INFRA-RED SPECTROSCOPY-I

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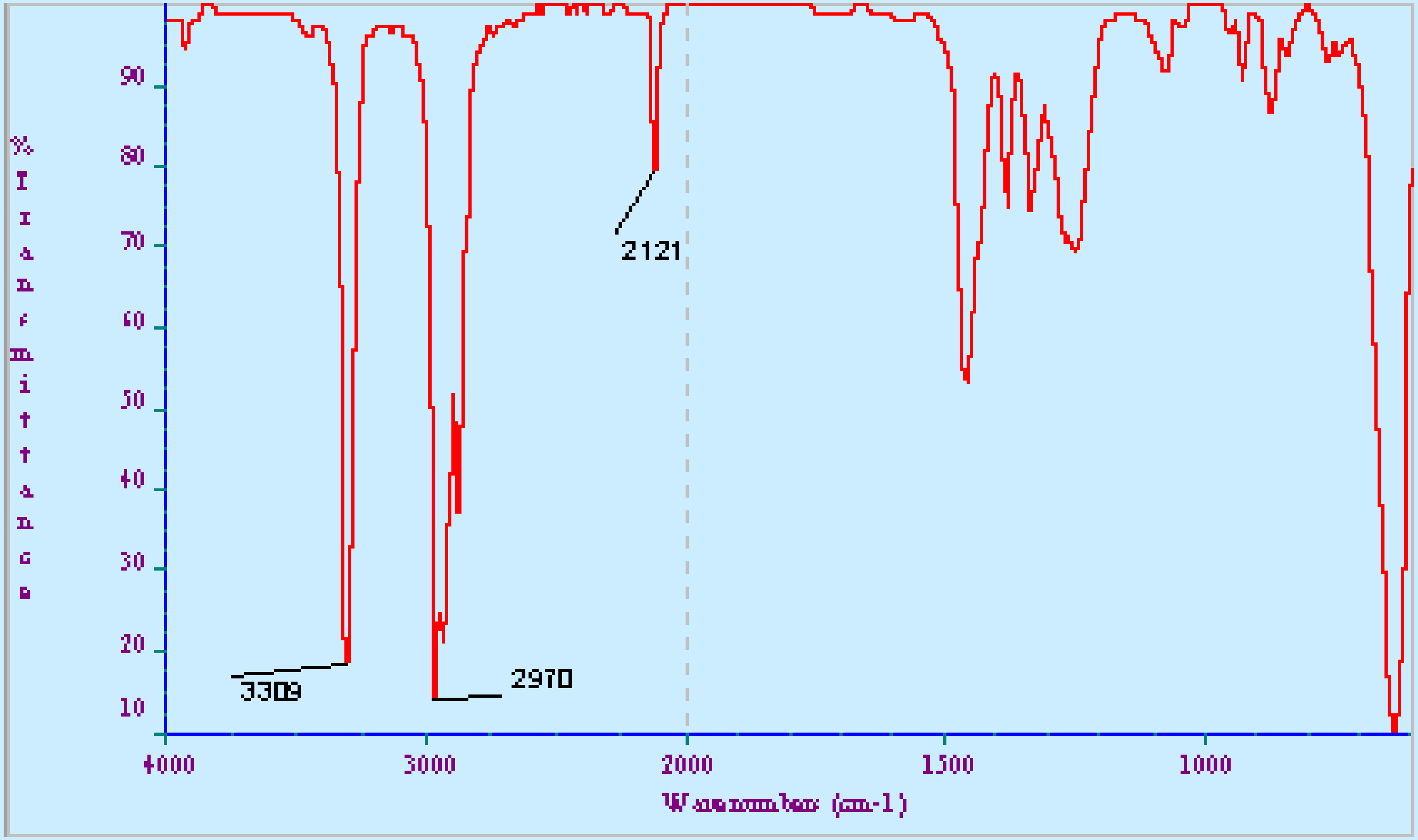
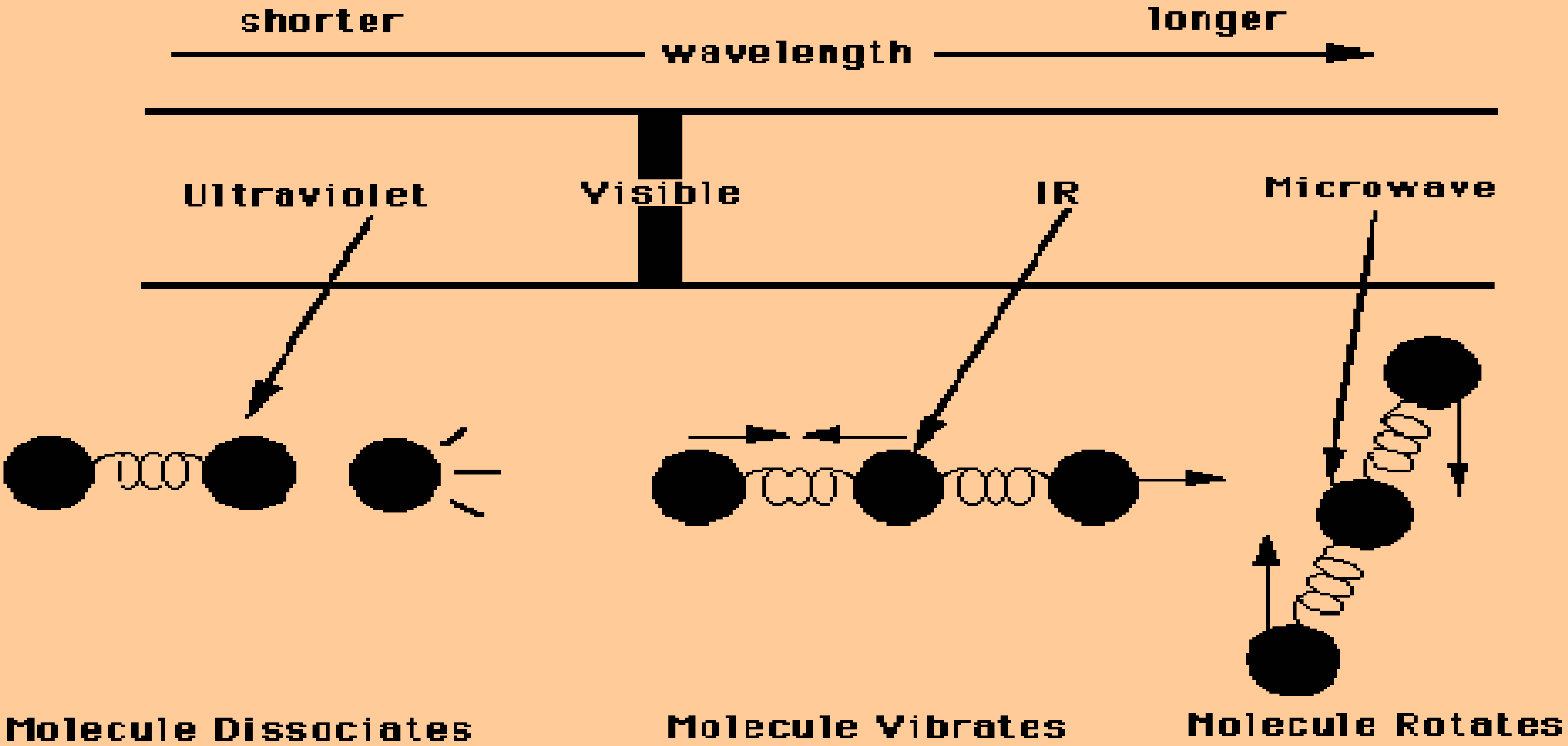
INFRA-RED SPECTROSCOPY

