



Vibrational Spectroscopy (Infrared, IR-Spect.)

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Vibrational (Infrared, IR) Spectroscopy

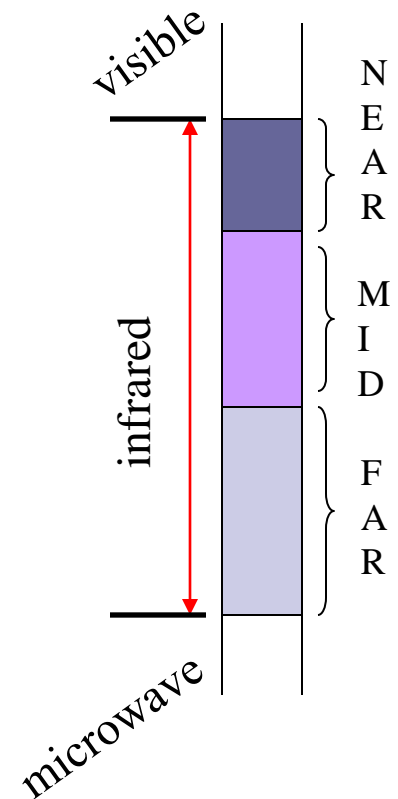
- It is the technique which is used to identify chemical compounds based on how infrared radiations are absorbed by the compounds' chemical bonds, and interacts with them.
- The most common technique used is absorption spectroscopy.
- Infrared spectroscopy exploits the fact that molecules have specific frequencies at which they vibrate corresponding to discrete energy levels.
- Gives information about the functional groups present in molecules.

■ IR region of electromagnetic spectrum:

- λ : 780 nm – 1000 μm
- Wavenumber : 12,800 – 10 cm^{-1}

■ IR region is subdivided into 3 sub-regions:

1. Near IR region (Nearest to the visible)
 - 780 nm to 2.5 μm (12,800 - 4000 cm^{-1})
2. Mid IR region
 - 2.5 to 50 μm (4000 – 200 cm^{-1})
3. Far IR region
 - 50 to 1000 μm (200 – 10 cm^{-1})



■ What happens when absorption of IR occurs?

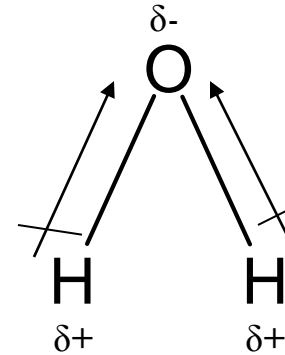
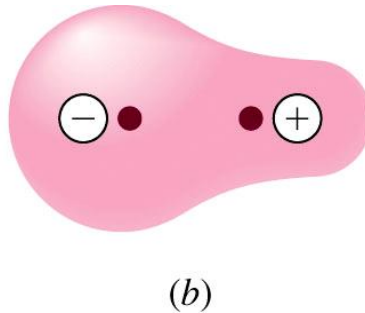
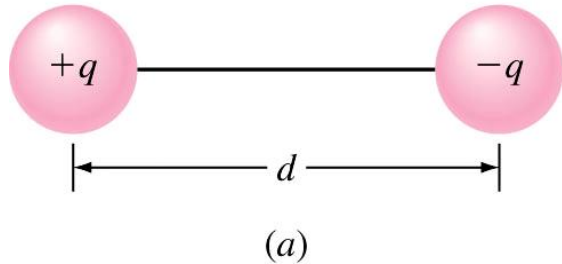
1. Changes in the shape of molecules such as stretching of bonds, bending of bonds, or internal rotation around single bonds.
2. IR absorption only occurs when IR radiation interacts with a molecule undergoing a change in dipole moment as it vibrates or rotates.
3. Infrared absorption only occurs when the incoming IR photon has sufficient energy for transition to the next allowed vibrational state to take place ($\Delta E = h\nu$).

Note: If the rules 2 and 3, above are not met, no absorption can occur.

SO, NOT ALL bonds in a molecule are capable of absorbing IR- energy.

Infrared Absorption

For a molecule to show infrared absorptions it must possess a specific feature: an electric dipole moment which must change during the vibration.



A dipole moment, μ is defined as the charge value (q) multiplied by the separation distance (d) between the positive and negative charges.

$$\mu = qd \text{ (C.m)}$$

In hetero-nuclear diatomic molecules, due to the difference in electronegativities of the two atoms, one atom acquires a small positive charge (δ^+), the other a negative charge (δ^-).

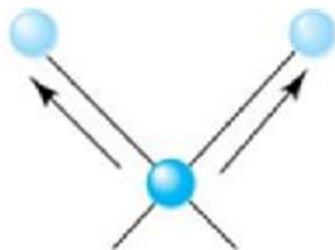
- **A molecule is IR active** if it has a permanent dipole moment; **HCl is active while N₂ is inactive.**
- **IR spectrum represents** the rotation-vibration spectrum of the molecule.
- **In solution,** the rotation of molecules is strongly hindered, bands are strongly broadened and the maxima of these bands correspond to the vibrational spectrum.
- **In the solid state,** the rotations are effectively frozen so that the spectrum appears as relatively sharp bands, which corresponds to the normal vibrations.
- **In gases,** the rotation-vibration spectrum can be also observed.

Modes of Vibration

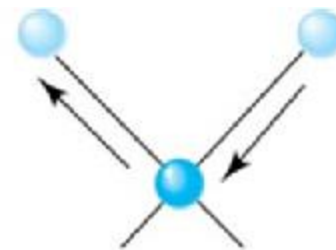
- The interaction of infrared radiations with matter can be understood in terms of changes in molecular dipoles associated with vibrations.
- Vibrations can involve either changes in bond length (stretching) or bond angle (bending).
- Some bonds can stretch in-plane (symmetric stretching) or out-of-plane (asymmetric stretching).
- Bending vibrations can be either in-plane (as; scissoring, rocking) or out-of-plane (as; wagging, twisting) bending vibrations.

Modes of Vibration

STRETCHING



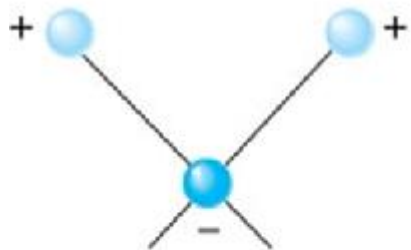
Symmetric



Asymmetric

(a) Stretching vibrations

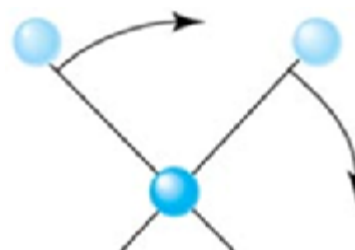
BENDING



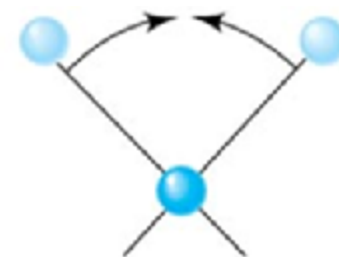
Out-of-plane wagging



Out-of-plane twisting



In-plane rocking



In-plane scissoring

(b) Bending vibrations

Molecular vibration

divided into

back & forth movement

stretching

involves change in bond angles

bending

symmetrical

asymmetrical

scissoring

wagging

rocking

twisting

in-plane vibration

out of plane vibration

Total number of modes of vibrations (normal modes)

- The number of coordinates required to specify the position of all atoms in a molecule is called the number of degree of freedom, thus, for a molecule with N -atoms, it has $3N$ degree of freedom.
- So, the degree of vibrational freedom (Total number of modes of vibrations) for polyatomic molecules containing (N) atoms is given by;
 1. $3N - 5$ (For linear molecules)
 2. $3N - 6$ (For non-linear molecules)
- Two other concepts are also used to explain the frequency of vibrational modes:
 - (1) The stiffness of the bond expressed as the force constant (called; k or F) and,
 - (2) The masses of the atoms at each end of the bond (μ).

- When the thermal energy is absorbed by molecules, it is stored in molecules in the form of;
 - (1) Transitional movement of the molecule. There are 3-translational degrees of freedom along X, Y and Z-axes, so the remaining $(3N-3)$ co-ordinates represent the internal degree of freedom. These are sub-divided into;
 - Rotational degree of freedom
 - Vibrational degree of freedom
 - (2) Internal motion of atoms present in the molecule (i. e. rotational and vibrational motions).

