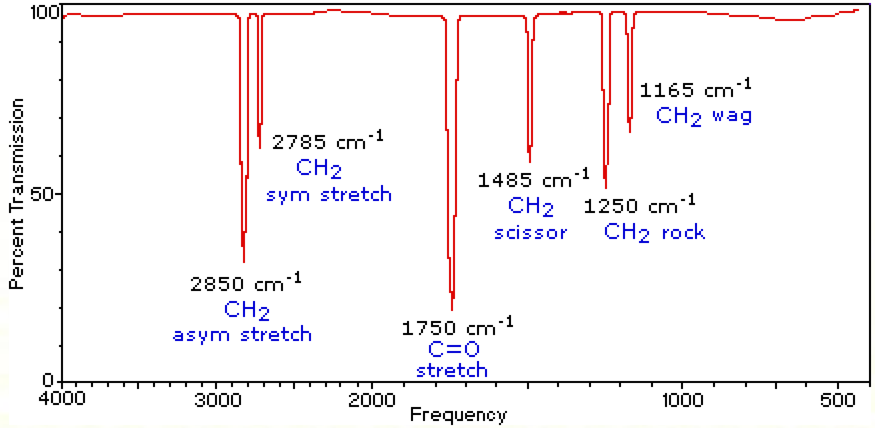
Typical IR Spectra



Note inverted peaks

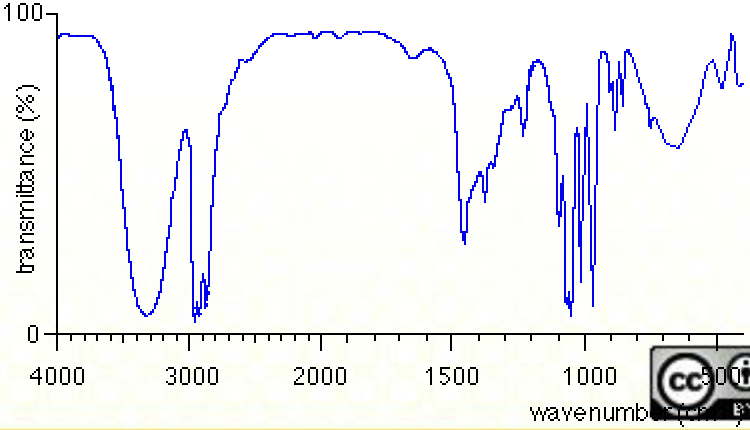
Top: 100% transmission

Bottom: No transmission



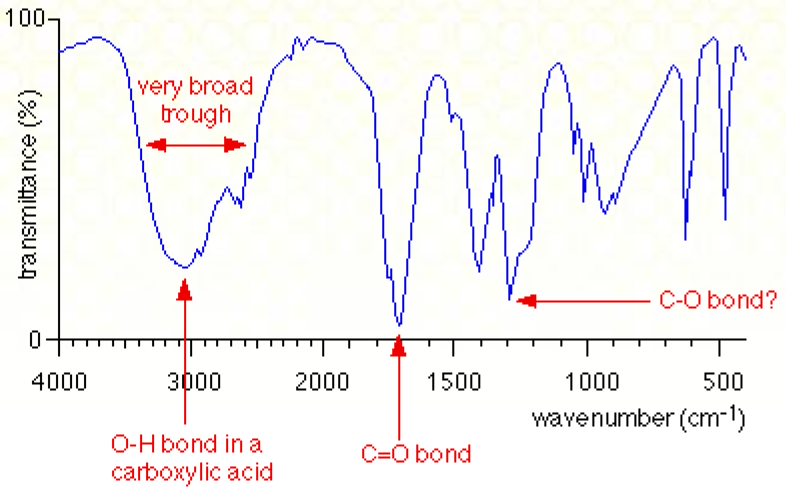
Formaldehyde

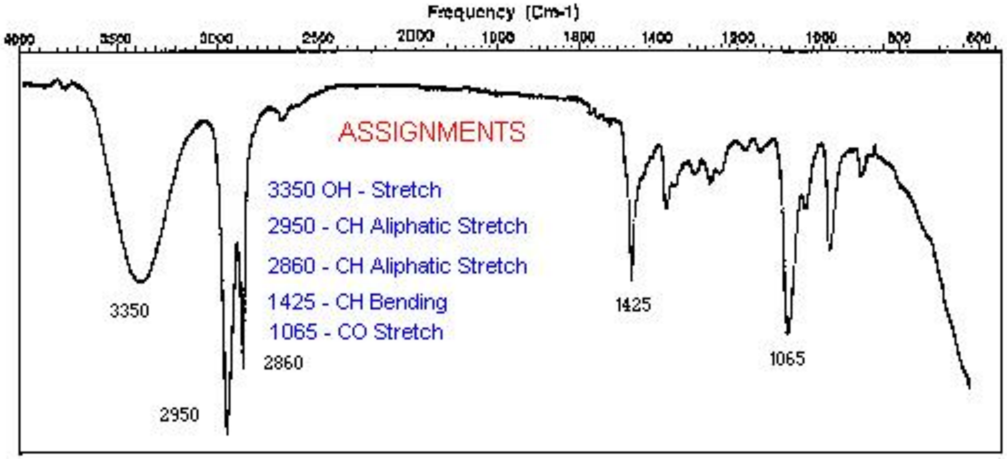
