Interaction of Light with Low-Energy Light
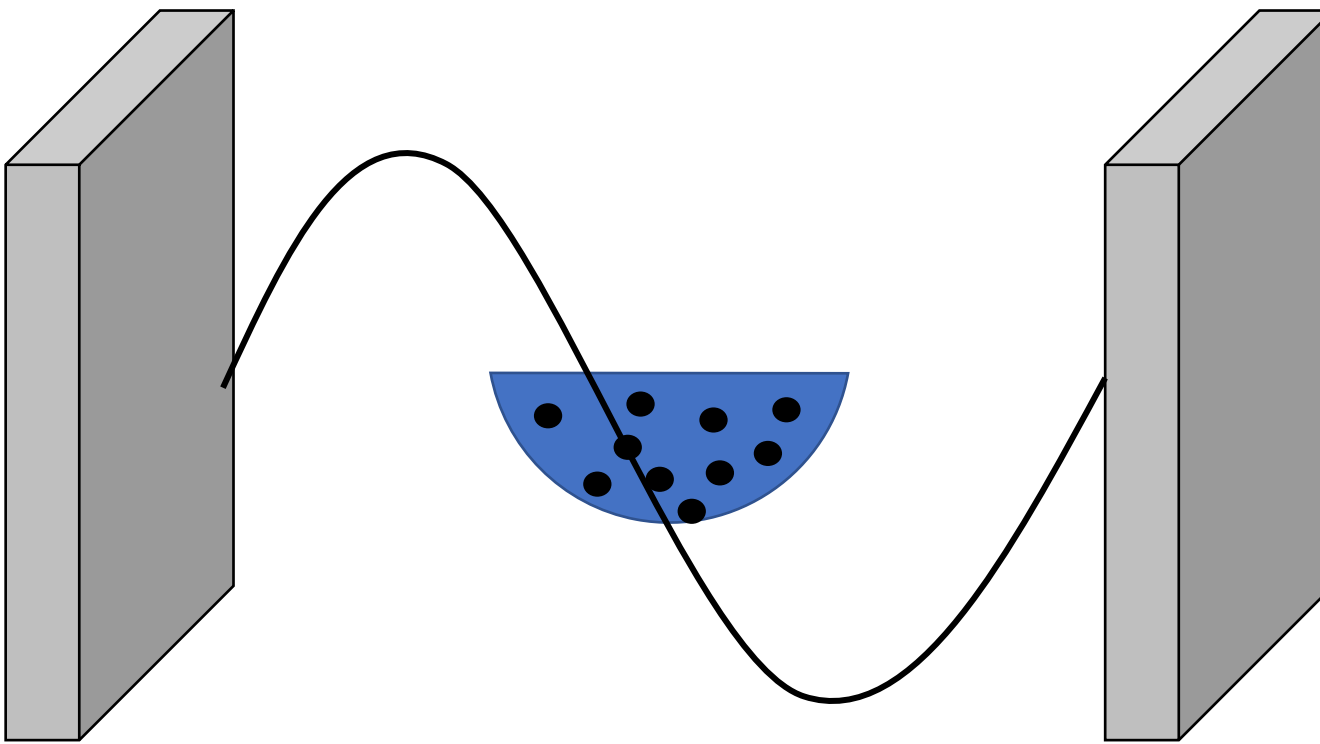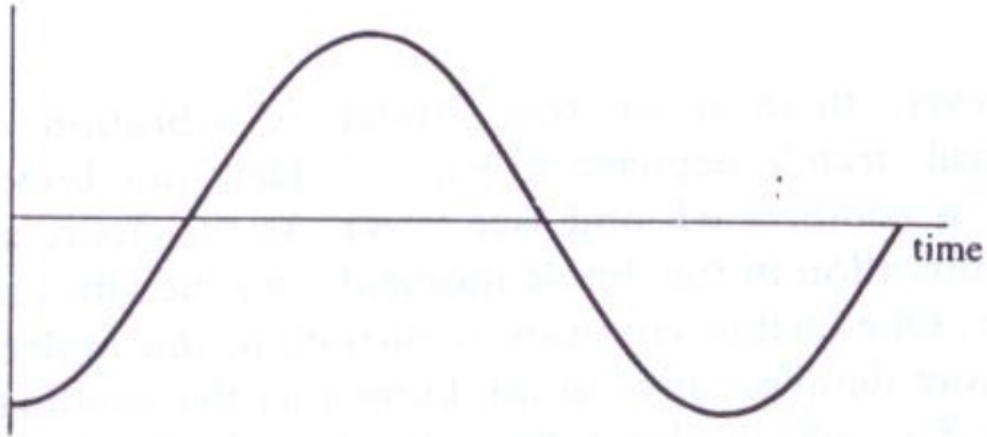
- From the schematic, how do we see the microwave interact with the mole of water ?
  - Water has an Avogadro number of molecules
  - Each molecule interacts with a single photon
  - The molecule gets excited to one of the accessible excited states

Rotation in molecules

An oscillating electromagnetic field

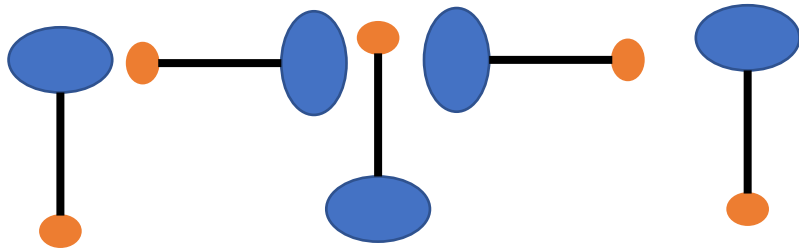A simple molecule with no dipole

O_2, H_2 ...

Molecule with permanent dipole

H-Cl

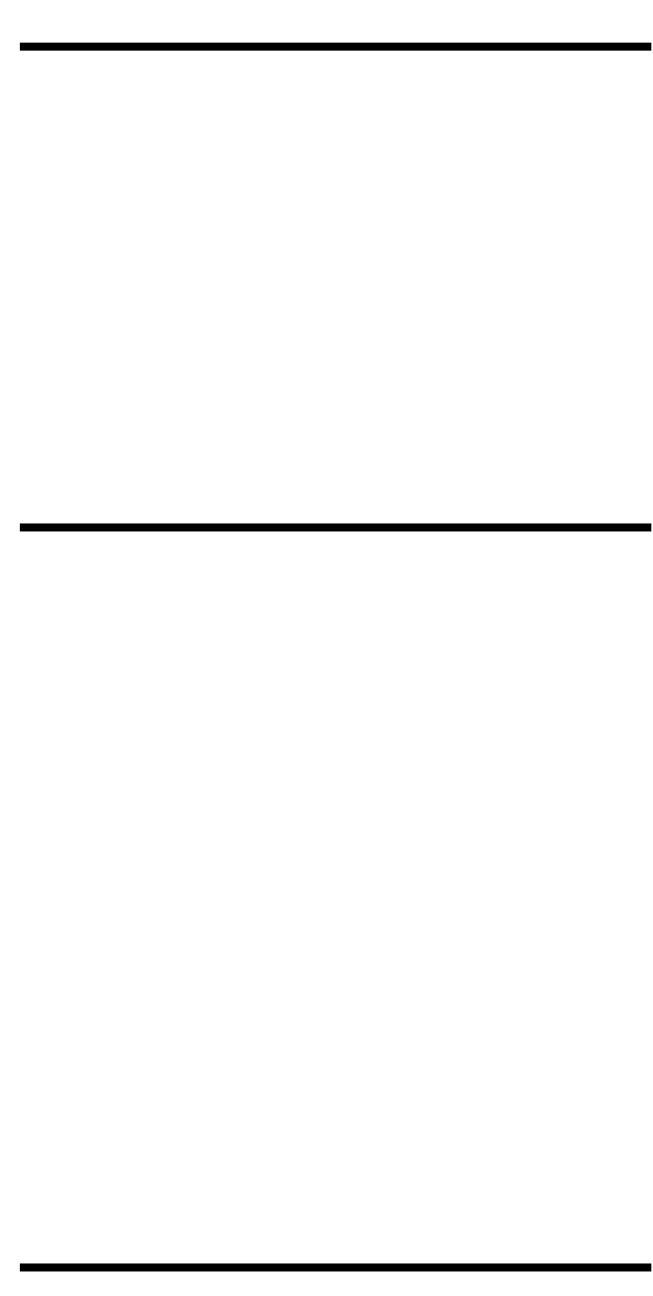Rotation of a polar molecule with the frequency of the incident radiation.

If you have two masses m_1 and m_2

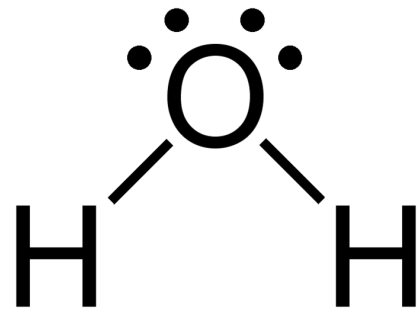Moment of inertia about a point C is given by $I = m_1 r_1^2 + m_2 r_2^2$

Rotational energy levels of a rigid diatomic molecule can be calculated to be $E_J = \dfrac{h^2}{8\pi I} J(J+1)$
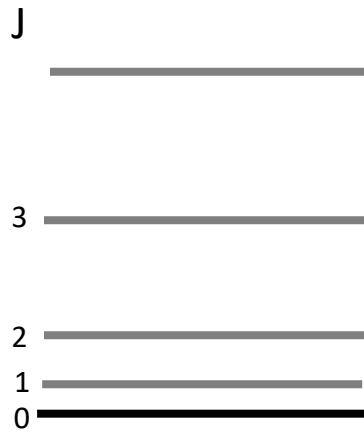
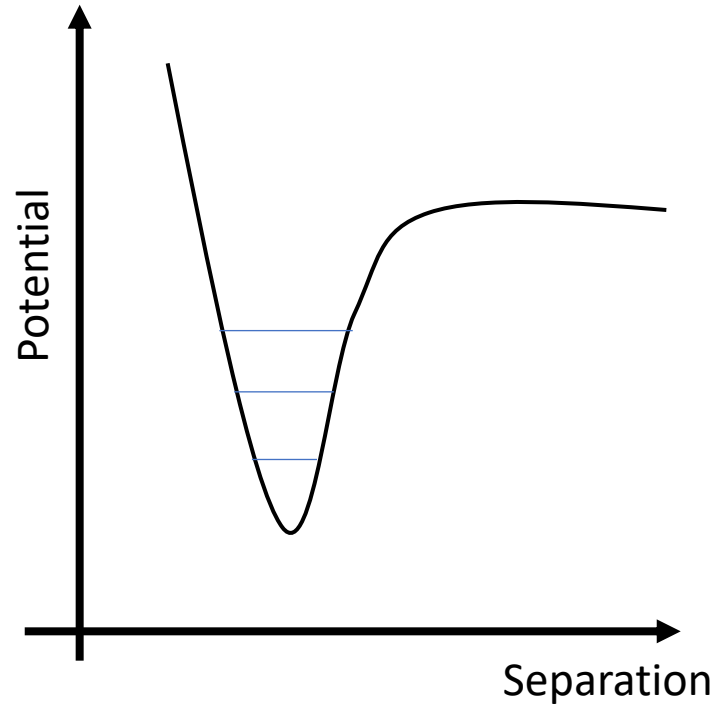Discrete J values leads to quantized rotational states.   J = 0,1,2,....