	TRANSLATIONAL	ROTATIONAL	VIBRATIONAL
For linear molecule	3	2	$3N-5$
For nonlinear molecule	3	3	$3N-6$

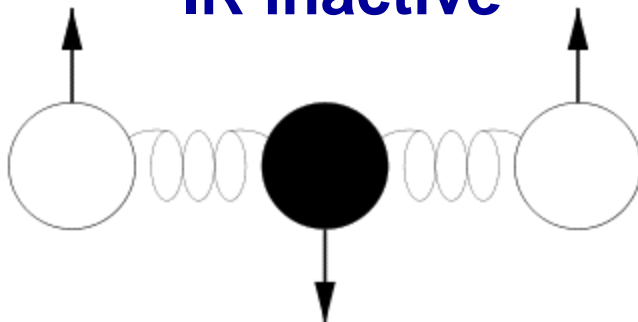
Molecular Vibrations of CO₂



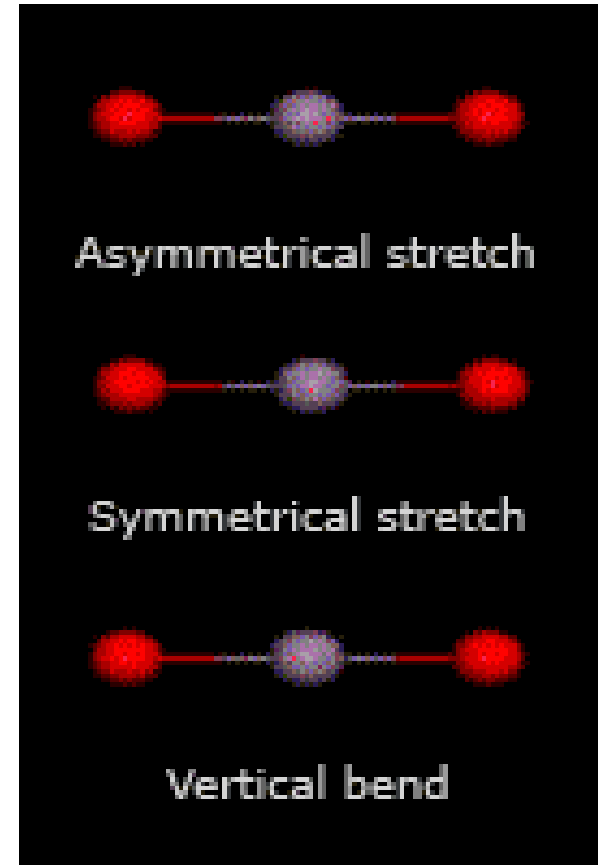
IR active



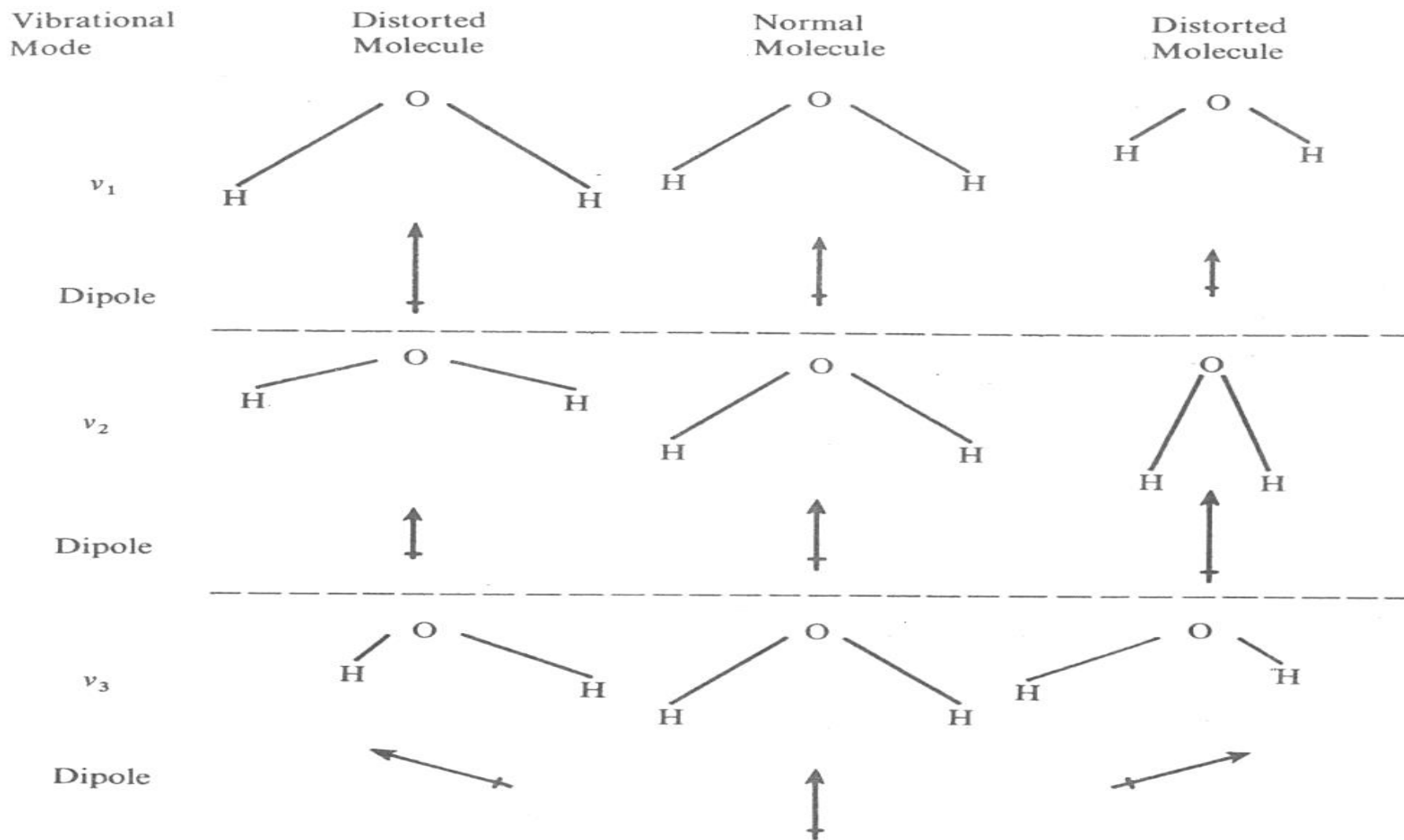
IR inactive



IR active

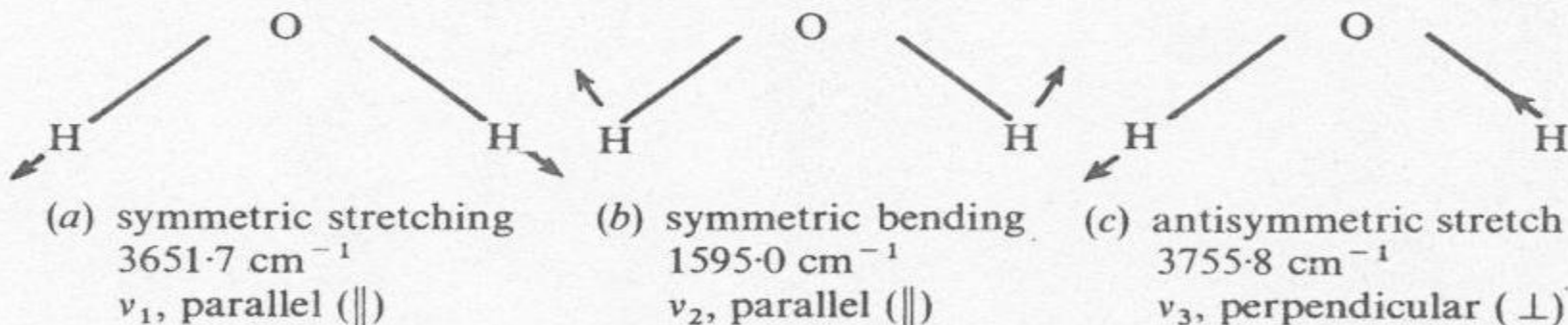
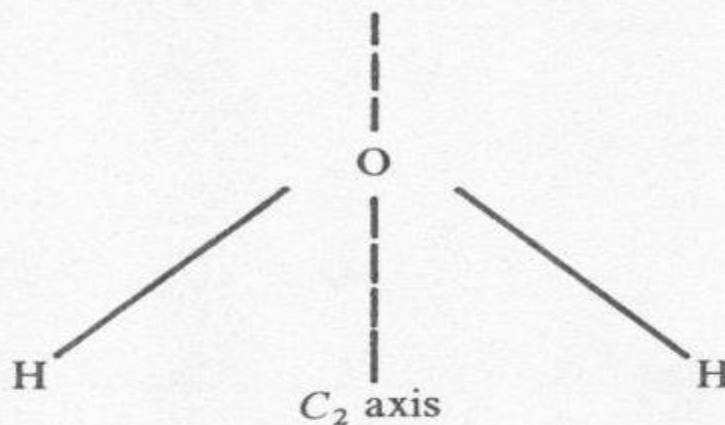