infra-red spectrum of propan-1-ol, $CH_3CH_2CH_2OH$



Typical IR Spectra

infra-red spectrum of ethanoic acid, CH_3COOH





ASSIGNMENTS

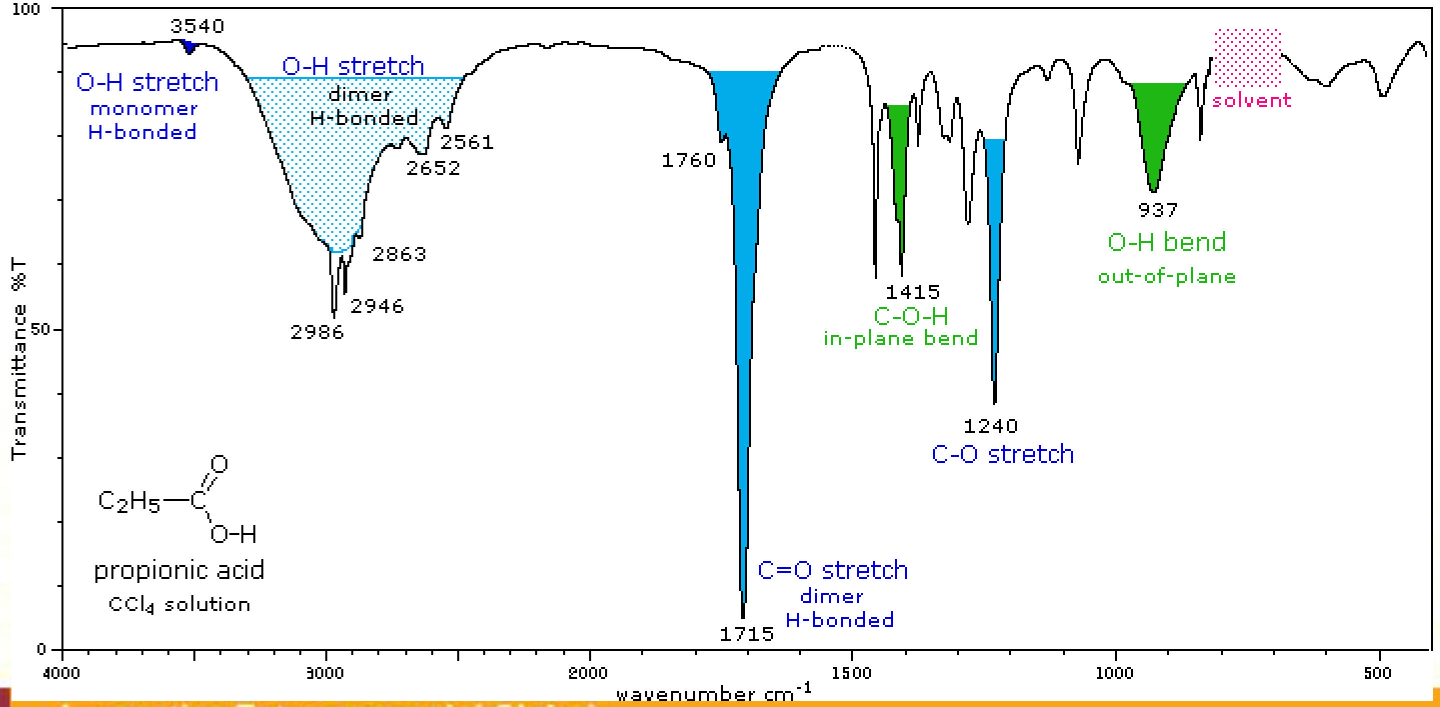
3350 OH - Stretch

2950 - CH Aliphatic Stretch

2860 - CH Aliphatic Stretch

1425 - CH Bending

1065 - CO Stretch



Questions ?

Thank You