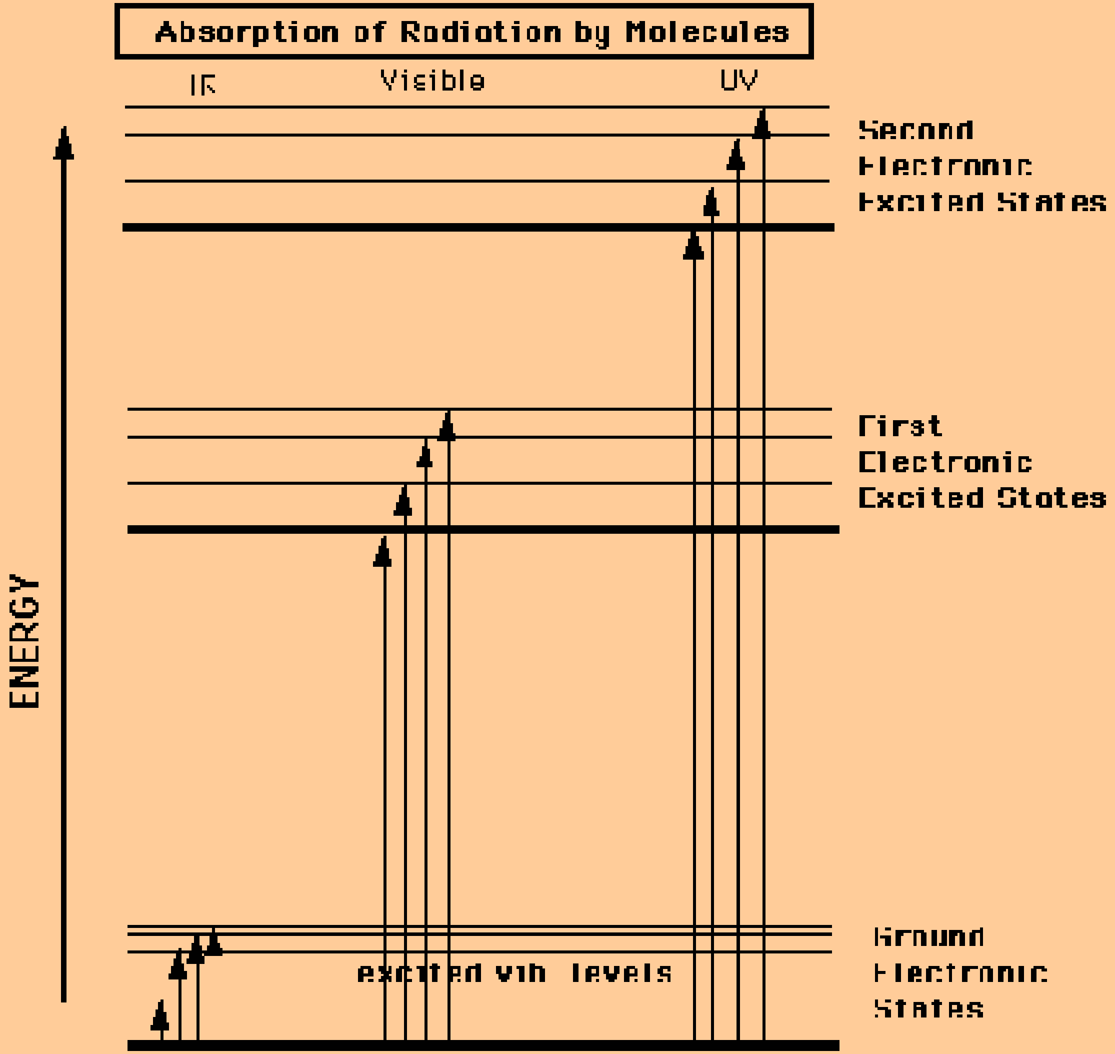
Can You Assign Stretches To These?



Comparison of the effect of different types of electromagnetic radiation on molecules

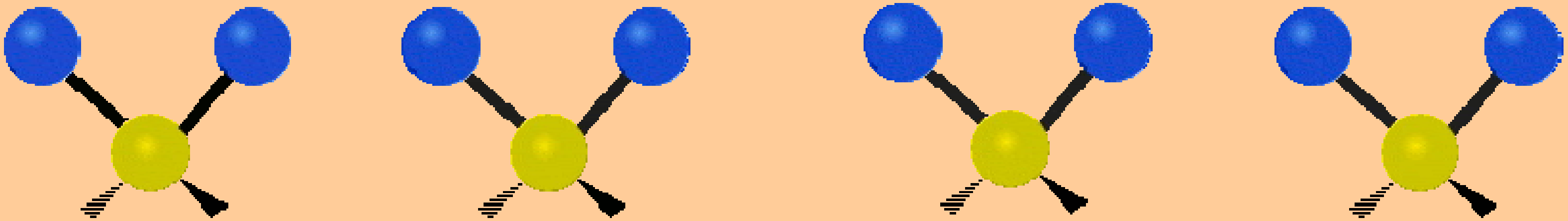


IR energy ranges from 2.6×10^{-19} to 2.0×10^{-22} J.
It is too small to induce electronic transition, but it is enough to bring about **vibrational** and **rotational** transition.



Principle

- IR causes bonds to vibrate
- Bonds vibrations can be **stretching, bending, wagging or scissoring**



- The bonds in a molecule vibrate all about **when IR energy hits it.**

Infrared radiation

λ = 2.5 to 17 μm

υ = 4000 to 600 cm^{-1}

These frequencies match the frequencies of covalent bond stretching and bending vibrations.

Infrared spectroscopy can be used to find out about **covalent bonds** in molecules.

IR is used to tell:

1. what type of bonds are present

2. some structural information

Principle

IR radiation

Vibrational

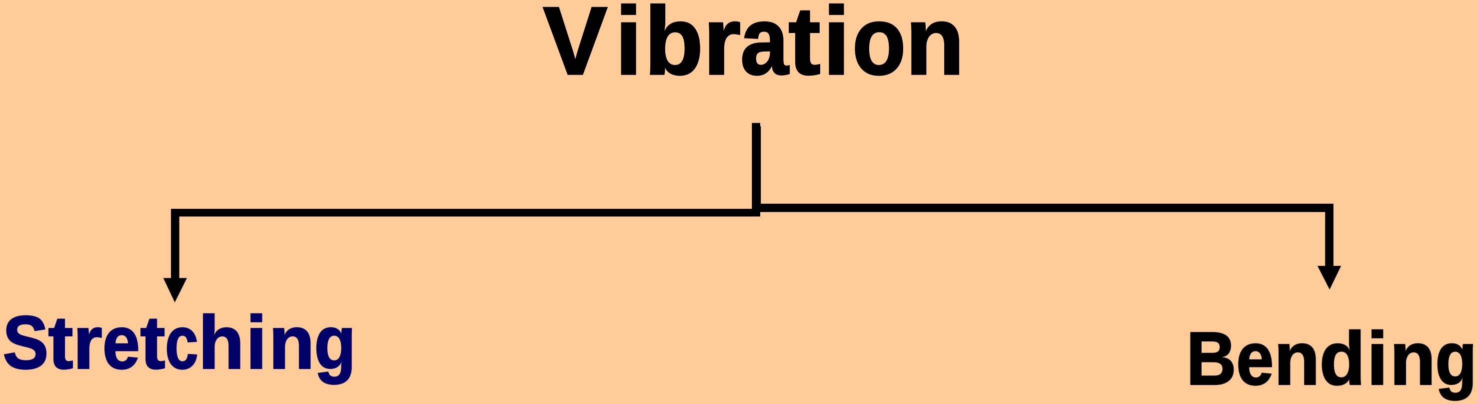
Useful in IR spectroscopy

Rotational

Not useful in IR spectroscopy

Collisions & interactions of liquids and solids

Principle



Vibration

Stretching

Bending

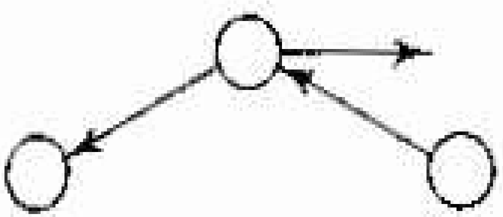
change in inter-atomic distance along the bond axis

change in the angle between two bonds

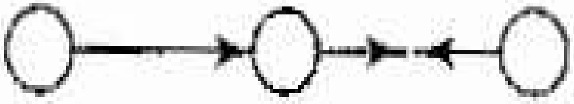
What is the relation between bond vibrations and IR?