Rotational transitions with $\Delta J = \pm 1$ are only possible

J

3

2

1

0

Rotational energy levels

Ground State

Electronic energy levels

Vibrational Energy levels

A restoring force acts on molecules separated away from the eq. distance r_{eq}

$$f = -k(r - r_{eq})$$

If this is the force, the potential tends to be parabolic

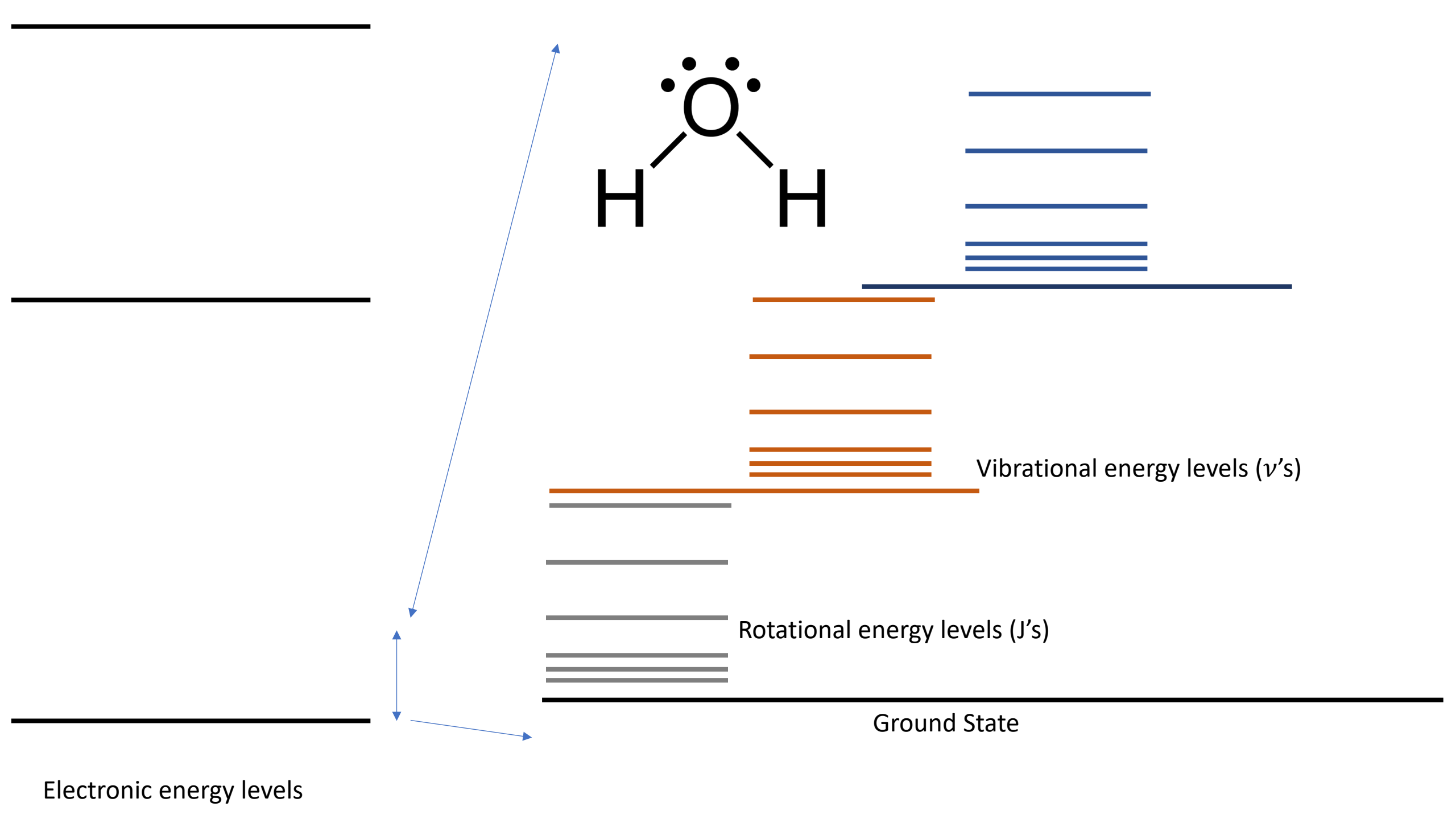$$U = \frac{1}{2}k(r - r_{eq})^2$$

This is a simple harmonic oscillator

The two atoms will vibrate at a frequency

$$\omega = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$

Quite like the rotational system, the vibrational states are also discrete.
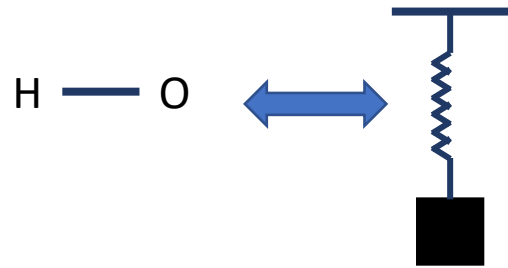
No atom can have 0 vibrational energy!

$$E_v = \left(v + \frac{1}{2}\right)h\omega \qquad v = 0,1,2,3\ldots$$

Vibrational energy levels (ν's)

Rotational energy levels (J's)

Ground State

Electronic energy levels

Characteristic Vibrational Energy levels

Any chemical bond can be represented as a spring

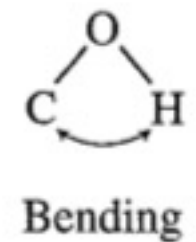H — O ⟷ 〰️▪️ A spring with a strength K, develops a force $F = -Kd$

The spring has natural frequency $\omega = \sqrt{\dfrac{K}{m}}$

Remember, energy can also be written in terms of wavenumber k, with the units of cm^{-1}

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

2150 cm^{-1} 1650 cm^{-1} 1200 cm^{-1}

← *Increasing K*

$C-H$ $C-C$ $C-O$ $C-Cl$ $C-Br$ $C-I$

3000 cm^{-1} 1200 cm^{-1} 1100 cm^{-1} 750 cm^{-1} 600 cm^{-1} 500 cm^{-1}

→ Increasing m

Absorption in a molecule

- An isolated molecule/large well-defined phase/long chain
  - All have characteristic bonding between constituent atoms

- Each atomic bond has well defined states
  - Rotational
  - Vibrational
    - Stretching – symmetric, asymmetric
    - Bending – scissoring, rocking, wagging, twisting
  - Electronic transition

C—H

Stretching

O
C   H

Bending

If a photon of energy matching the energy difference is provided, an excited state reached in which the bonds either vibrate/rotate

Typical energy scales:

Rotation - 1- 20 cm^{-1}, Vibration – 2000 – 4000 cm^{-1}, Electronic - 10000 – 50000 cm^{-1}

Types of Vibrations

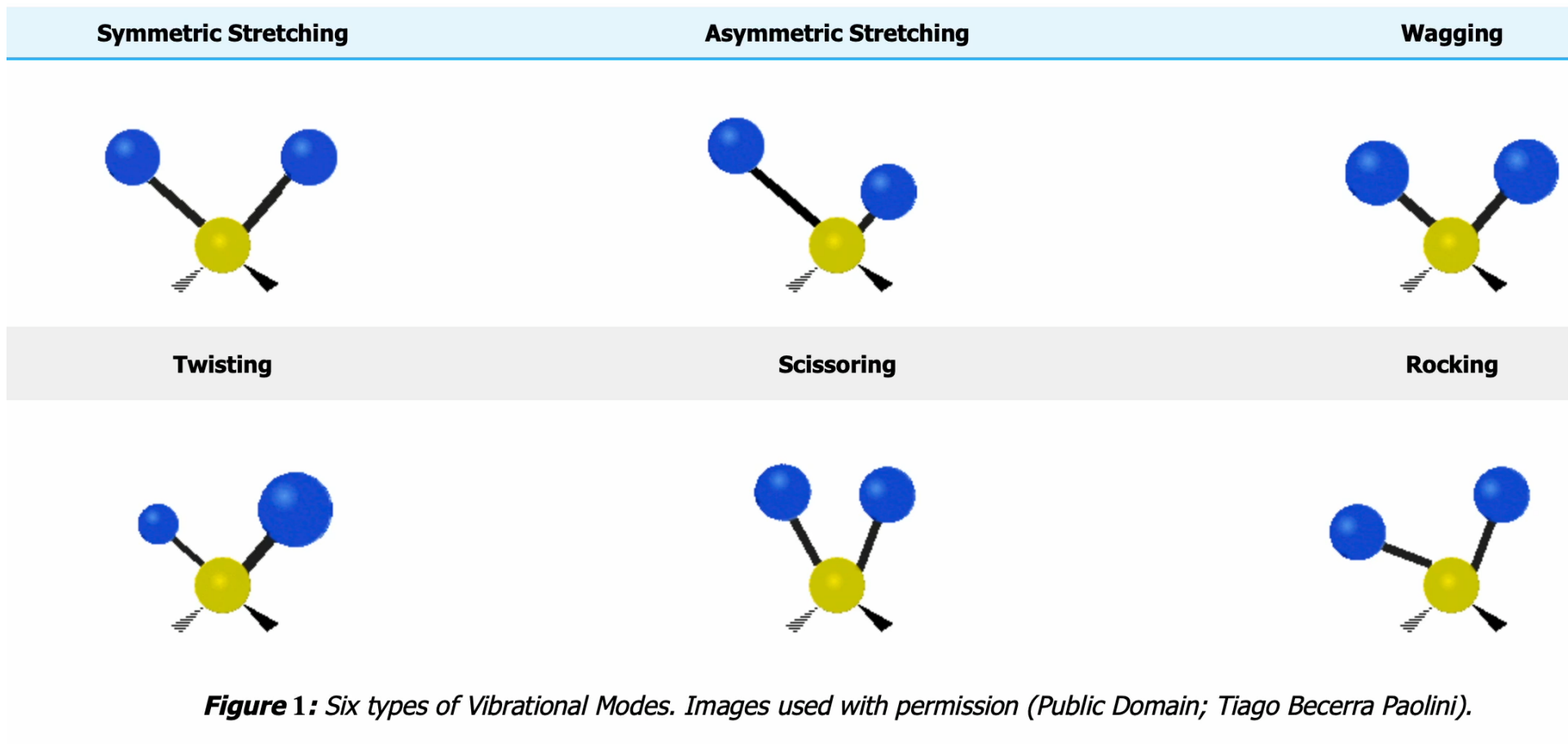| Symmetric Stretching	Asymmetric Stretching	Wagging
Twisting	Scissoring	Rocking