Vibrational Modes for Water



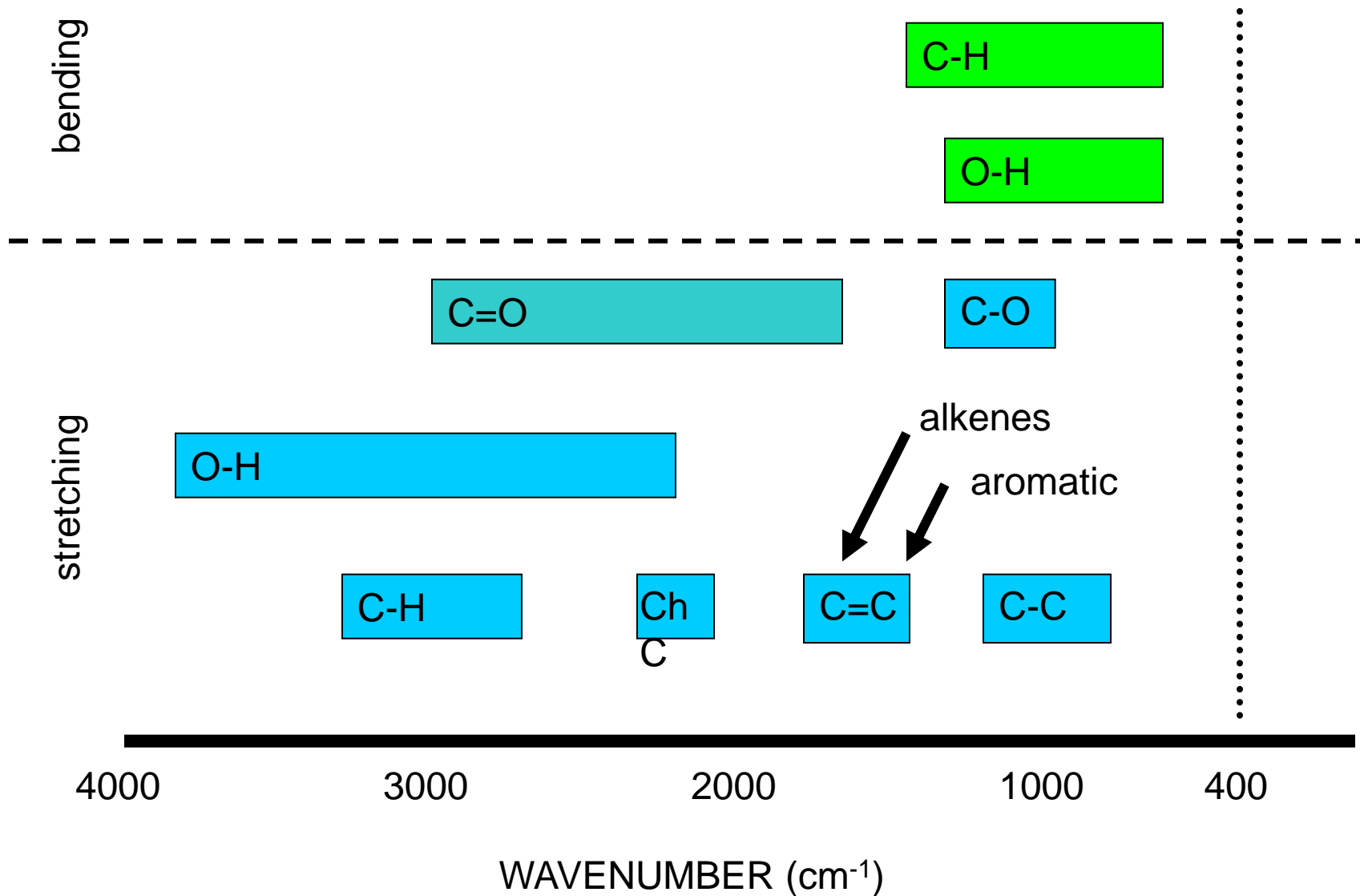
The change in the electric dipole moment produced by each vibration of the water molecule; this is seen to occur either along (\parallel) or across (\perp) the symmetry axis. The amplitudes are greatly exaggerated for clarity.

Fundamental IR Bands for Water

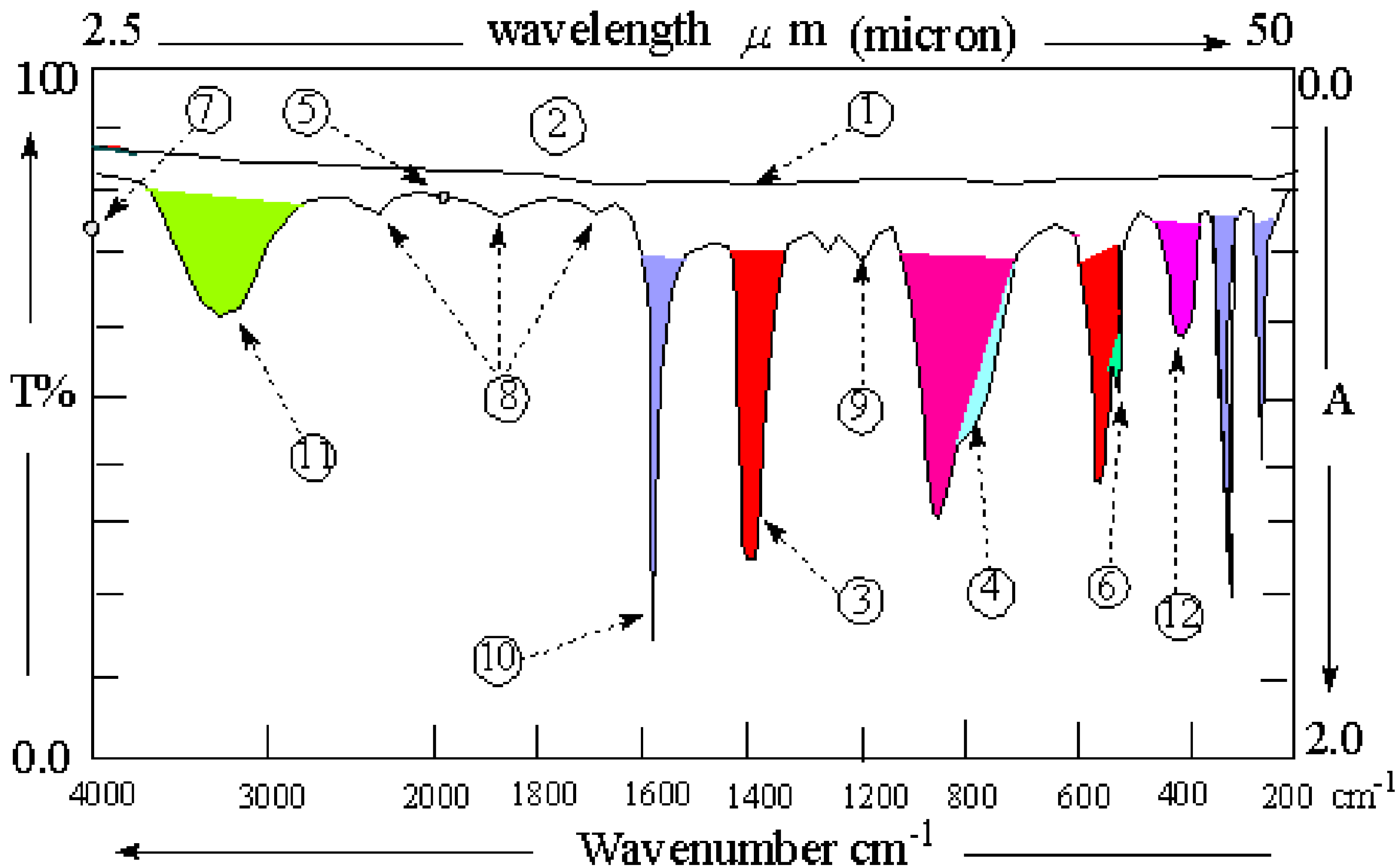


The symmetry of the water molecule and its three fundamental vibrations. The motion of the oxygen atom, which must occur to keep the centre of gravity of the molecule stationary, is here ignored.