Different types of vibrations (streching, bending,..etc) required different amount of IR energy

The same type of vibration between different type of bonds also required different amount of IR



Asymmetric streching



Asymmetric

Strong bonds require more IR energy to vibrate

More IR energy is required to stretch strong short bonds than it does for long weak bonds.

$C\equiv C$ $C=C$ $C-C$

It takes more IR energy to stretch a bond between two heavy atoms than it does if the bond is between two light atoms.

$C-H$ $C-O$

Principle

Weaker bonds vibrate easily by absorbing IR corresponds to the difference between two vibrational energy levels

↑ atoms in a molecule

↑ bonds

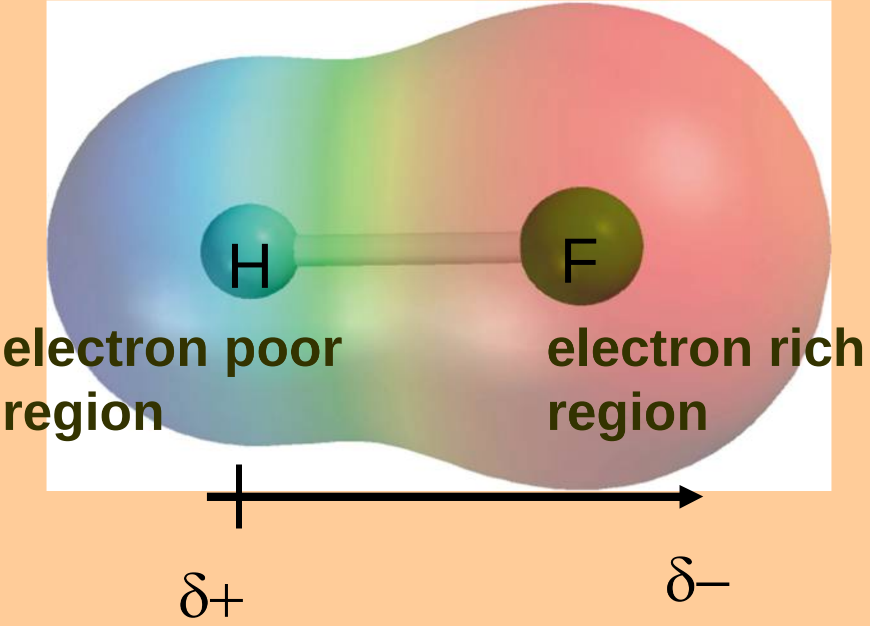
↑ modes of vibrations.

For a vibration to be observed in the IR spectrum (IR active)

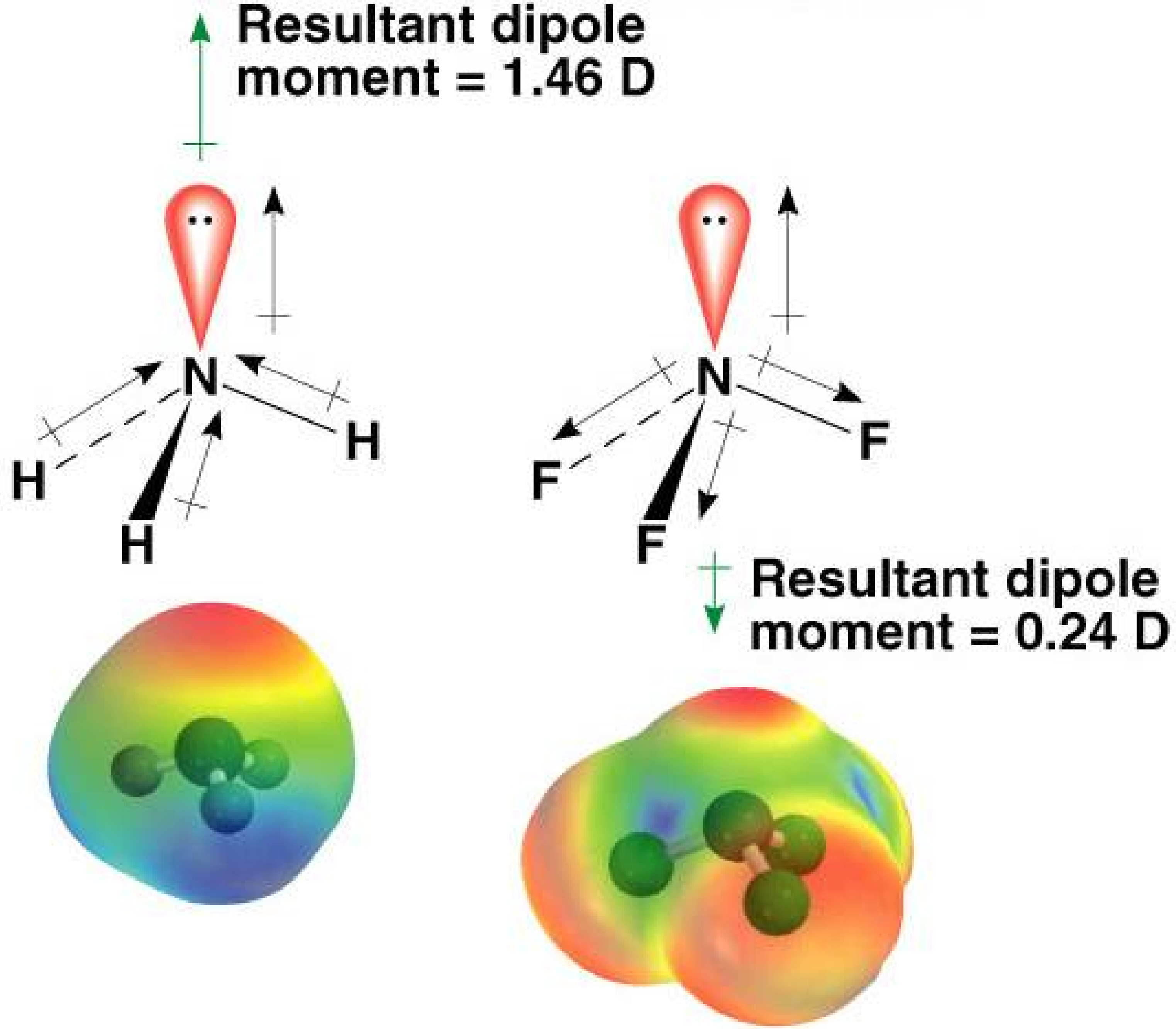
It must cause a change in the dipole moment of the molecule

IR active molecules

1- Molecules that are **electrically asymmetrical.** i.e. **molecules that have dipole moments, e.g. HF**



2- Molecules that have **change in dipole moments in** some of their vibrational modes, **e.g. CO_2**



Resultant dipole moment = 1.46 D

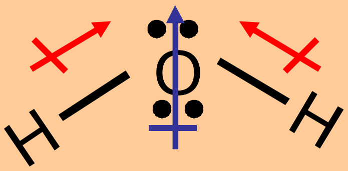
Resultant dipole moment = 0.24 D

When You stretch a bond

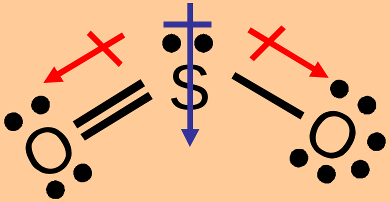
As the a bond stretches the atoms move a part from each other