Figure 1: *Six types of Vibrational Modes. Images used with permission (Public Domain; Tiago Becerra Paolini).*

Vibrational Modes and Selection Rules
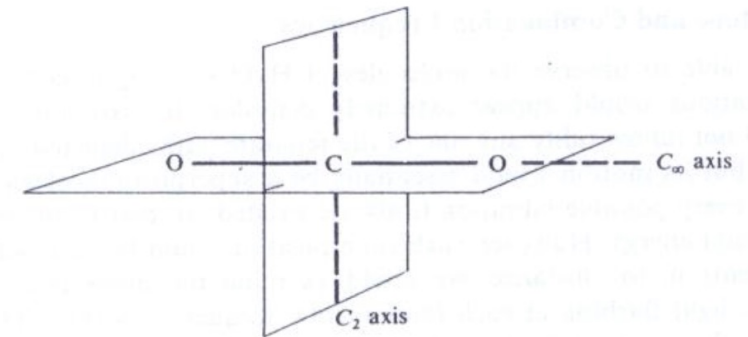
If a molecule has N atoms:

    -> If we are worried only about translational in 3D world, DOF = 3 * N

    -> If molecules are bonded, then some of the translations become rotational (because of constraints)
        - Any rotation can be described by 3 rotational axes.
        - So total DOF = 3*N – 6 (3 rotational DOF x 2 chirality)

    -> However, if the molecule is linear, then rotational along the linear axis leaves the molecule unchanged.
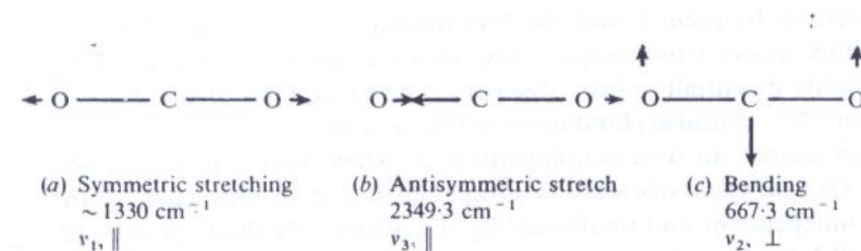
      - so DOF = 3*N - 5

So, how many vibrational modes for CO_2 ?

$$3 * 3 - 5 = 4$$
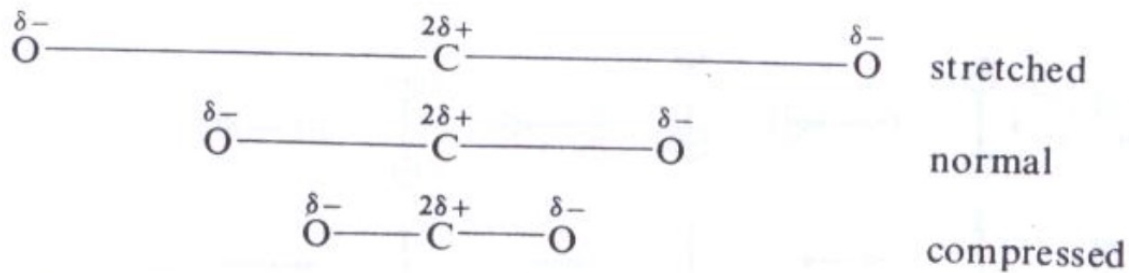
For methane :

$$3 * 5 - 6 = 9$$

C_∞ axis

C_2 axis

(a) Symmetric stretching
~1330 cm^{-1}
v_1, ||

(b) Antisymmetric stretch
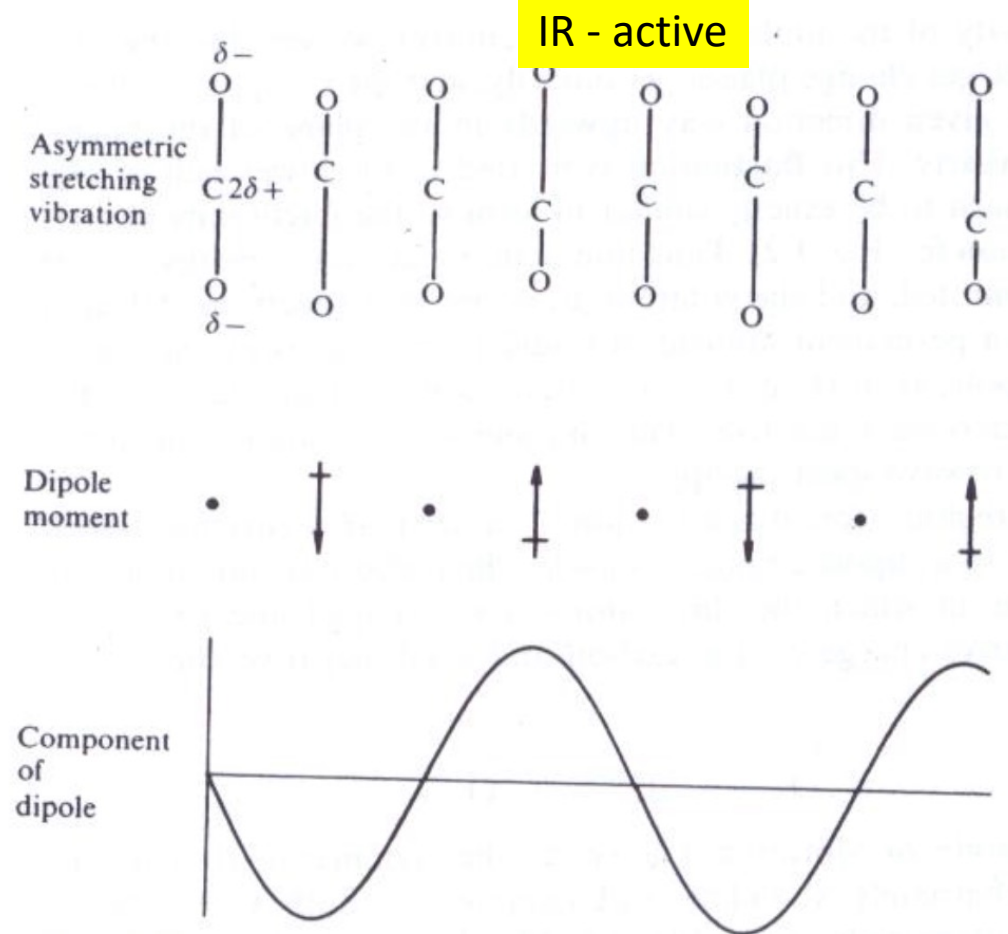2349·3 cm^{-1}
v_3, ||