Basic Functional Groups



Infrared Spectrum



IR Spectrum of Complex Molecules

- There are many possible vibrational modes giving rise to complicated spectra with many peaks.
- **IR spectra are mainly used to identify unknown compounds**
- Peak positions can demonstrate what functional groups are present in the molecule. Each functional group gives rise to an absorption peak at a characteristic frequency, no matter what the rest of the molecule contains.
- **The peak positions and intensities of an unknown can be compared with the spectrum of known suspects in the same manner that police use fingerprints.**

group	Approximate frequency cm⁻¹	Group	Approximate frequency cm⁻¹
- OH (free)	3600	-SH (free)	2580
- NH₂ (free)	3400	- C ≡ N	2250
≡ CH	3300	- C ≡ C -	2220
Ph-H	3060	C = O	1750-1600
= CH₂	3030	C = C	1650
CH₃	2970 $\bar{\nu}_{\text{asym.}}$	C-C, C-N, C-O	1200-1000
	2870 $\nu_{\text{sym.}}$	C = S	1100
	1460 $\delta_{\text{asym.}}$	C-F	1050
	1375 $\delta_{\text{sym.}}$	C-Cl	725
-CH₂-	2930 $\bar{\nu}_{\text{asym.}}$	C-Br	650
	2860 $\bar{\nu}_{\text{sym}}$	C-I	550

Harmonic oscillator

Assuming that the two atoms are point masses connected by a massless spring with simple harmonic motion:

Restoring force, $F = -k x$,

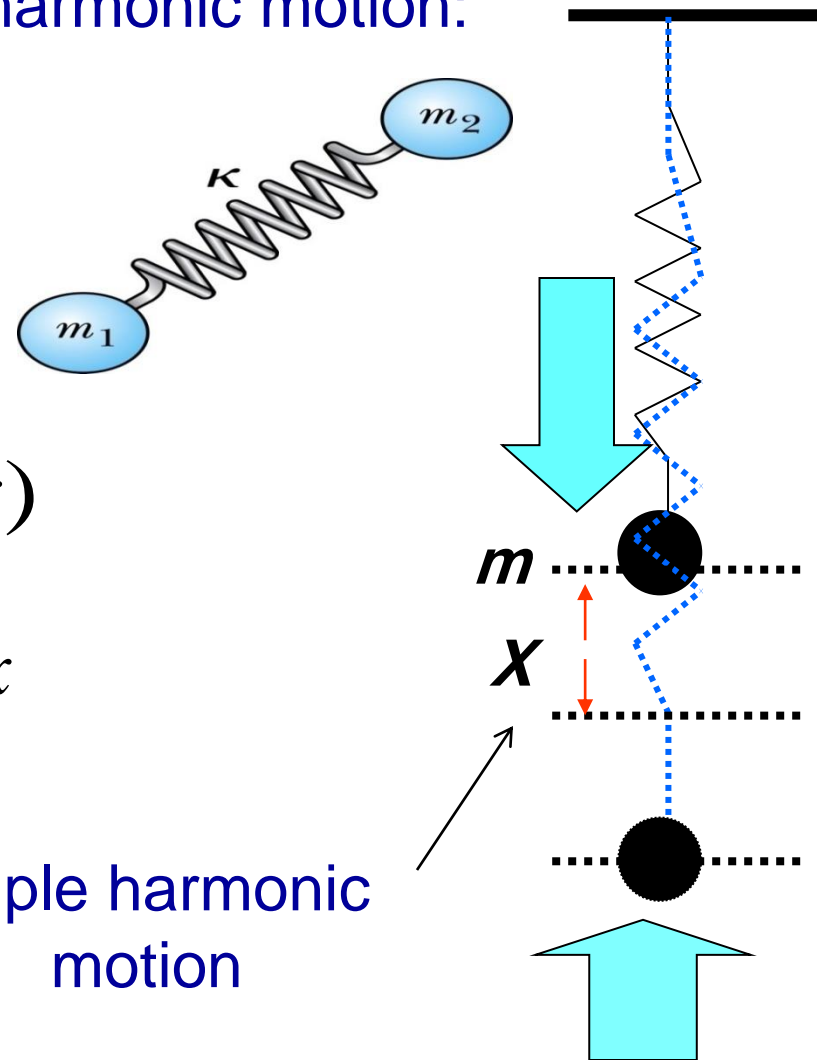
$k =$ forceconst.
(sometimes called F)

Potential energy $V(x)$

$$V(x) = -Fdx, \quad V(x) = \int_0^x k x dx$$

$$V(x) = \frac{1}{2} k X^2$$

simple harmonic motion



For stretching of the bond A-B, the frequency of oscillation ν as harmonic oscillator is given by the relation;

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \quad \text{or in cm}^{-1} \quad \bar{\nu} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}}$$

$$\mu = \frac{m_A m_B}{m_A + m_B}$$

μ Is the “reduced mass” where m_1 , m_2 are the masses on either side of vibration

k is the “force constant”, like the Hooke’s Law restoring force for a spring. Known and tabulated for different vibrations.

k (single bond) = 5×10^5 dyne/cm.,

k (double bond) = 10×10^5 dyne/cm.,

k (triple bond) = 15×10^5 dyne/cm.

Harmonic oscillator

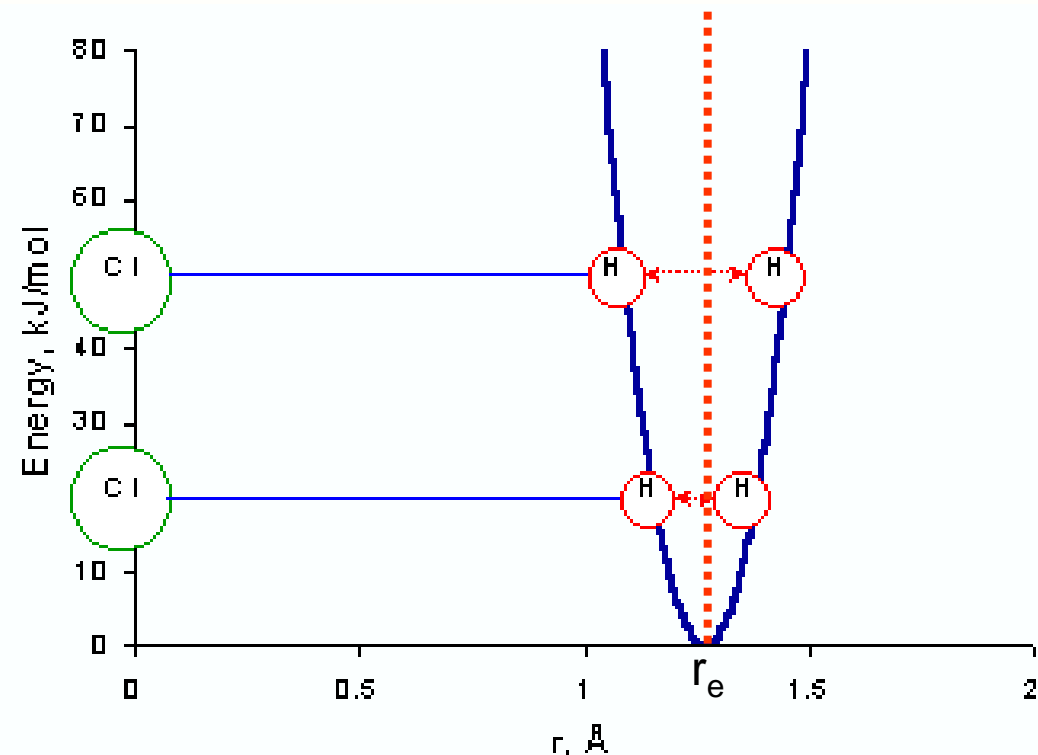
harmonic oscillator obeys Hooke's law: $F = k \cdot \Delta x$, where $\Delta x = (r - r_{eq})$
energy of harmonic oscillator is

$$E = \frac{1}{2} k (r - r_e)^2$$

the oscillating frequency is:

$$\omega_{osc} = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \quad \text{units: Hz}$$

$$\bar{\omega}_{osc} = \frac{1}{2\pi \cdot c} \sqrt{\frac{k}{\mu}} \quad \text{units: cm}^{-1}$$



μ - effective mass, k - force constant

for H-Cl molecule:

$$k = 516 \text{ N/m}; \mu = 1.629 \cdot 10^{-27} \text{ kg}; \omega_{osc} = 8.96 \cdot 10^{13} \text{ Hz}; \bar{\omega} = 2989 \text{ cm}^{-1}$$

Example

A strong absorption of infrared radiation is observed for $^1\text{H}^{35}\text{Cl}$ at 2991 cm^{-1} .