If the bond elongation changes the net dipole moment of the molecule; an **IR** peak is manifested

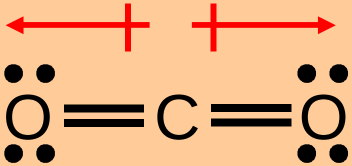
Which of the following molecules have a dipole moment?
H_2O, CO_2, SO_2, and CH_4



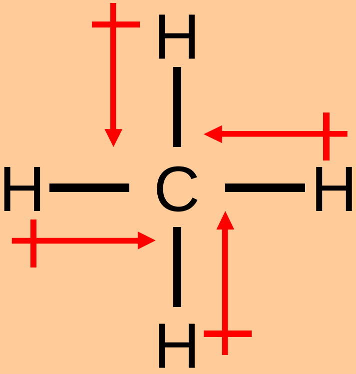
dipole moment
polar molecule



dipole moment
polar molecule



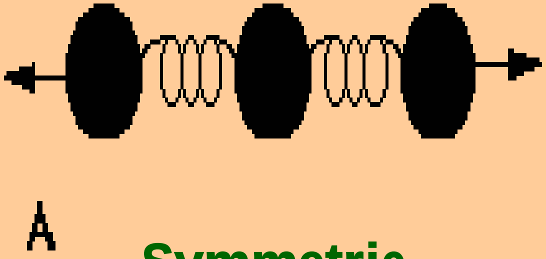
no dipole moment
nonpolar molecule

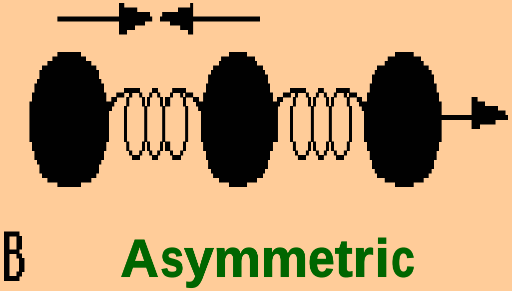


no dipole moment
nonpolar molecule

Principle

vibrational modes of CO_2





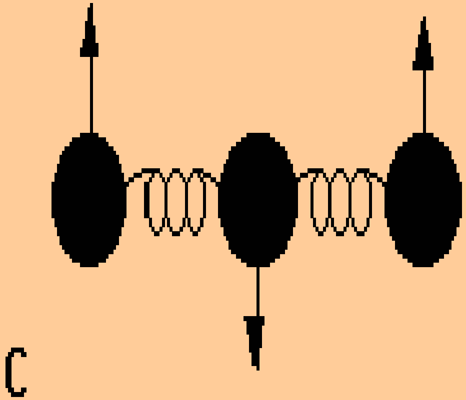
stretching

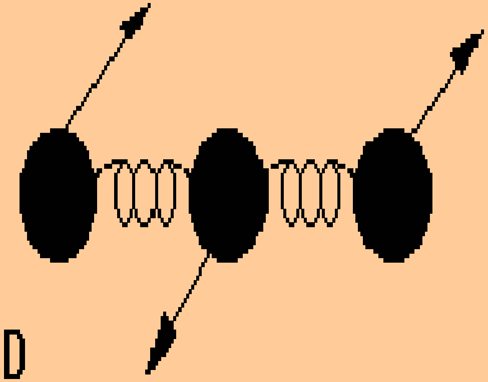
Symmetric

Not IR active
No changes in the molecular dipole moment

Asymmetric

IR active
changes the molecular dipole moment





bending

Principle

Molecules

linear

vibrational modes = 3n-5

How many vibrational modes for CO_2?

= 3 x 3 -5

= 4 fundamental vibrations

non-linear

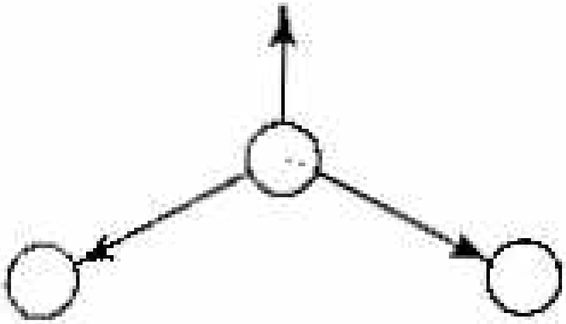
3n-6

How many vibrational modes for H_2O?