(c) Bending
667·3 cm^{-1}
v_2, ⊥

Selection Rule for IR activeness

- A vibration is said to be IR-active if dipole moment changes during the vibration.
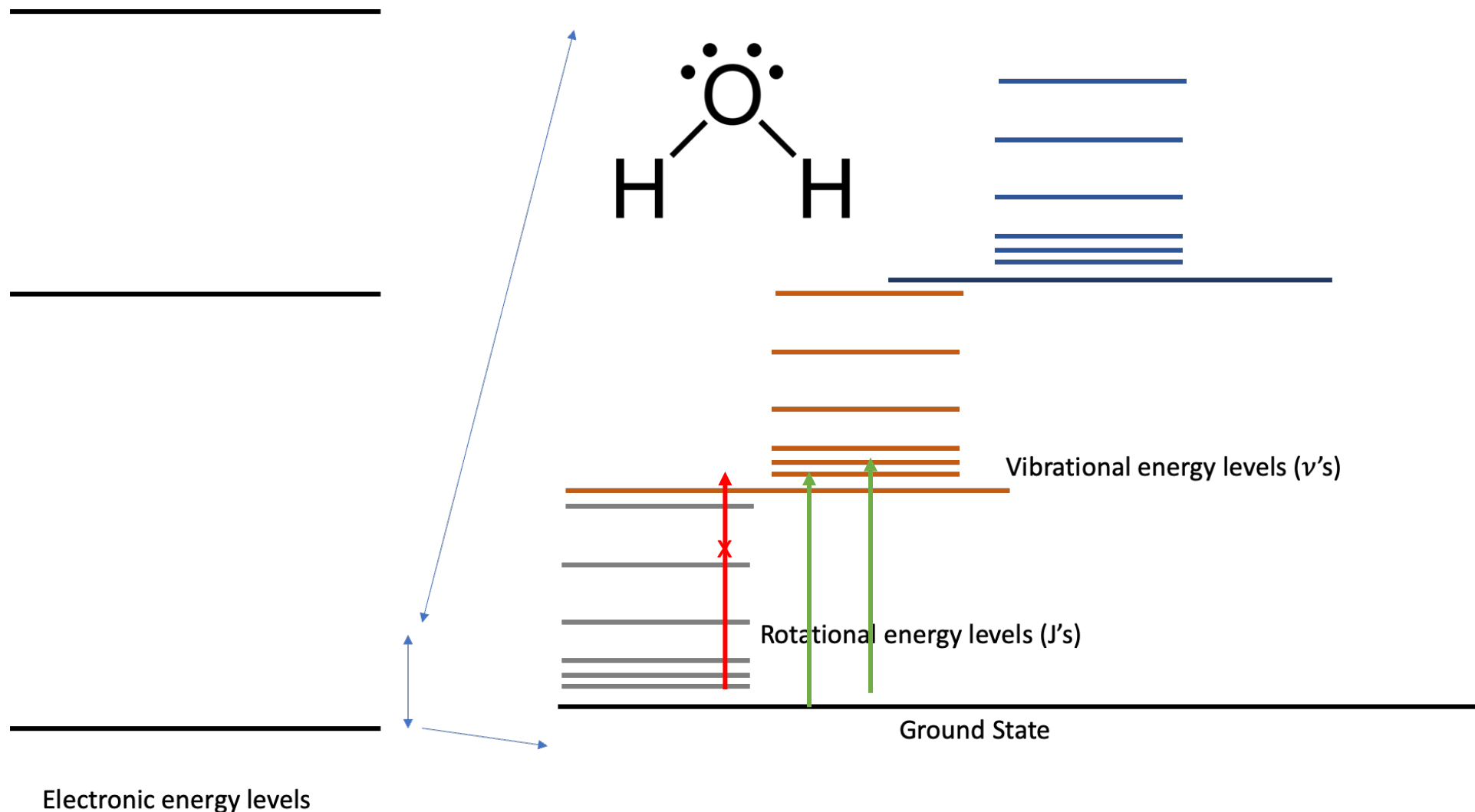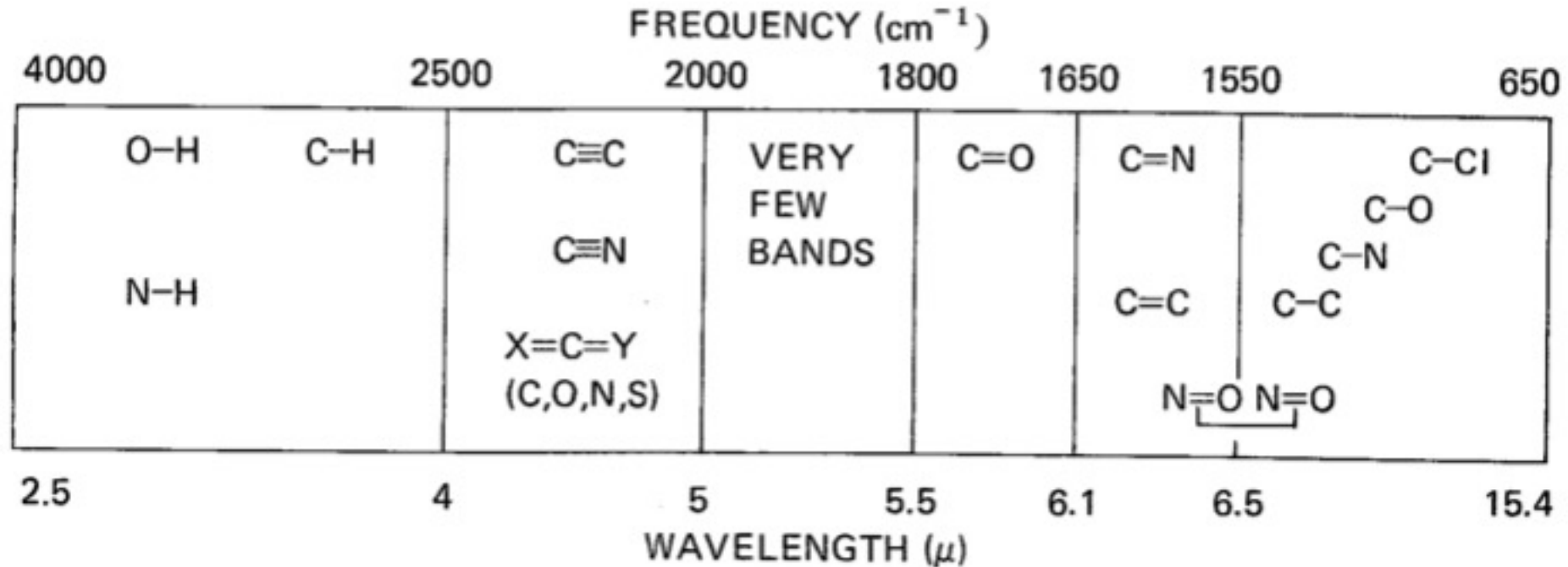
Selection Rule:

This means, you cannot have a vibrational energy change without rotation.

$$\Delta v = \pm 1 \text{ and } \Delta J = \pm 1$$

Vibrational energy levels (v's)

Rotational energy levels (J's)

Ground State
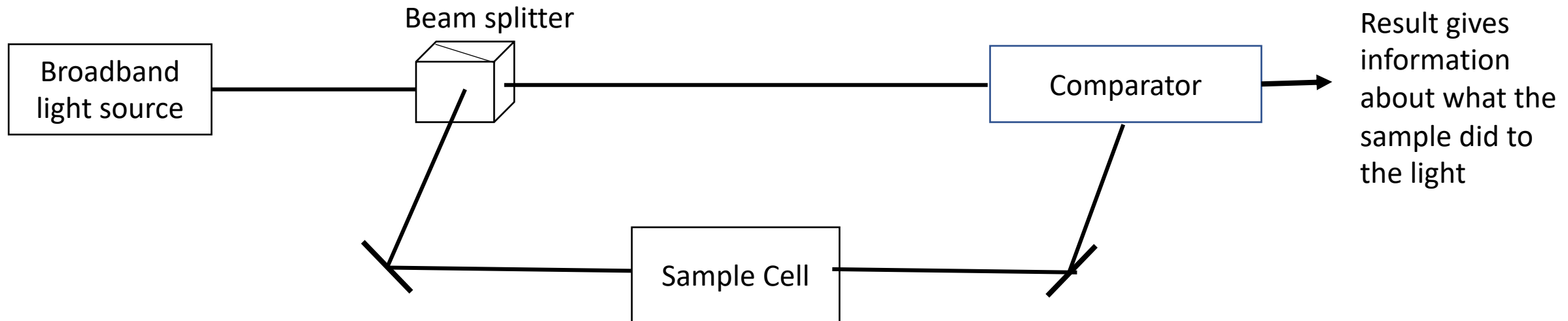
Electronic energy levels

Infrared spectroscopy

- Most common bonds have characteristic frequencies between 2.5 – 25 μm
- This lies in electromagnetic spectrum called Infra-red (infra – meaning lower/below)

General Idea of Spectrometer

Beam splitter

Broadband light source

Comparator

Result gives information about what the sample did to the light
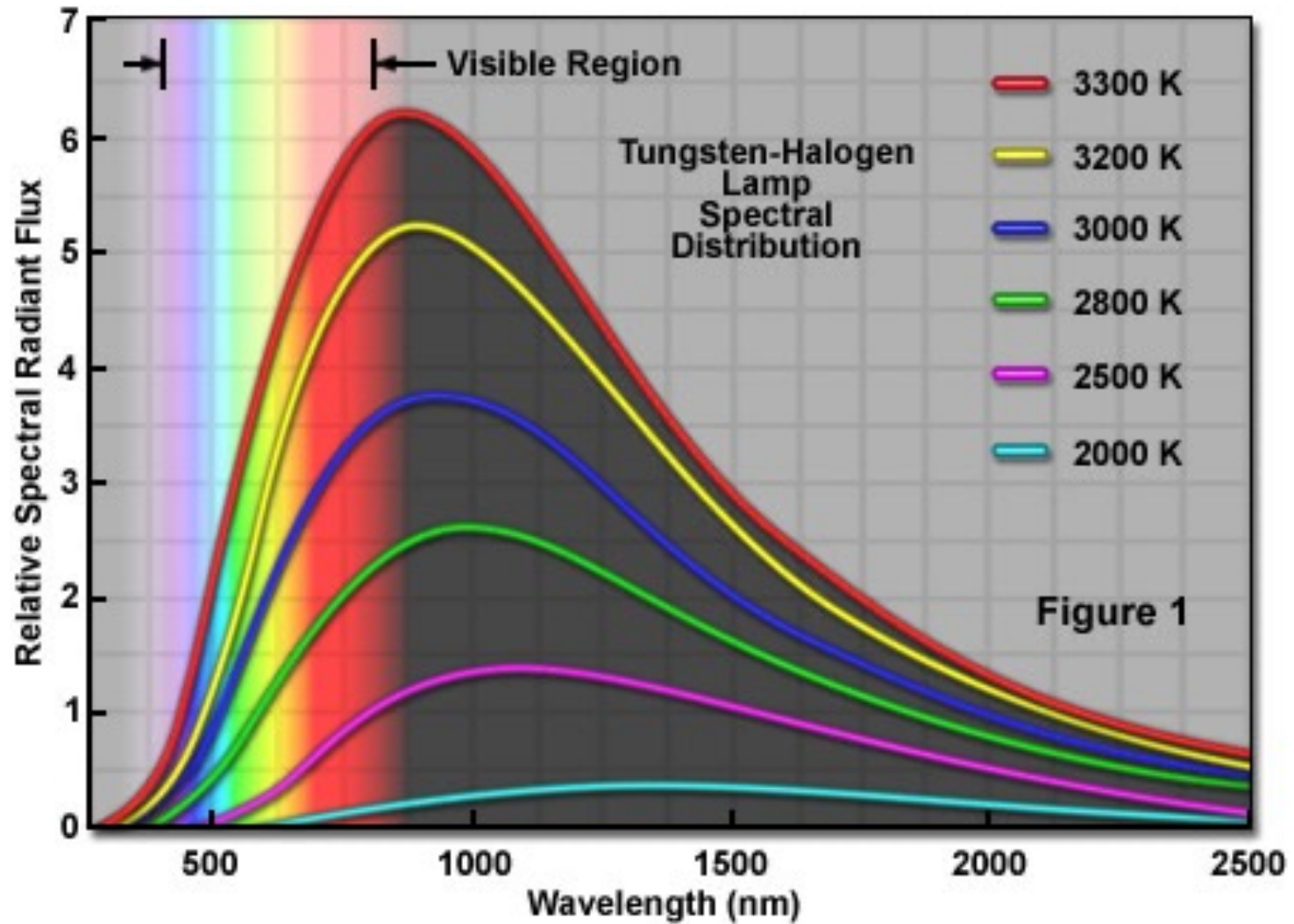
Sample Cell

Broadband light: A electromagnetic source which has many wavelength contributions. Eg: Tungsten bulb.

A typical specification of this source is its intensity distribution vs wavelength

Black-Body Radiation

Eg: Tungsten halogen lamp

Homework: Get the solar spectrum plot! How does it compare with the T-H lamp and why ?

Design of Absorption cell - Beer-Lambert Law

- If I_R is the intensity of the reference, and I_S is the intensity of the light through the sample cell, the % transmittance is given by

$$T = \frac{I_S}{I_R} * 100$$

From theory, transmittance through a sample is given by

$$T = e^{-\tau} = 10^{-A}$$

Where τ is called as optical path, A is called as absorbance.