- Calculate the force constant, k , for this molecule.
- By what factor do you expect this frequency to shift if deuterium is substituted for hydrogen in this molecule? The force constant is unaffected by this substitution.

Solution

a. We first write
Solving for k ,

$$\Delta E = hv = hc / \lambda = \sqrt{k / \mu}.$$

$$\Delta E = hv = \frac{hc}{\lambda} = \frac{h}{2\pi} \sqrt{\frac{k}{\mu}} \text{ and}$$

$$k = 4\pi^2 \left(\frac{c}{\lambda} \right)^2 \mu = 4\pi^2 \left(2.998 \times 10^8 \right) (2991 \times 100)^2 \frac{(1.008)(34.969)}{(35.977)} \times 1.661 \times 10^{-27} = 516.3 \text{ N/m}$$

b. The vibrational frequency for DCl is lower by a substantial amount.

$$\sqrt{\frac{\mu_{\text{HCl}}}{\mu_{\text{DCl}}}} = \sqrt{\frac{m_{\text{H}} m_{\text{Cl}} (m_{\text{D}} + m_{\text{C}})}{m_{\text{D}} m_{\text{Cl}} (m_{\text{H}} + m_{\text{C}})}} = \sqrt{\left(\frac{1.0078}{2.0140} \right) \left(\frac{36.983}{35.977} \right)} = 0.717$$

From the Schrödinger equation;

Vibrational energy is quantized, so; $\epsilon_v = (v + \frac{1}{2}) \cdot \omega_{osc}$

$v = 0; 1; 2; \dots$ is the vibrational quantum number

units = cm^{-1}

$\epsilon_v = \frac{1}{2} \cdot \omega_{osc}; \frac{3}{2} \cdot \omega_{osc}; \frac{5}{2} \cdot \omega_{osc}; \frac{7}{2} \cdot \omega_{osc}$

$\epsilon_0 = \frac{1}{2} \cdot \omega_{osc}$ - zero-point energy

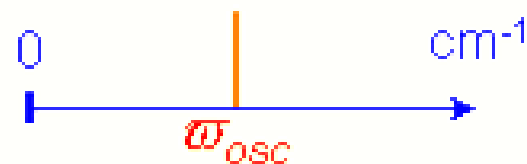
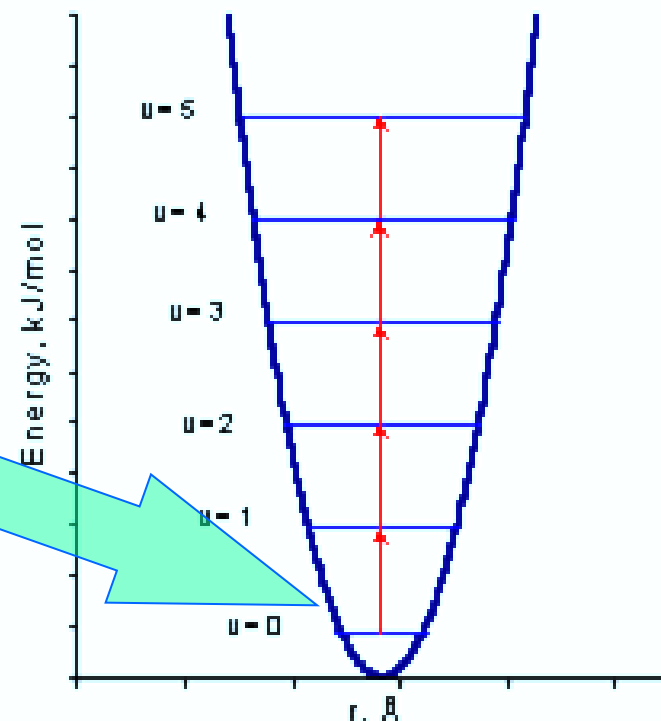
Selection rules:

dipole moment must change

$\Delta v = \pm 1$ (+1=absorption; -1=emission)

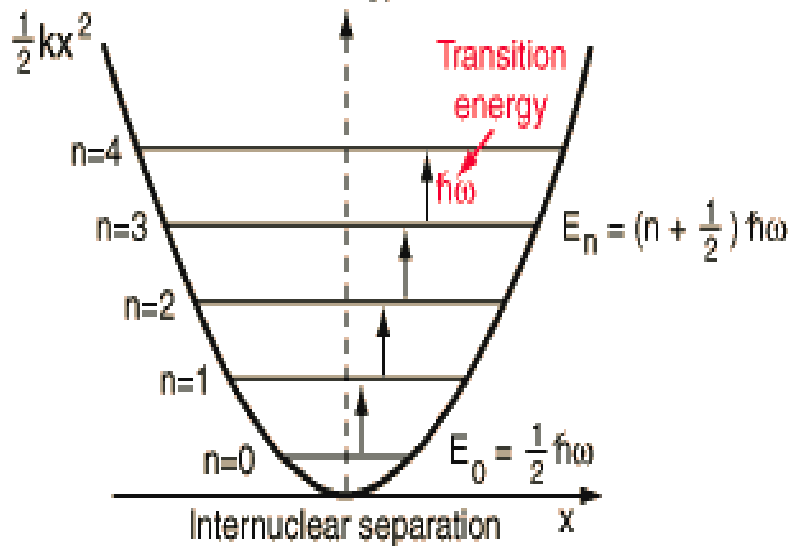
$\epsilon_{v \rightarrow v+1} = \omega_{osc}$ units = cm^{-1}

The vibrating molecule interacts with EMR of its own oscillating frequency



Vibrational energy states of a harmonic oscillator

Potential energy
of form



Second selection rule

$$\Delta v = \pm 1$$

Thus expect only one vibrational peak in the IR spectrum

Vibration levels are quantized, like everything else ($\Delta E = h\nu$)

The energy difference between v_0 and v_1 in harmonic oscillator $(\epsilon_{0 \rightarrow 1}) = \varpi_{osc}$.

Classical explanation of molecular vibrations:

If the oscillation frequency ν of the electric field of a radiation is similar to the frequency $\nu = \omega/2\pi$ of one vibrational motion in a molecule (which involves a variation of the charge distribution), then the molecule can absorb the energy $h\nu$ of one photon from the radiation. Intuitively, we can see this absorption of energy like the resonance phenomenon in classical mechanics.