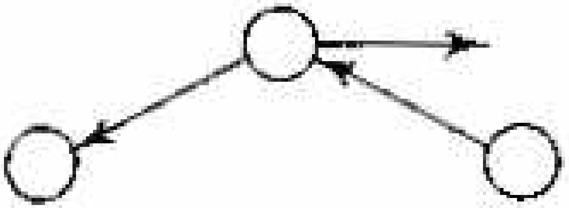
= 3 x 3 -6

= 3 fundamental vibrations

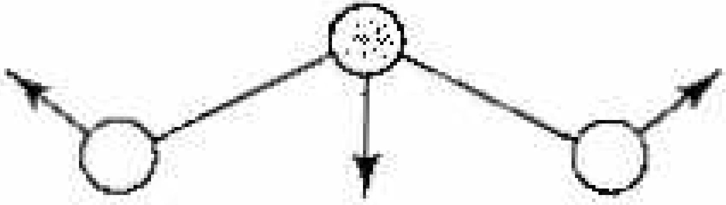
H_2O Vibrations



Symmetric stretching



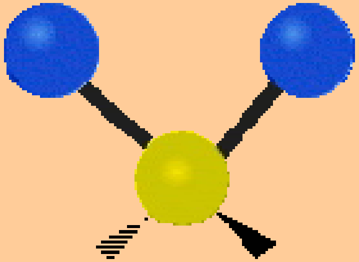
Asymmetric streching



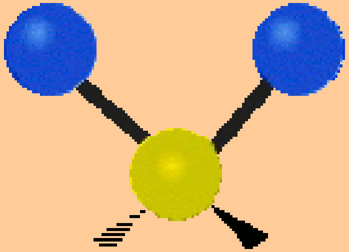
Scissoring

Additional Vibrational modes For complicated molecules

- ***Rocking***



- ***Twisting***



- **Coupling**

Principle

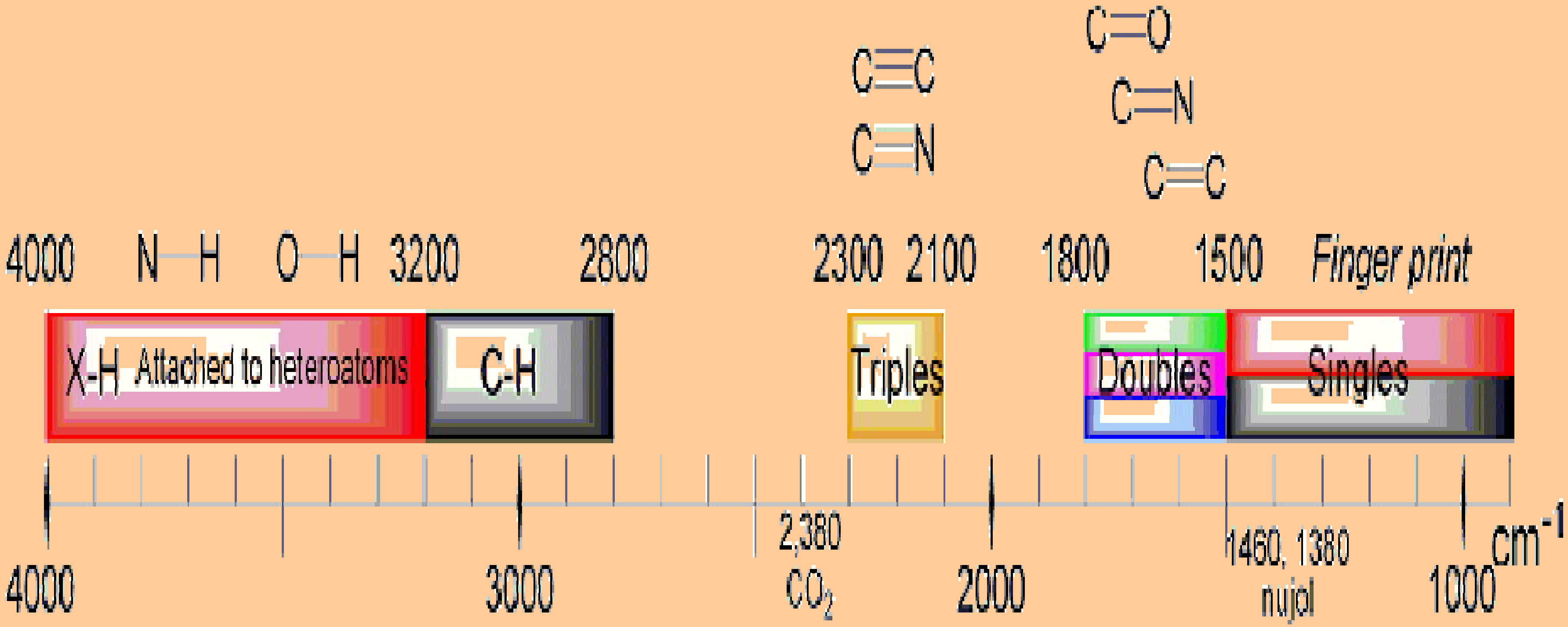
Factors affecting IR frequency

(a) The masses of the bonded atoms

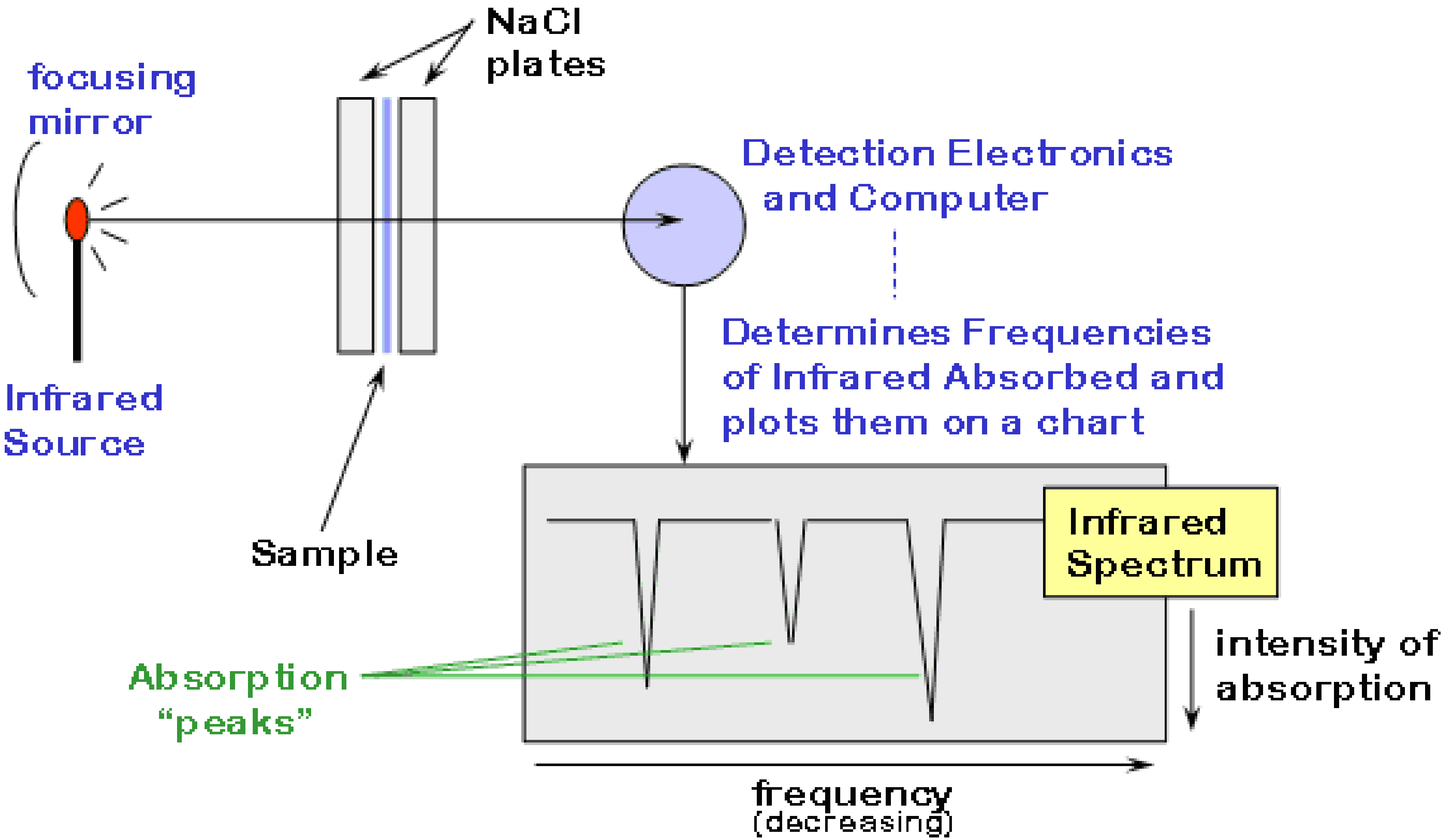
(b) The strength of the bond

(c) The overall structure of the molecule

Each type of bond has a characteristic range of IR wavelengths it can absorb



Instrumentation



Instrumentation

IR source → Sample → Monochromator → Detector

A- Conventional spectrometer

IR source → Interferometer → Sample → Detector

B- FTIR spectrometer

Fourier transformation

an interferometer is used in place of a monochromator.

1. IR Source

Resistors that are heated by an electric current to emit infra-red (heat) radiation

Common IR source;

Nernst glower
light emitting diodes (LEDs)
tunable diode lasers (TDLs)

2. Sampling

Method by which a sample is held in the path of the IR light.

Glass and plastics are never used as sample holders

sample holders are made of ionic compounds (NaCl & KBr)
analytes must be prepared with water-free organic solvents

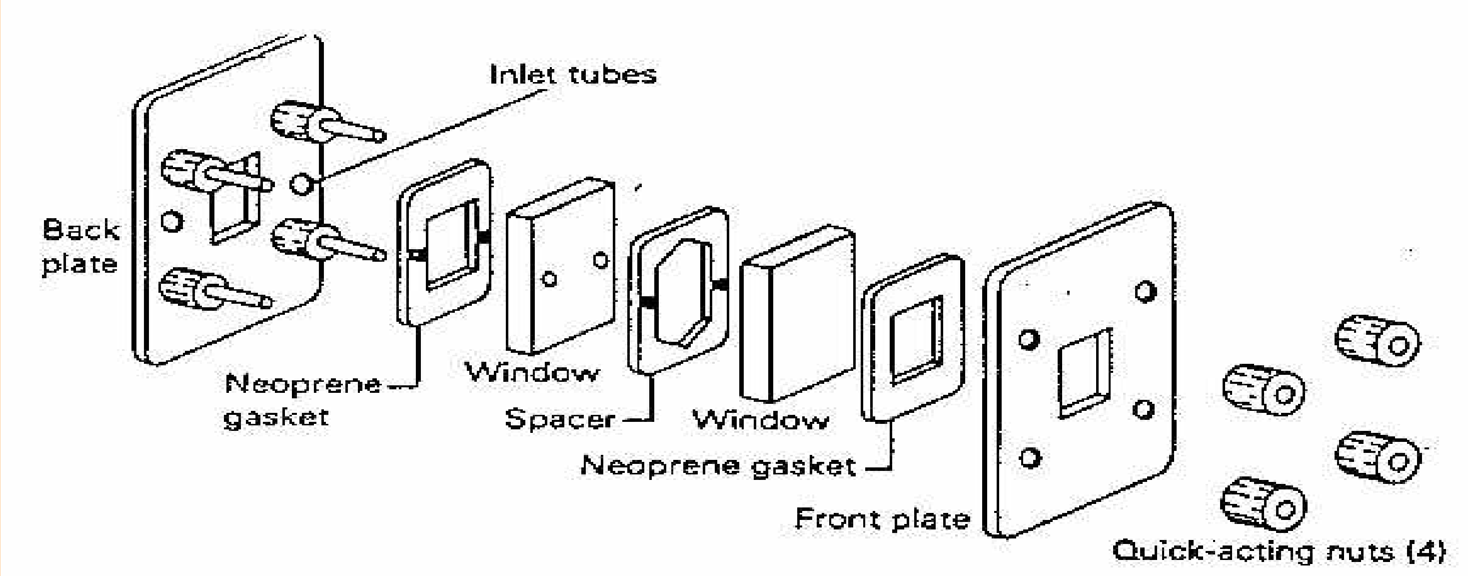
Common solvents used;