Absorbance is dependent on specific details of sample cell. So, we use Beer-Lambert law which is given by
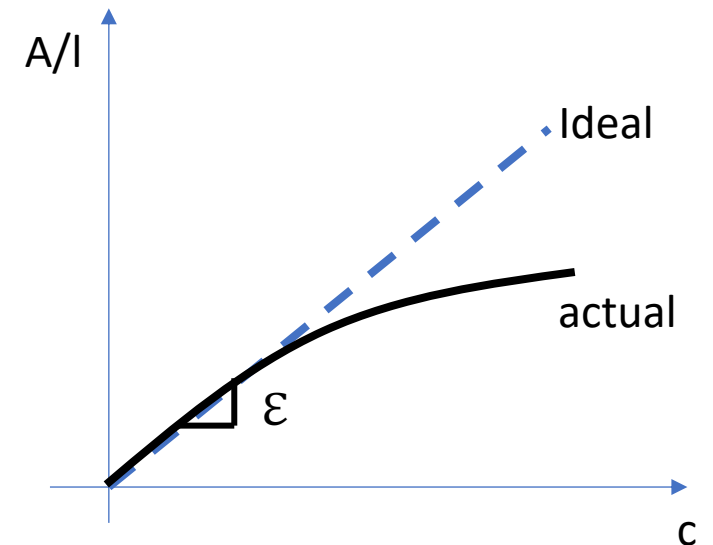
$$A = \epsilon l c$$

l – optical path length
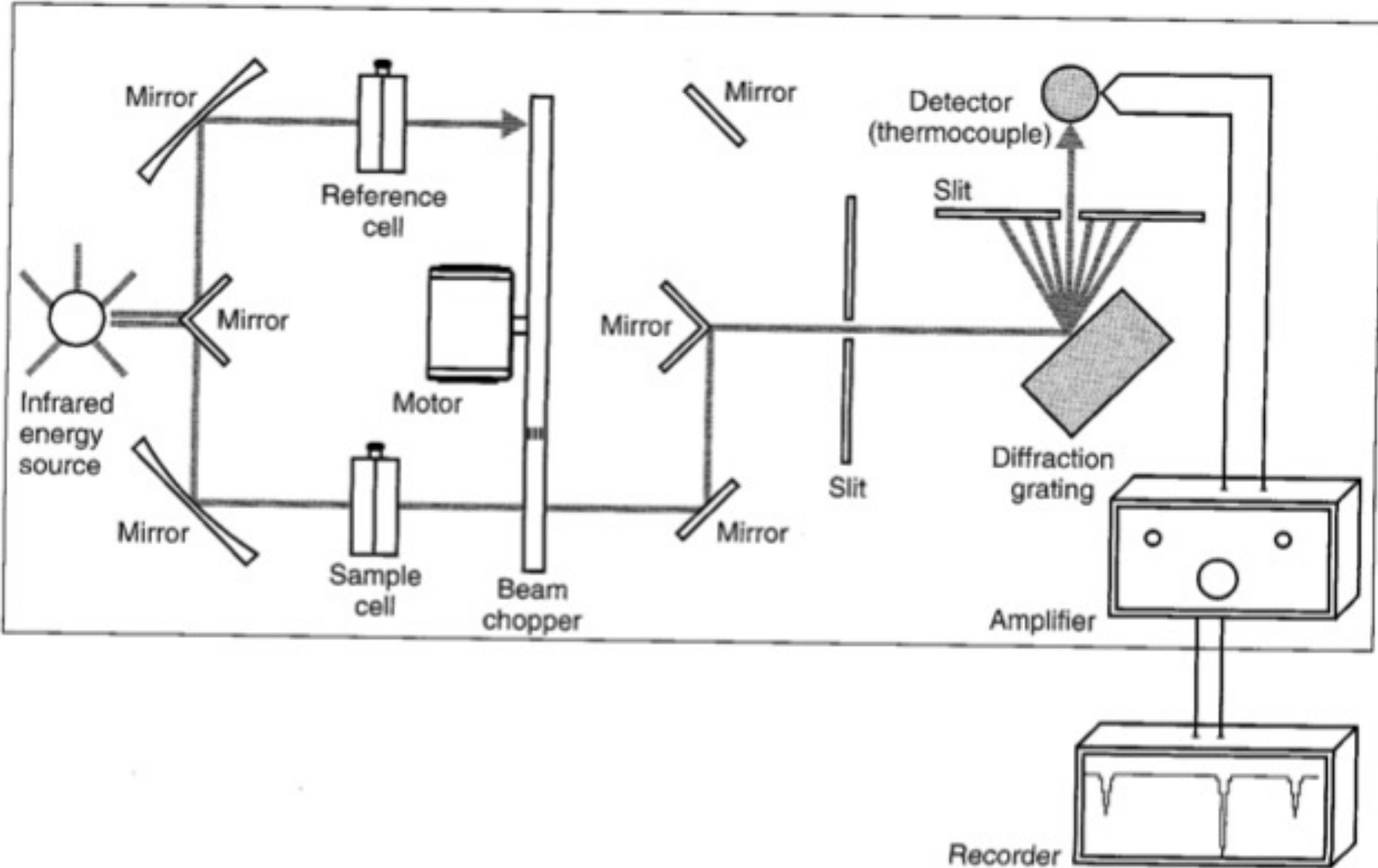
c – concentration of the absorbing species

Ɛ - molar attenuation coefficient or absorptivity

Properties of Absorbance

- Absorbance is additive
  - A mixture of n components has total absorbance $A_T = \sum_i A_i$
  - Extent of linearity
  - Absorptivity depends on lot of factors
    - Polarizability and rate of polarizability
    - Interaction cross-section
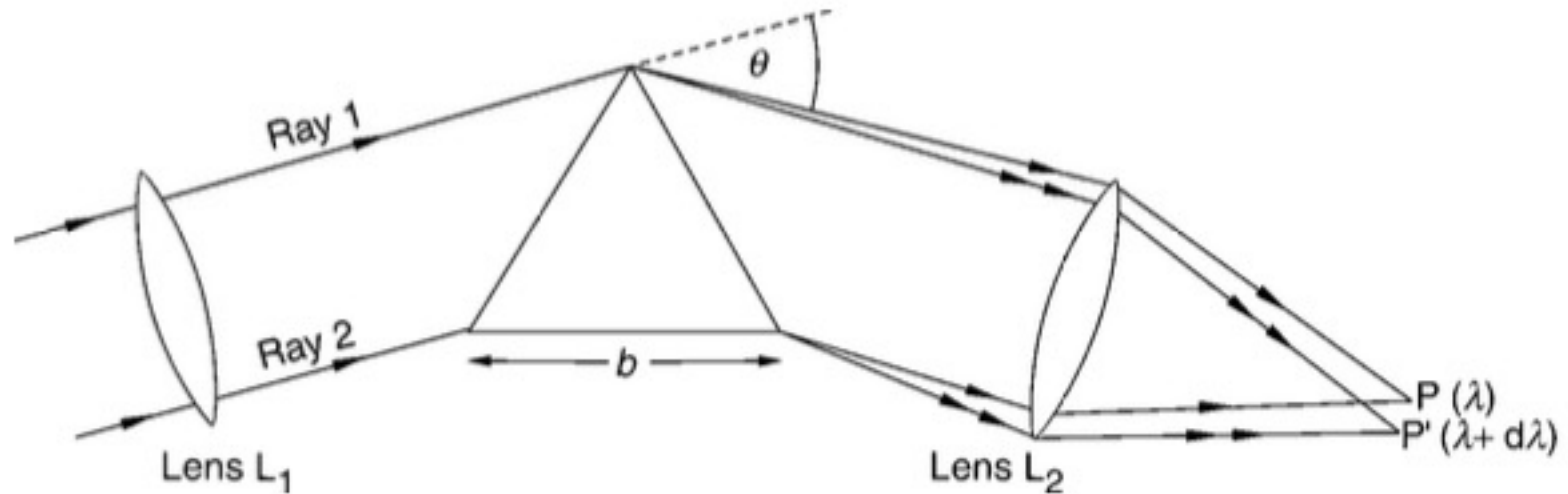   - Energy levels and correlation with energy of photon

A simple setup

Dispersing Element

• Disperse: Separate in space light with differing wavelength

Simplest method: A prism with base 'b'

If we assume the light is incident on an entire face as shown in the figure,
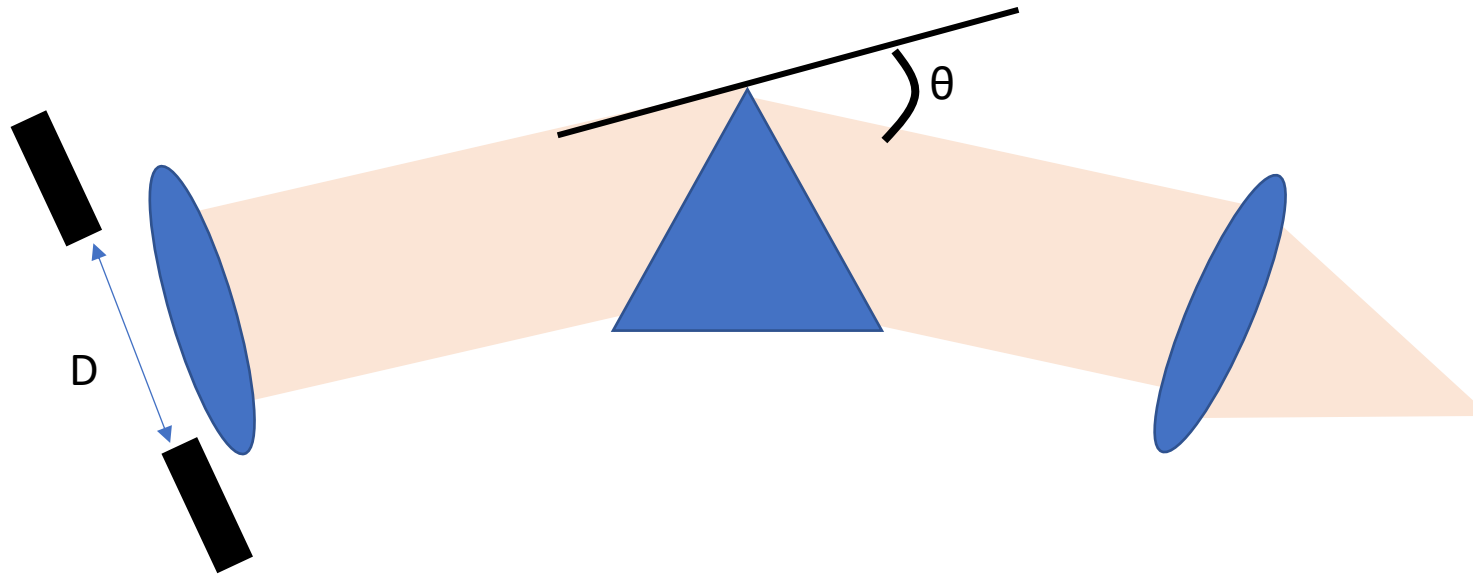
n – refractive index of the material.