Consequences of the harmonic approximation

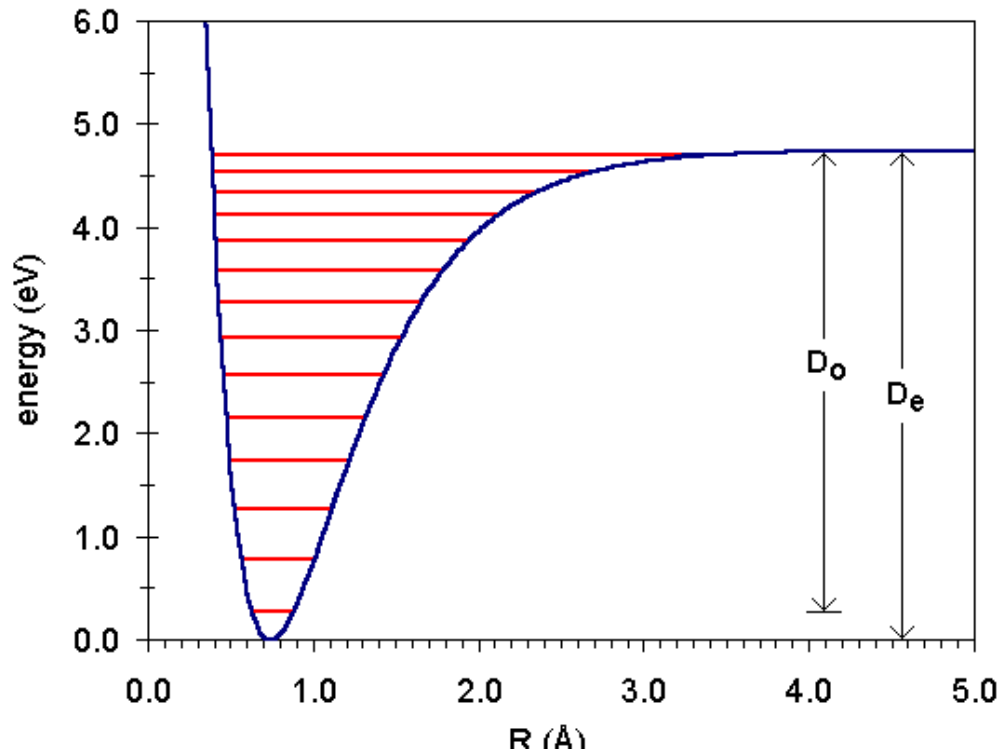
- ◆ **At room T**, molecules are mainly in their vibrational ground state. Hence, in IR absorption spectroscopy, the molecules are excited from the ground state to the first excited state: $0 \rightarrow 1$, since the selection rule is $\Delta v = \pm 1 \rightarrow$ the IR spectrum should contain only one line for diatomic molecule.
 - ◆ **At higher T**, other transitions can occur: $2 \rightarrow 3$ or $3 \rightarrow 4$, but all of them need the absorption of a photon with the same energy, i.e. the absorption lines appear at the same frequency, because the energy between two states is constant.
- \rightarrow Although the main features are there, it is not exactly what shows the actual absorption spectra.... The potential is not harmonic.
- ◆ According to the harmonic oscillator, a chemical bond cannot break.

Anharmonic Oscillator

Real molecules do not obey exactly the laws of simple harmonic motion. If the bond between atoms is stretched, there comes a point at which the bond will break i. e. **the molecule dissociates into atoms.**

A parabola cannot be correct at all extensions because it does not allow the bond to dissociate. So, a parabolic approximation is not the actual potential energy curve, then the motion becomes anharmonic and represented by the Morse potential energy curve.

Potential energy curve for anharmonic oscillator



D_0 = Dissociation energy

D_{eq} is the depth of the potential energy minimum

Therefore, the Morse potential energy is the most closely to the true potential energy curve.

The solution of Schrödinger equation for the Morse function gives the allowed vibrational energy levels (ϵ_v) for anharmonic oscillator, where;

$$\epsilon_v = \left(v + \frac{1}{2} \right) \omega_e - \left(v + \frac{1}{2} \right)^2 \omega_e x_e \quad \begin{array}{l} v = 0; 1; 2; 3; \dots \\ x_e \approx 0.01 \end{array}$$

and x_e = anharmonicity constant
 ω_e = equilibrium vibrational frequency

- When v increases, the second term becomes more negative than the first term, so the energy levels become less widely spaced at high excitation → Also, at high temperature, several weak lines appear due to population of higher vibrational states.
- ♦ Moreover, the selection rule $\Delta v = \pm 1$ indicates the more intense lines, however, weak transitions of $\Delta v > 1$ are now also allowed.

The relation between;

$$\omega_{osc} = \omega_e \left(1 - x_e \left(v + \frac{1}{2} \right) \right)$$

Anharmonic Oscillator - Selection Rules

1) the dipole moment must change

2) $\Delta v = \pm 1, \pm 2, \pm 3 \dots$

+ = absorption; - = emission

fundamental absorption

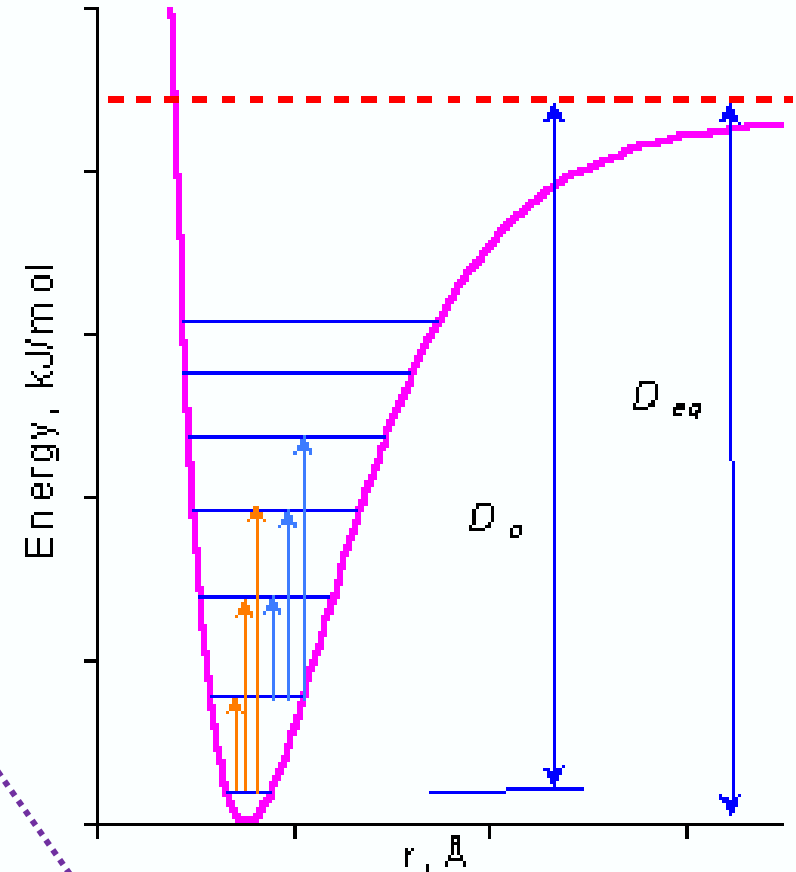
$$\tilde{\nu}_{v=0 \rightarrow v=1} = \epsilon_{v=1} - \epsilon_{v=0} = \omega_e - 2\omega_e x_e$$

first overtone

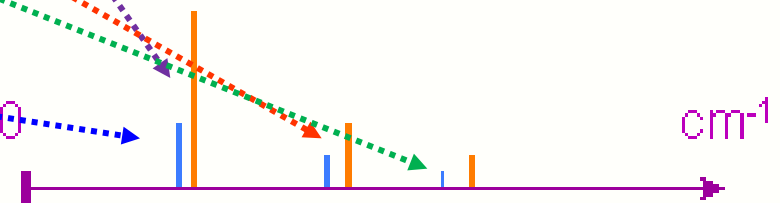
$$\tilde{\nu}_{v=0 \rightarrow v=2} = \epsilon_{v=2} - \epsilon_{v=0} = 2\omega_e - 6\omega_e x_e$$

second overtone

$$\tilde{\nu}_{v=0 \rightarrow v=3} = \epsilon_{v=3} - \epsilon_{v=0} = 3\omega_e - 12\omega_e x_e$$



Why do hot bands have low intensity?



• Example

• The fundamental and first overtone of $^1\text{H}^{35}\text{Cl}$ are observed at 2886 cm^{-1} and 2668 cm^{-1} , respectively. **Calculate:**

- 1- Equilibrium vibration frequency.
- 2- Anharmonicity constant.
- 3- Exact zero-potential frequency.
- 4- The force constant of the molecule.