CCl_4
$CHCl_3$
CH_2Cl_2

2. Sampling

a. Liquid Sampling

container **is called liquid sampling cells**
a thin layer of liquid is sandwiched between two blocks of NaCl or KBr crystals (windows or salt plates)



Types of IR Cells

- salt plates are held permanently in place with fixed path-length and holes that allow small volumes of samples to be introduced and drained out with a syringe
- for qualitative and quantitative analysis

a. Sealed cells

- liquid sample is applied on one salt plate and the second plate is positioned over the first to smear the liquid between the two plates.
- for qualitative analysis only

b. demountable cells

- cells that can be opened if desired
- for qualitative and quantitative analysis

c. sealed demountable cells

2. Sampling

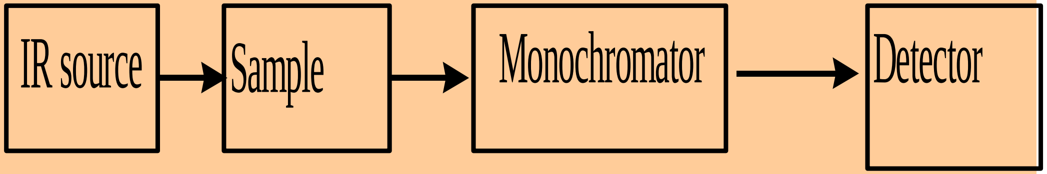
c. Gas Sampling

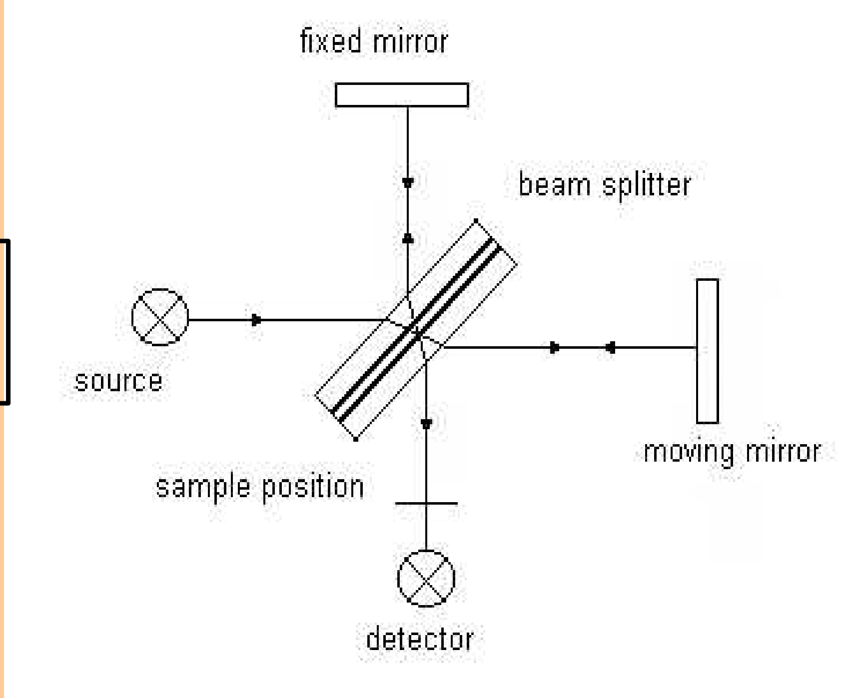
Gases are held in a special cylindrical container with salt windows (10-20 cm).

3. Monochromators and Interferometers

1- Conventional IR spectrometers (*dispersive instruments*): monochromators that consist of diffraction gratings

2- FTIR spectrometers: sample is placed between an interferometer and the detector.





4. Detectors

- ***Thermopile***
- ***Bolometers***
- ***Pyroelectric detectors***
- ***Pneumatic detectors***
- ***Photoconductive sensors***
- ***Photovoltaic detectors***

IR Spectrum

Plot IR energy vs. %transmittance (%T)

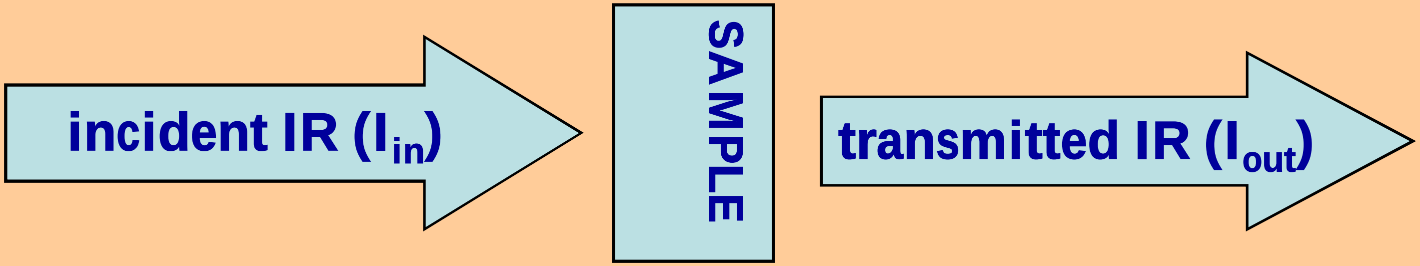
– Energy scale in wave numbers, wn (cm^{-1})

– %T scale

Compares intensity of IR striking sample (I_{in}) with intensity of IR leaving sample (I_{out})