We define dispersion power/wavelength resolution as R

$$R = \frac{\lambda}{d\lambda}$$

Where $d\lambda$ is the smallest change in wavelength that is visibly separated.
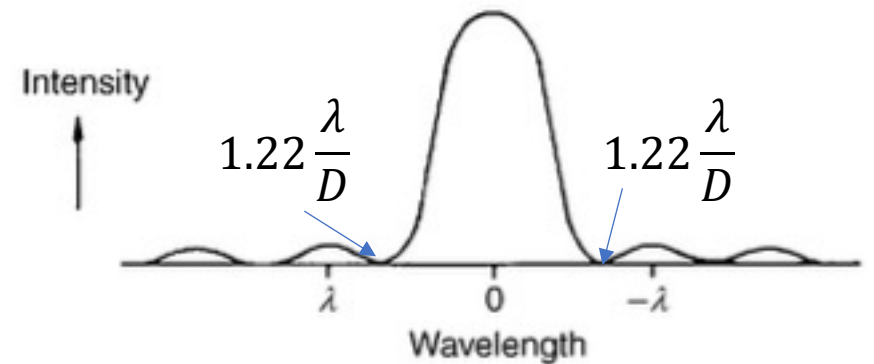
How small can the light be focused ?

θ

D

- Limit of visible separation of two light spots is given by Rayleigh's criteria:

If the light is obtained from a slit of width 'D', then the first minima in the Airy disk formed by the focused light is obtained at angle $\theta = \frac{1.22\lambda}{D}$

Intensity

$1.22\frac{\lambda}{D}$

$1.22\frac{\lambda}{D}$

λ

0

−λ

Wavelength
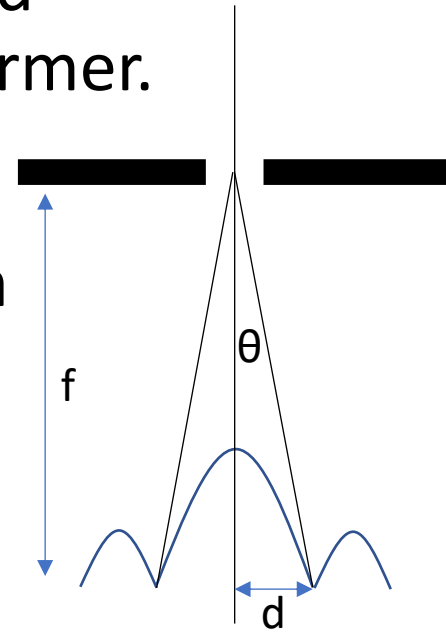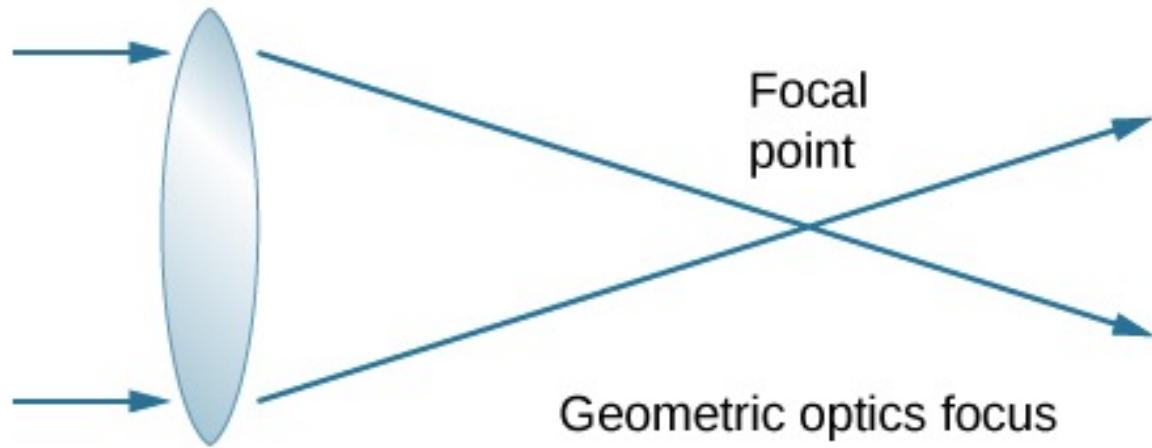
What is visible separation ?

Lord Rayleigh: Two Airy disks can be resolved if they are separated such that the maxima of one co-incides with the minima of the former.

If f is focal length of the lens, interparticle separation at maximum resolution is given by

$$d = f * \tan \theta$$

In small angle approximation $d = f\theta = \dfrac{1.22\lambda f}{D}$

Focal point

Geometric optics focus

(a)

Focal region

Wave optics focus

(b)

- The point is broadened by the size of the disk as calculated before

$$R = 1.22 \frac{\lambda f}{D}$$

We define a term Numerical aperture NA as the acceptance angle of a lens

$$NA = n \sin \alpha$$

By simple trigonometry, we get $R = 1.22 \frac{\lambda}{2 \tan \alpha} = 1.22 \ \frac{\lambda}{2 \sin \alpha} = 0.61 \frac{\lambda n}{NA}$

Microscope
Objective

Acceptance
angle θ

D

θ

α

f

P

- Prism dispersion = $\dfrac{d\theta}{d\lambda}$
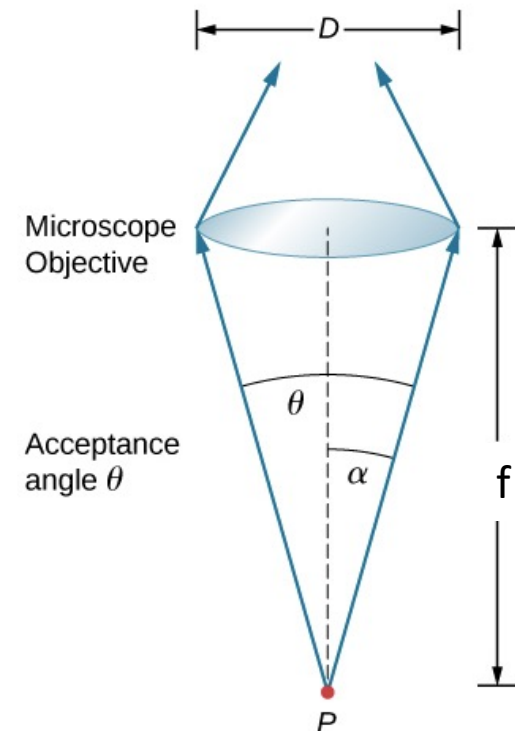
Finally, the prism dispersion also depends on $\dfrac{d\theta}{dn}\dfrac{\color{red}{dn}}{\color{red}{d\lambda}}$

Glass prisms are not great for IR radiations as the index rarely changes in the IR region!

Diffraction Grating

0th order diffraction   1st order diffraction

If we have a periodic structure such as one shown below:

With a period 'd'
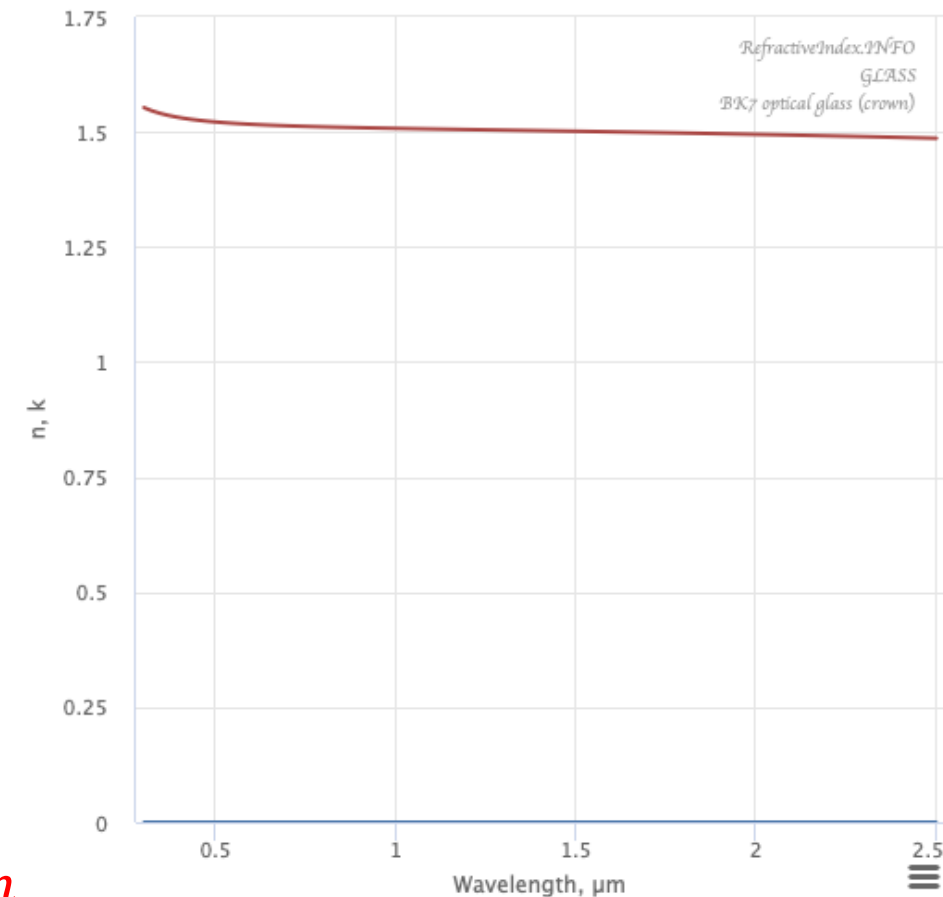
Total path difference between the two radiations: $OA - O'A' = d \sin \theta_r + d \sin \theta_i$

As before, we get constructive interference when the path length is equal to integer multiples of λ

$$d \left(\sin \theta_r - \sin \theta_i \right) = n\lambda$$

If the incident angle is 90°, the equation simplifies to $d \sin \theta_r = n\lambda$