equilibrium vibration frequency = ω_e ;

anharmonicity const. = x_e

fundamental vibration = $\omega_e(1 - 2x_e) = 2886 \dots \dots \dots (1)$

First overtone = $2\omega_e(1 - 3x_e) = 5668 \dots \dots \dots (2)$

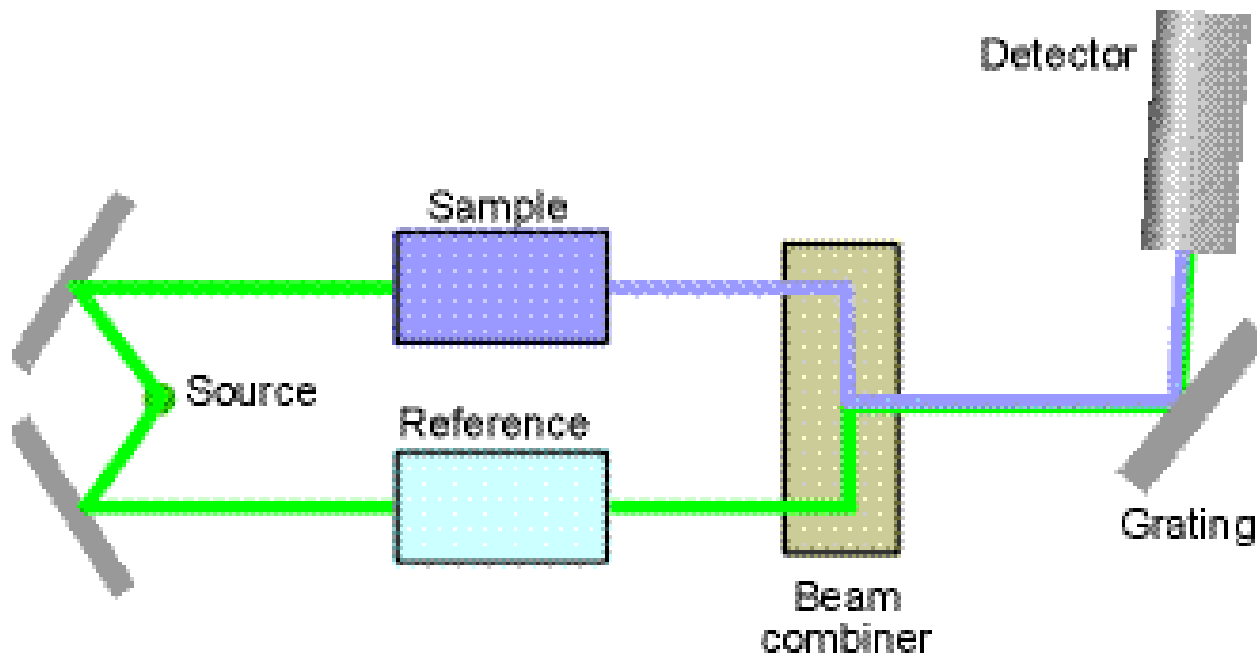
By solving equations (1), (2)

$\omega_e = 2990 \text{ cm}^{-1}$, $x_e = 0.0174 \text{ cm}^{-1}$

exact zero potential $\varepsilon_0 = \frac{1}{2}\omega_e - \frac{1}{4}\omega_e x_e = 14819 \text{ cm}^{-1}$

force const. = $k = 4\pi^2\omega_e^2 c^2 \mu = 516 \text{ Nm}^{-1}$

Typical IR-Spectrophotometer



The layout of a typical dispersive Infra-red absorption spectrometer

From the comparison between the reference beam and the one passing through the sample, we can deduce the frequencies absorbed by the excitation of molecules in their vibrational energy levels. So, the IR spectrum is recorded.

Sample preparation

1- Gaseous samples; require little preparation beyond purification, but a sample cell with a long path-length (typically 5-10 cm) is normally needed. The walls are of glass or brass.

2- Liquid samples; use solution cells. Two types of solution cells – permanent and demountable. Permanent cell is difficult to clean and can be damaged by water.

Demountable cell is easy to maintain as it can be readily dismantled and cleaned and the windows can be repolished.

3- Solid samples; can be prepared in two ways:

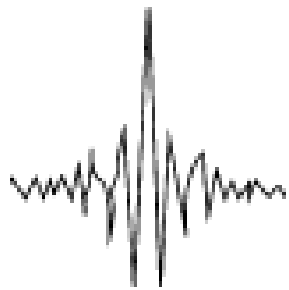
- 1. Crush the sample with a mulling agent (as paraffin oil) in a marble or agate mortar, with a pestle. A thin film of the mull is applied onto salt plates and measured.**
- 2. Grind a quantity of the sample with a specially purified salt (usually potassium bromide) finely (to remove scattering effects from large crystals). This powder mixture is then crushed in a mechanical die press to form a translucent pellet through which the beam of the spectrometer can pass.**

Fourier Transform FT-IR Spectrometer

- A spectrometer is an optical instrument used to measure properties of light over a specific portion of the electromagnetic spectrum, 5 microns to 20 microns.
- FTIR (Fourier Transform Infrared) spectrometer obtains an infrared spectra by first collecting an interferogram of a sample signal using an interferometer, then performs a Fourier Transform on the interferogram to obtain the spectrum.
- An interferometer is an instrument that uses the technique of superimposing (interfering) two or more waves, to detect differences between them. The FTIR spectrometer uses a Michelson interferometer.

■ Interferometer

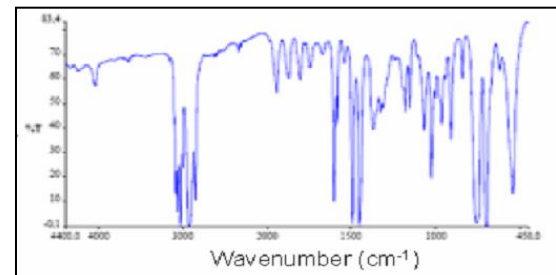
- Special instrument which can read IR frequencies simultaneously.
- faster method than dispersive instrument.
- interferograms are transformed into frequency spectrums by using mathematical technique called Fourier Transformation



interferograms

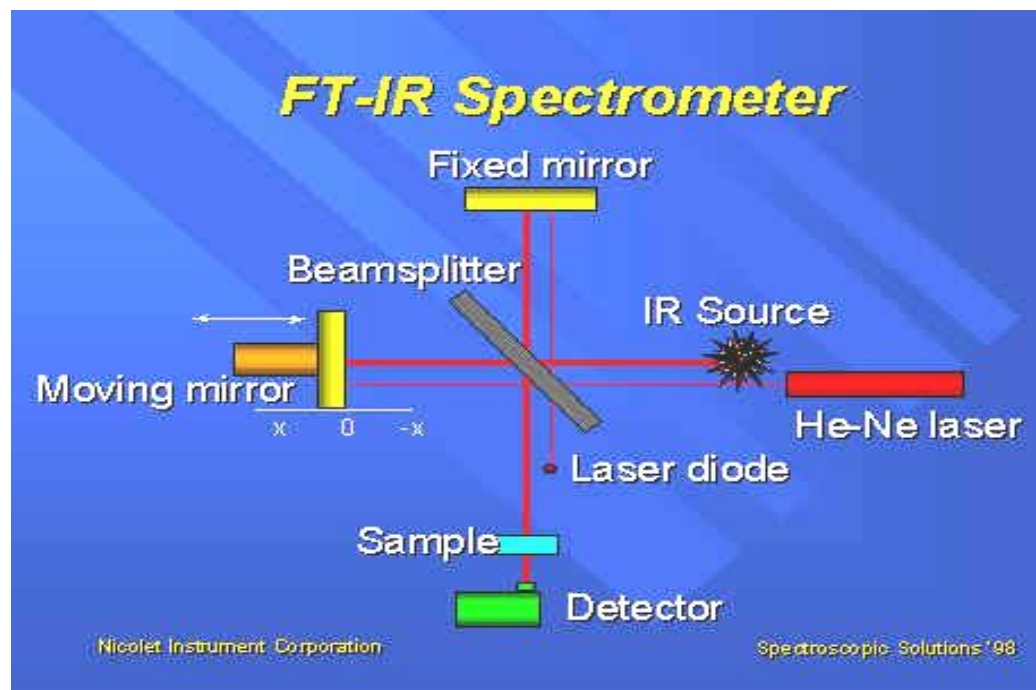
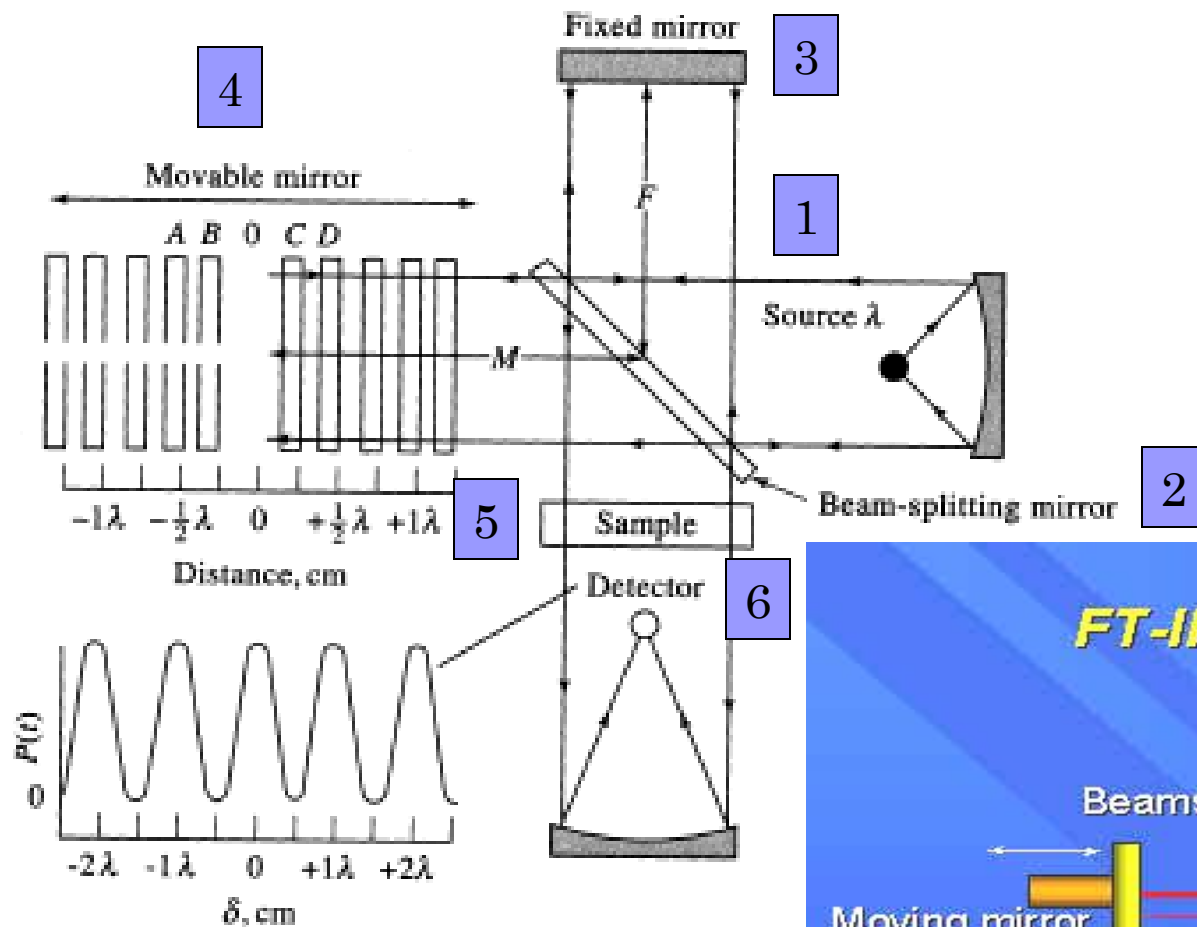