100%T no light absorbed by sample

0% all light absorbed by sample



$$\%T = 100 \times (I_{out} \;/\; I_{in})$$

IR Spectrum

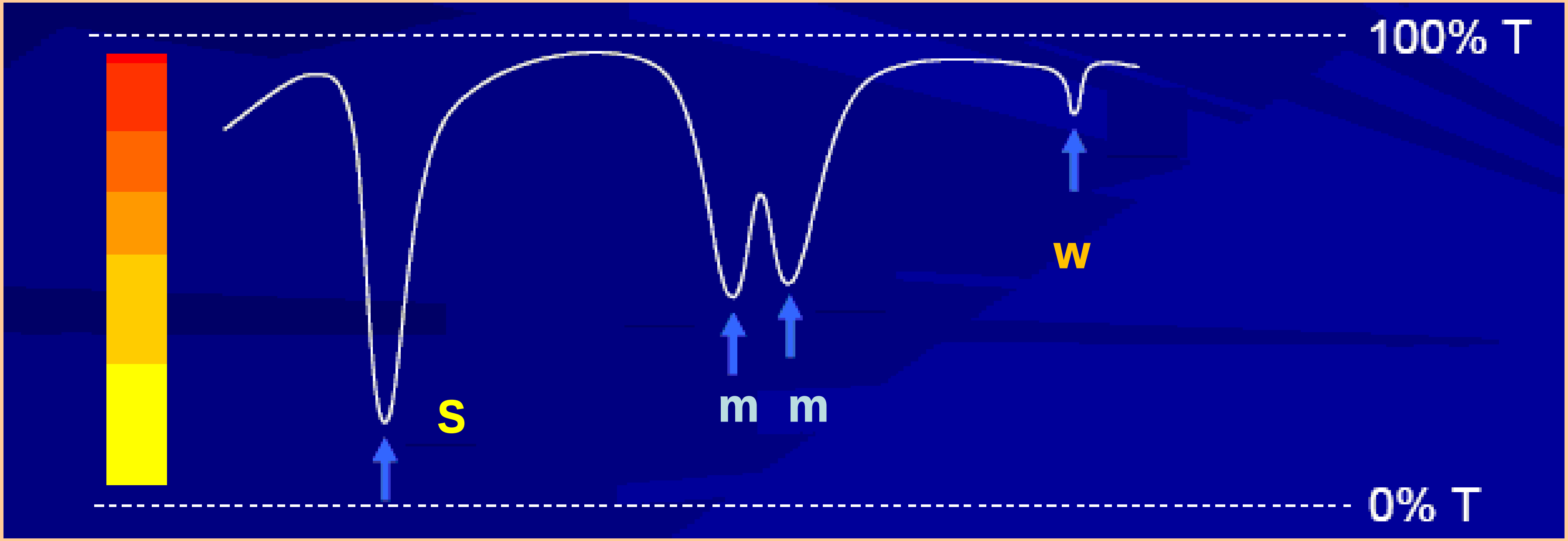
Record;

– Wave number location of IR “band” (position of max %T)

– Intensity of IR “band”

s = strong (low %T), m = medium, w = weak (high %T)