White light incidence on diffraction grating

1st order diffraction

0th order diffraction

1st order diffraction

Consider normal incidence

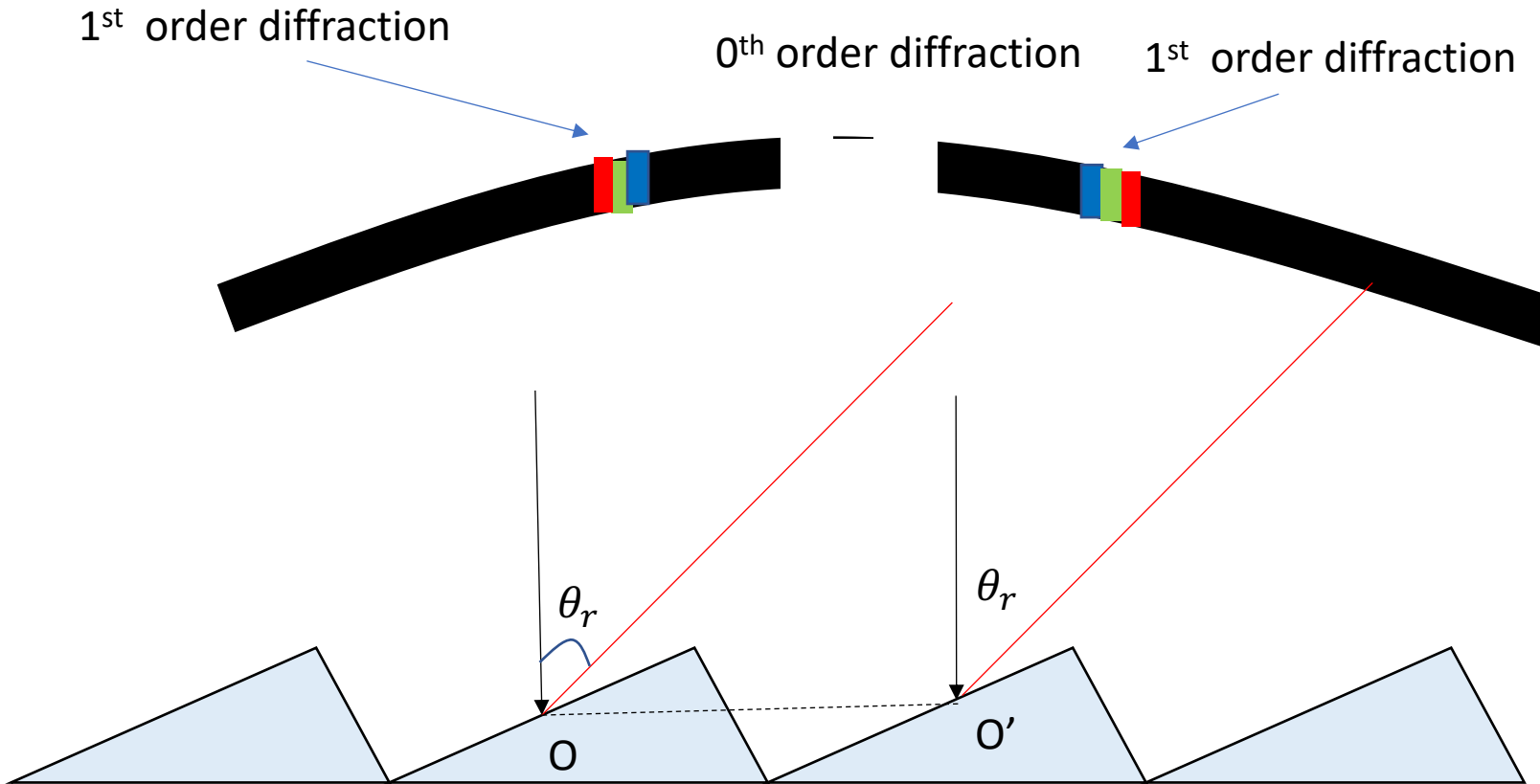$$d \sin \theta_r = n\lambda$$

0th order, the beams with different wavelengths does not have angular separation.

So, a bright white spot is obtained.

For the first order, when n = 1,

The dispersion

$$\frac{d\theta_r}{d\lambda} = \frac{n}{d \cos \theta_r}$$

θ_r

θ_r

O

O'

Higher dispersion is observed, when smaller 'd' is taken;

However, also remember, that no solution for constructive interference can be obtained when d < λ

Better dispersion can also be obtained when we take higher orders;
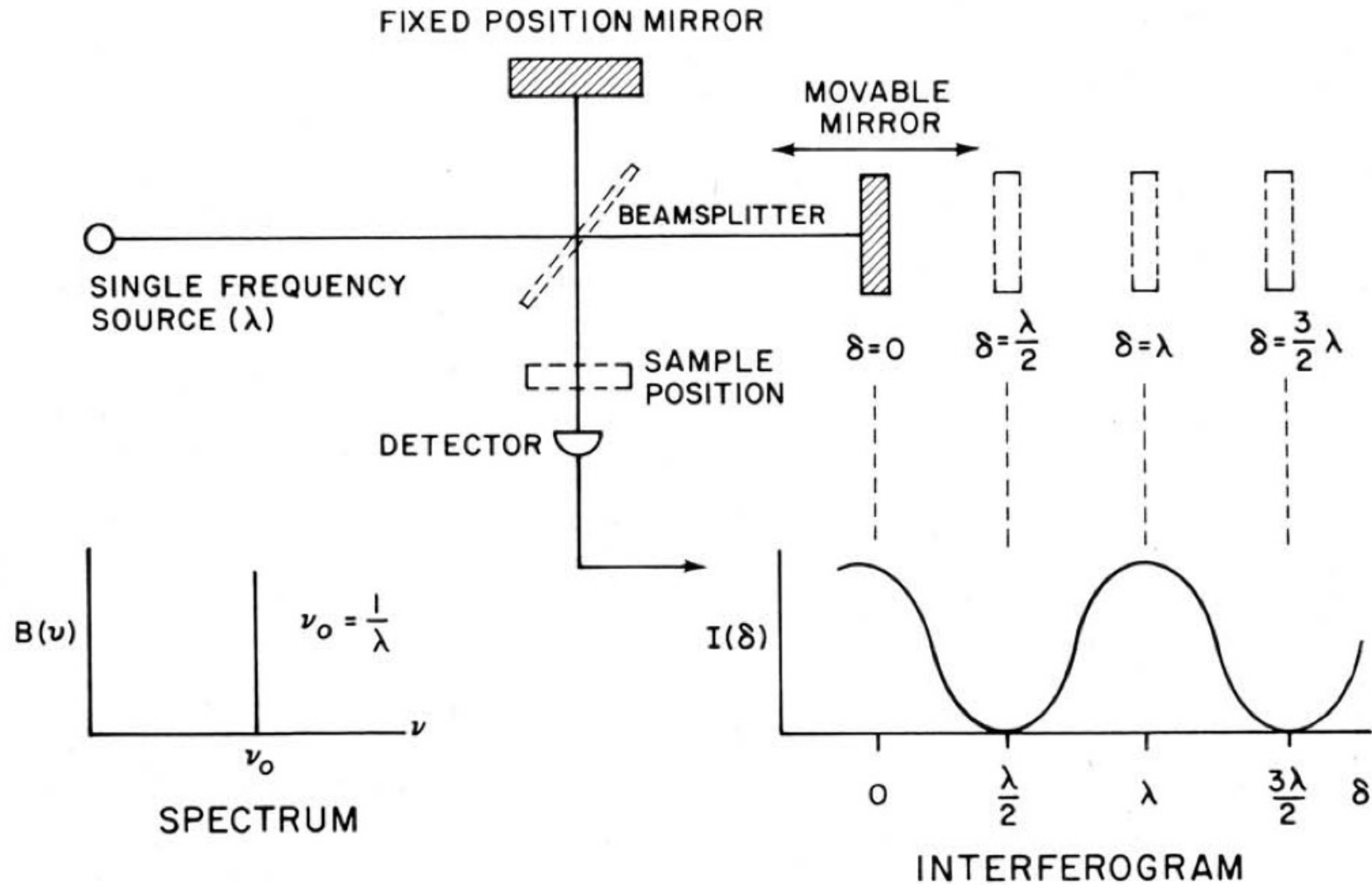
However, this has two fold problems:

     1. The light intensity is significantly lower in higher orders

     2. There will be significant overlap between the orders

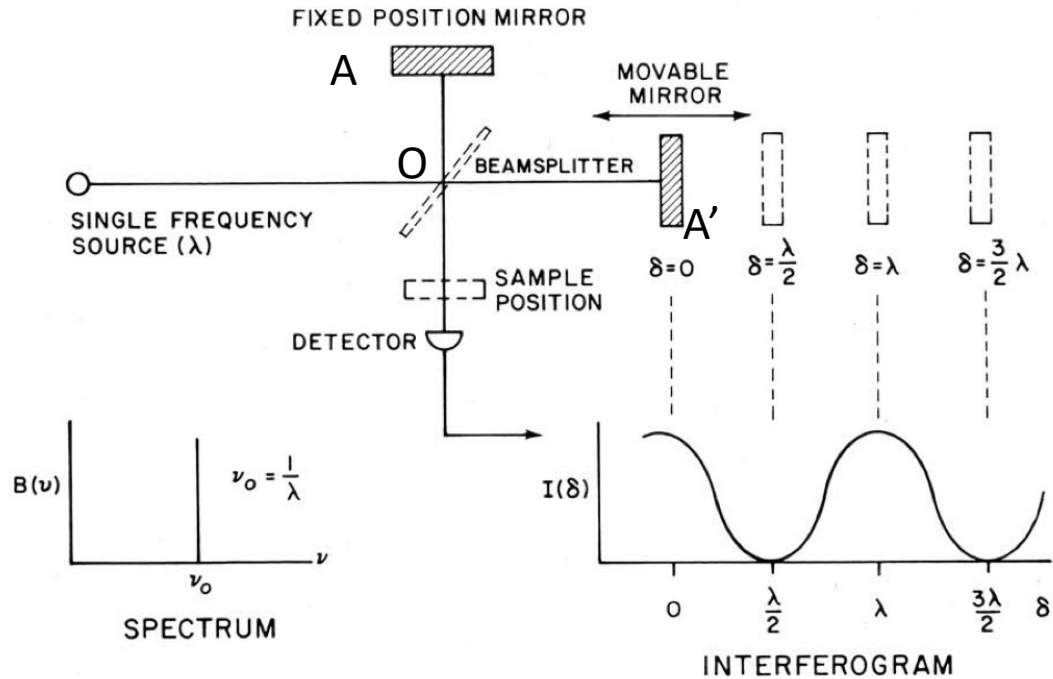General sources are weak in this part of spectrum   Solution is therefore FTIR

Detectors are weak.

Michelson Interferometer

Michelson Interferometer

FIXED POSITION MIRROR

A

MOVABLE MIRROR

O BEAMSPLITTER

SINGLE FREQUENCY SOURCE (λ)

A'

SAMPLE POSITION

DETECTOR

$\delta = 0$ $\delta = \frac{\lambda}{2}$ $\delta = \lambda$ $\delta = \frac{3}{2}\lambda$

$B(\upsilon)$ $\upsilon_0 = \frac{1}{\lambda}$

υ

υ_0

SPECTRUM

$I(\delta)$

O $\frac{\lambda}{2}$ λ $\frac{3\lambda}{2}$ δ

INTERFEROGRAM

Light is split at point O into two paths.