FT
Calculations



IR spectrum

Components of Fourier Transform Instrument



Theory and Instrumentation (contd.)

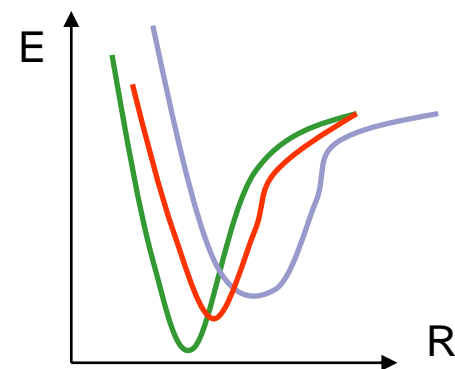
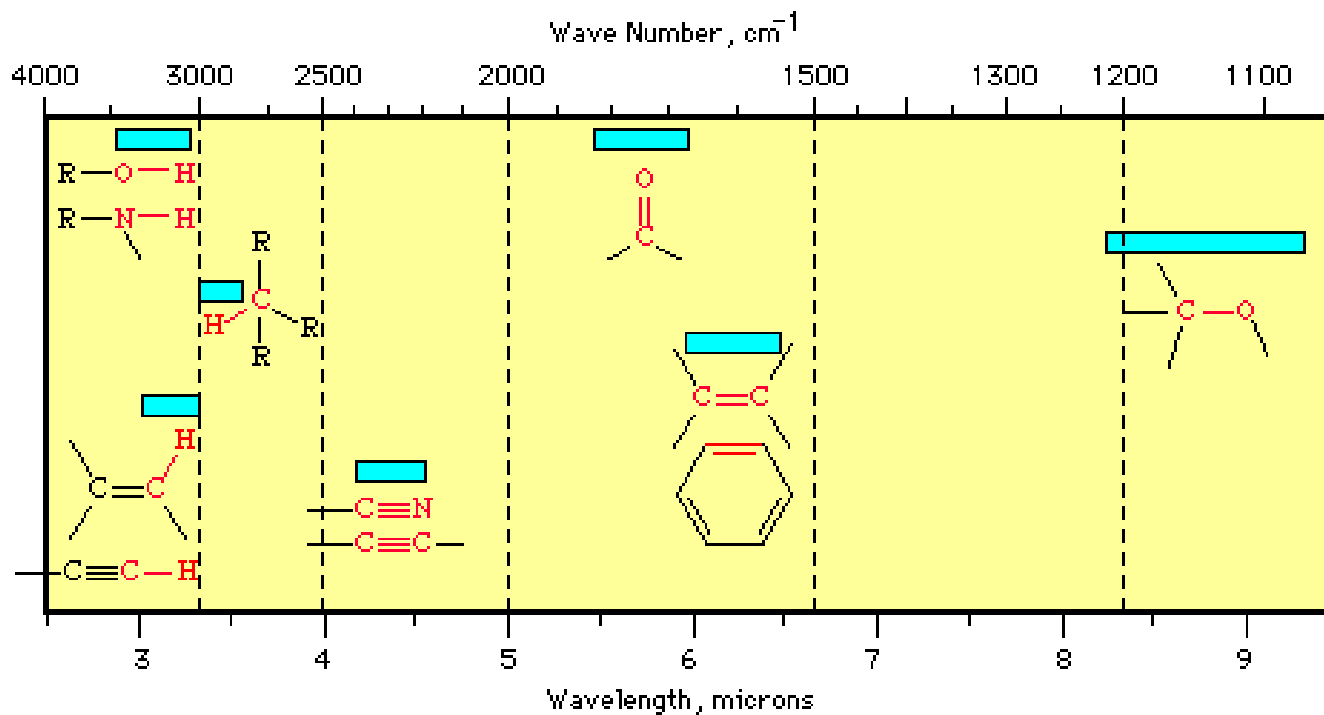
- The light originates from the He-Ne laser
- Half of the light is reflected 90 degrees and hits a fixed mirror, while the other half passes through the beam splitter and hits the moving mirror
- The split beams are recombined, but having traveled different distances, they exhibit an interference pattern with each other
- As they pass through the sample, the detector collects the interfering signals and returns a plot of response vs. mirror displacement known as an interferogram

Advantages of FT-IR (over dispersive instrument)

- high sensitivity**
- high resolution**
- speed of data acquisition (data for an entire spectrum can be obtained in 1 s or less)**

Applications of IR and FT-IR spectroscopy

- Identification of inorganic and organic compounds.
- Identification of components of an unknown mixture.
- Analysis of solids, liquids, and gasses.
- In remote sensing.
- In measurement and analysis of atmospheric spectra.
- Can also be used on satellites to probe the space.
- In Forensic labs. to identify chemicals in samples such as; paints, polymers, coatings, drugs, contaminants, explosive residues.
- Analysis of aircraft exhausts and measurement of toxic gas in fuels, as well as in oil industry.



Vibrational frequency: $\nu_{(\text{C}-\text{C})}$ [700-1200 cm^{-1}] < $\nu_{(\text{C}=\text{C})}$ [1620-1680 cm^{-1}] < $\nu_{(\text{C}\equiv\text{C})}$ [2100-2260 cm^{-1}]

Bond lengths: $R_{e(\text{C}-\text{C})}$ [1.54Å] > $R_{e(\text{C}=\text{C})}$ [1.35Å] > $R_{e(\text{C}\equiv\text{C})}$ [1.20Å]

Bond dissociation energy: $D_{0(\text{C}-\text{C})}$ [368 kJ/mol] < $D_{0(\text{C}=\text{C})}$ [720 kJ/mol] <

$D_{0(\text{C}\equiv\text{C})}$ [962 kJ/mol]

→ $k(\text{C}-\text{C}) < k(\text{C}=\text{C}) < k(\text{C}\equiv\text{C})$