vs = very strong, vw = very weak



Energy Trends

Identification of the functional groups in the molecule.swf

Energy follows vibration frequency of atoms

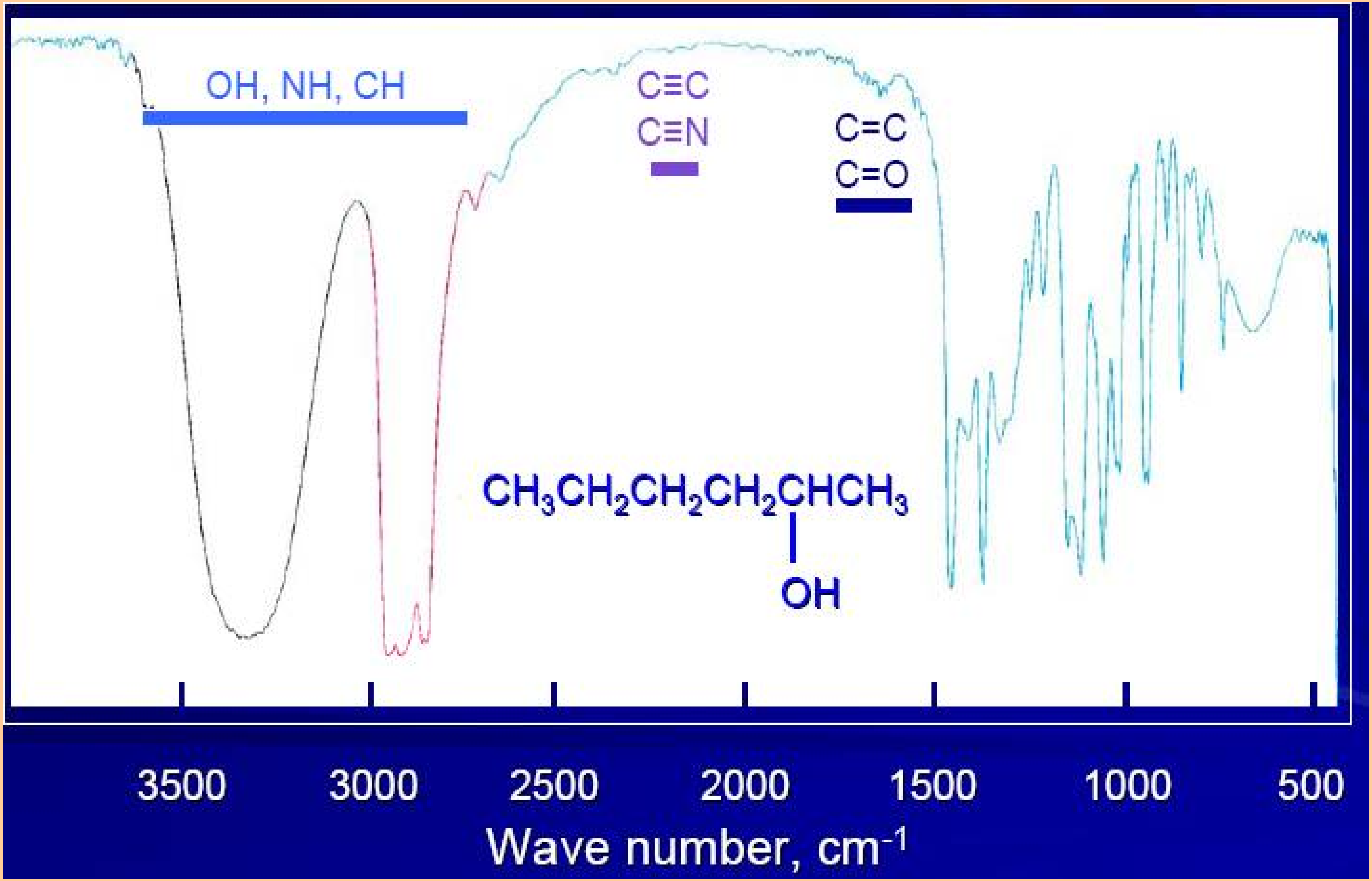
Light atoms vibrate more rapidly

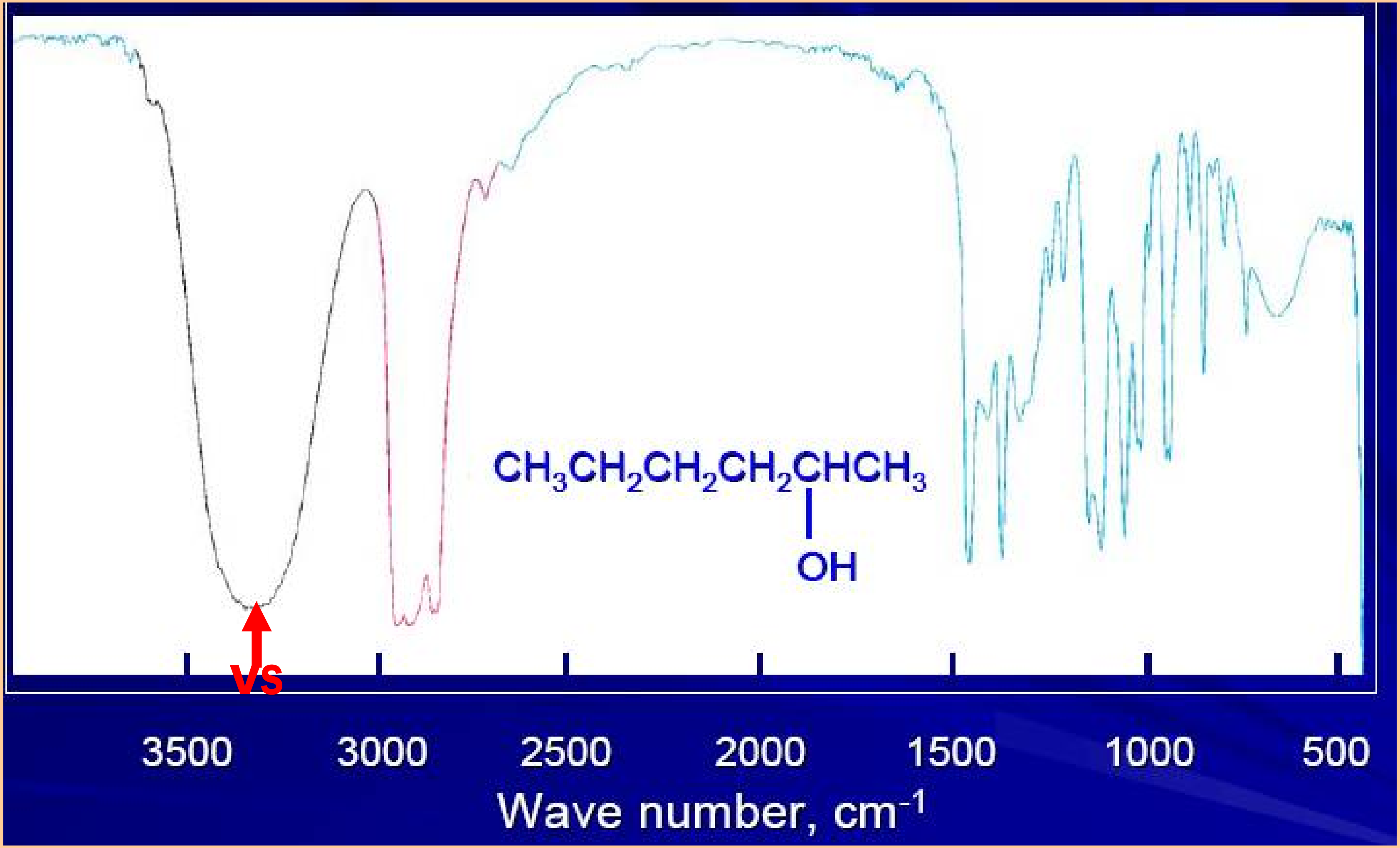
- CH, NH, OH vibrations > 2800 cm-1

Multiple bonds vibrate more rapidly

- Triple bonds : C≡C (2100-2200) C≡N (2240-2280)
- Double bonds : C=O (1680-1750) C=C (1620-1680)
- Single bonds : C–O (1025-1200)

Stretching > Bending > wagging/Twisting


OH, NH, CH
C≡C
C≡N
C=C
C=O
CH3CH2CH2CH2CHCH3
OH
3500
3000
2500
2000
1500
1000
500
Wave number, cm-1



Where do you measure the position of the "black" band? What is its intensity?

Fingerprint Region (<1500 cm^{-1})

Many bands & *many overlaps*

– Heavy atom stretches

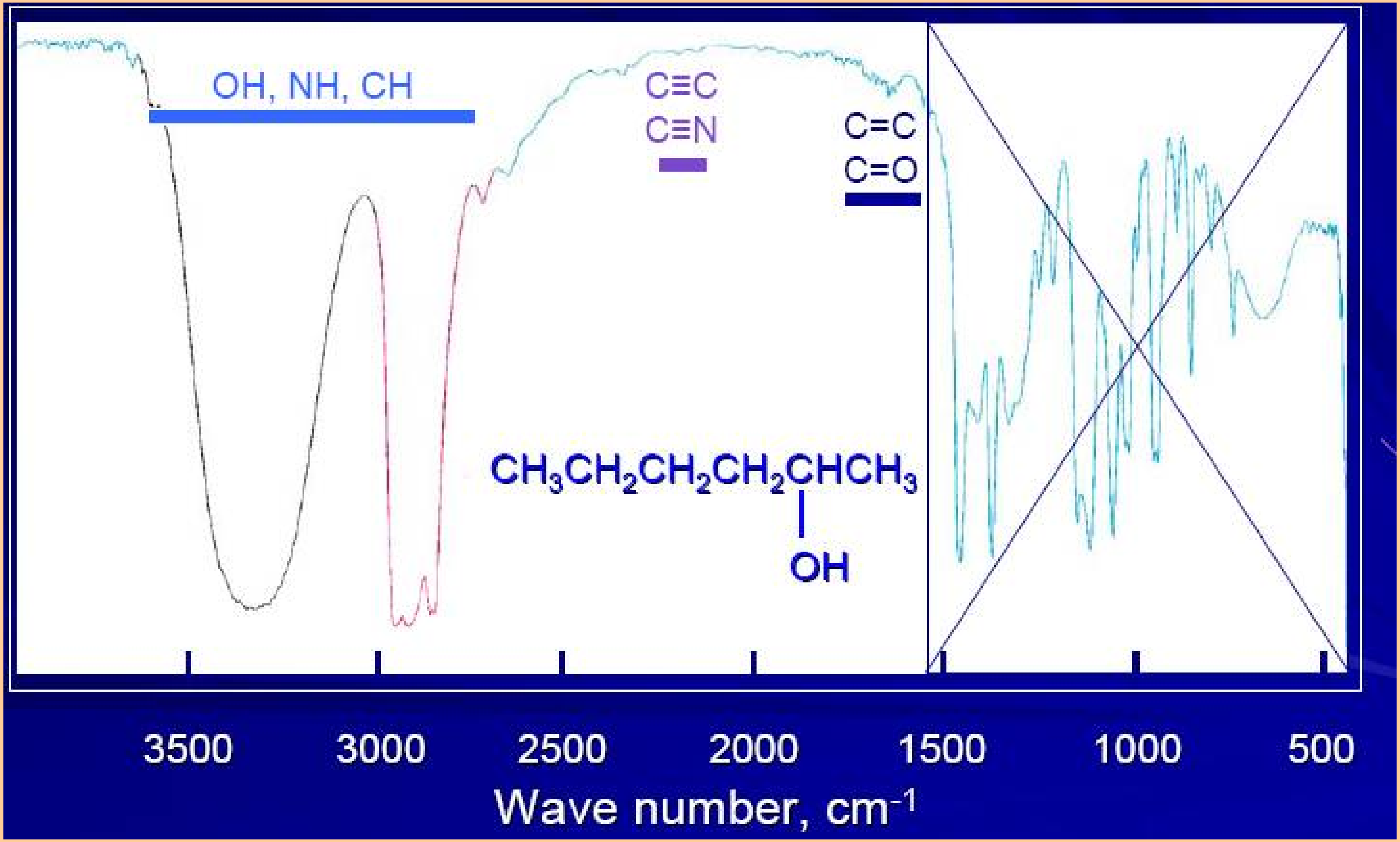
– All bends, etc.

Should have simple molecule (or *other* evidence for structure) before *interpreting* bands in this region

Overall pattern reflects molecular structure

Pattern from 1400-600 = “molecular fingerprint”

Fingerprint Region



Intensity Trends

Follows change in dipole caused by vibrating atoms

Polar bonds (strong bond dipoles) absorb strongly

- O–H
- C=O, C≡N
- C–O

Nonpolar bonds absorb weakly

- C≡C, C=C

Follows # overlapping bands

CH bands tend to overlap

Molecules contain many CH

CH absorptions tend to be strong

How to analyze IR spectra

Instead, look for tell-tale bands the region from 4000-1300 cm^{-1} is particularly useful for determining the presence of specific functional groups.

3500-3300 cm^{-1}	**N–H stretch**	**amines**
3500-3200 cm^{-1}	**O–H stretch**	**alcohols,** *a broad,* *strong band*
3100-3000 cm^{-1}	**C–H stretch**	**alkenes**
3000-2850 cm^{-1}	**C–H stretch**	**alkanes**
1760-1665 cm^{-1}	**C=O stretch**	**ketones,** **aldehydes,** **esters**
1680-1640 cm^{-1}	**C=C stretch**	**alkenes**

Begin by looking in the region from 4000-1300.
Look at the C–H stretching bands around 3000:

	Indicates:
Are any or all to the right of 3000?	alkyl groups (present in most organic molecules)
Are any or all to the left of 3000?	a C=C bond or aromatic group in the molecule

Contd.....