First one with fixed mirror

Second one with a movable mirror.

Constructive interference, when the total path difference is an integer multiple

Lets define $\delta = OA - OA'$

If the source is a monochromatic (single wave)

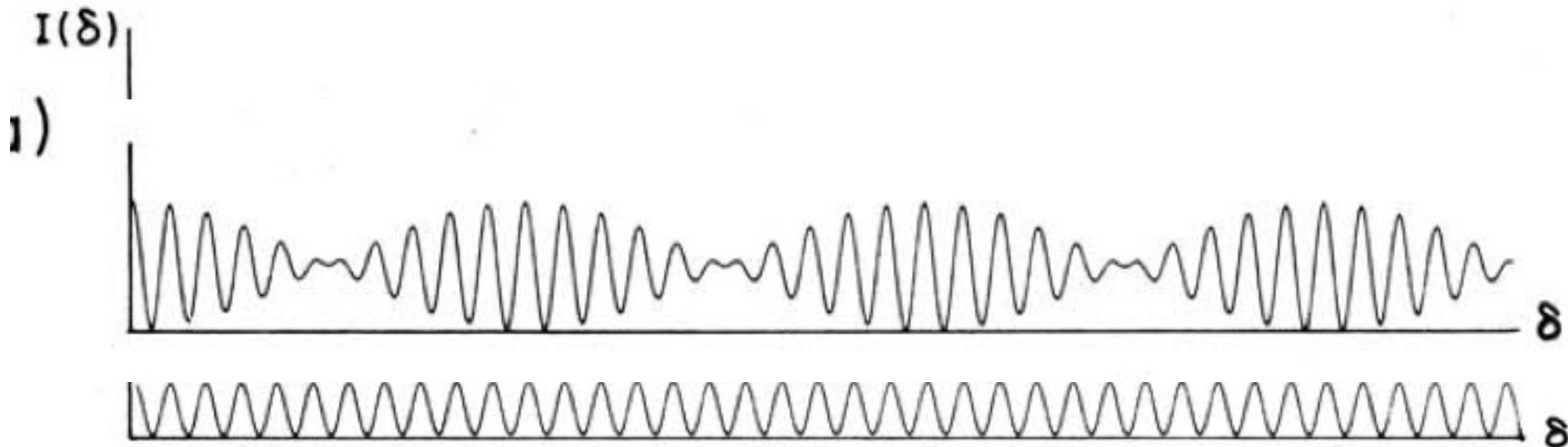It can be proved that the intensity of the wave at the detector: $I \; \alpha \; B[\cos k\delta]$ <mark>HW</mark>

Where $k = \dfrac{2\pi}{\lambda}$

W. D. Perkins *Journal of Chemical Education* **1986** *63* (1), A5

Interferometer with many colors:

- Lets say, if the interferometer is made incident with light with many colors.

- The different colors do not interfere. So, the net intensity is given by

$$I(\delta) = \sum_{\lambda_i} B(\lambda_i) \cos\frac{2\pi\delta}{\lambda_i}$$

If we have a continuum of wavelengths, we can use the 'chemist' notations for wavenumber $\bar{v} = \frac{1}{\lambda}$

$$I(\delta) = \int_0^{\bar{v}} B(\bar{v}) \cos 2\pi\delta\bar{v} \ d\bar{v}$$
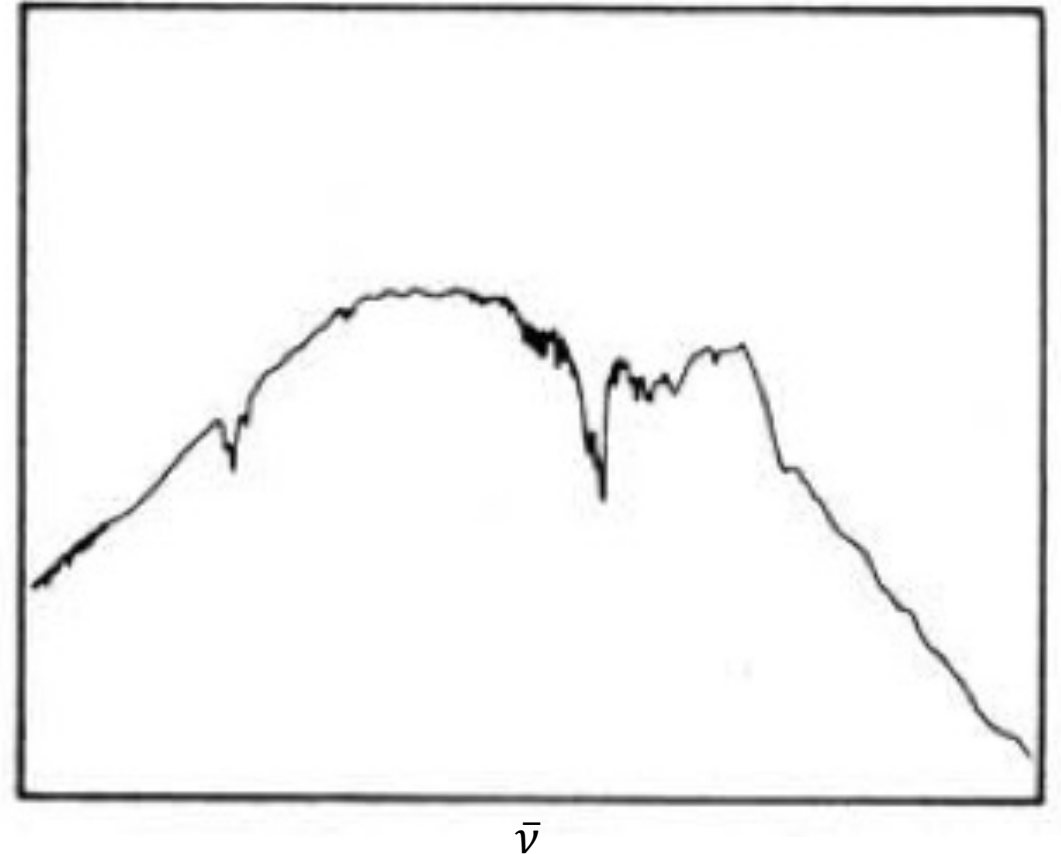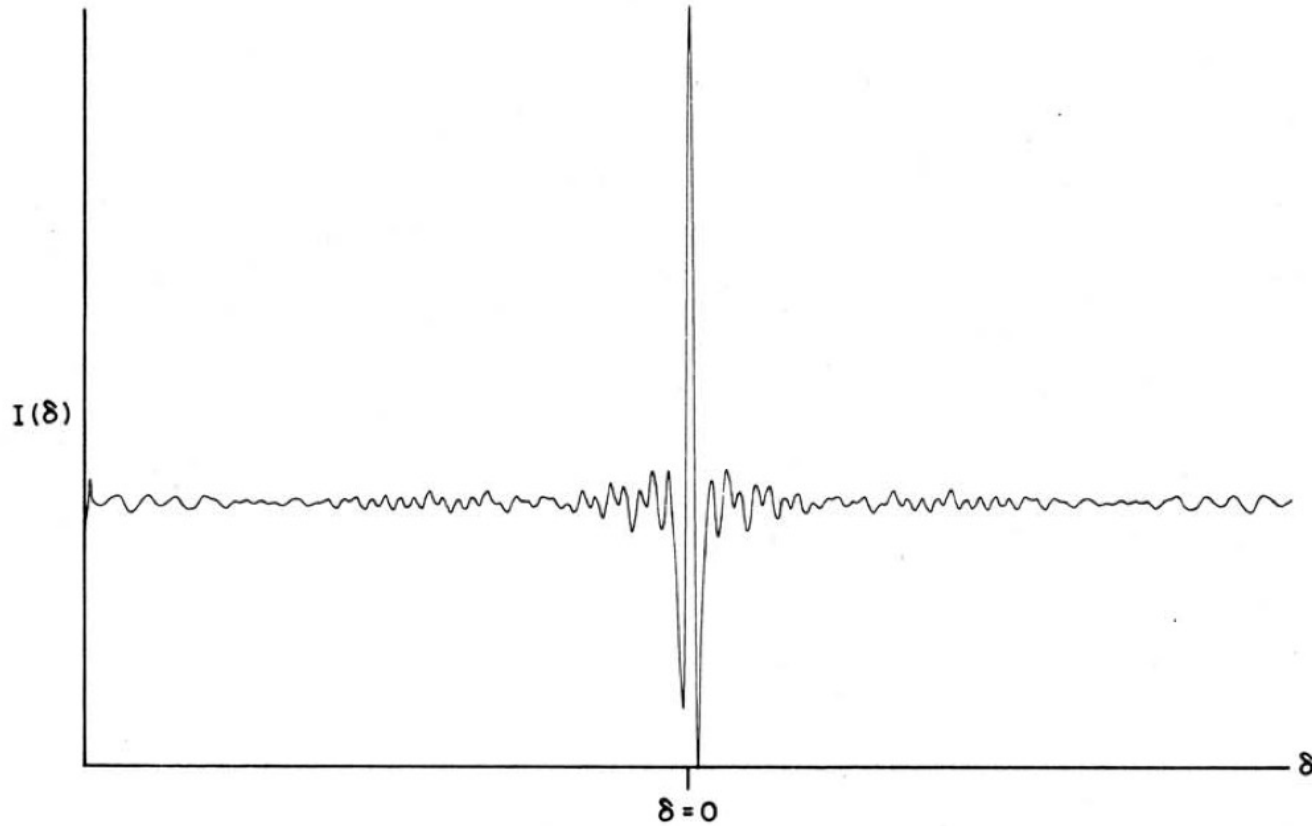
Does this expression look familiar to you ?

We can do inverse Fourier transform of the measured intensity signal in each frequency

$$B(\bar{v}) = \int_{-\infty}^{\infty} I(\delta) \cos 2\pi v\delta \ d\delta$$

Thus, if we record, the intensity as a function of different mirror positions $I(\delta)$, we can extract the intensity of the light as a function of wave-vector $(\bar{v})$, which is the frequency spectrum!
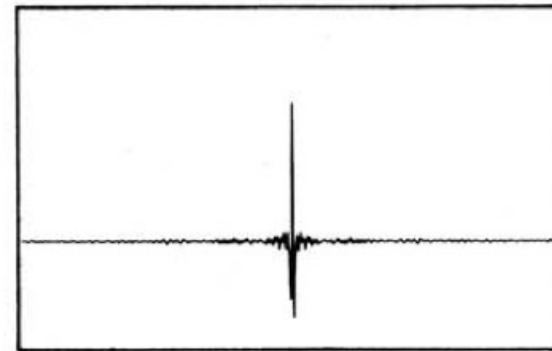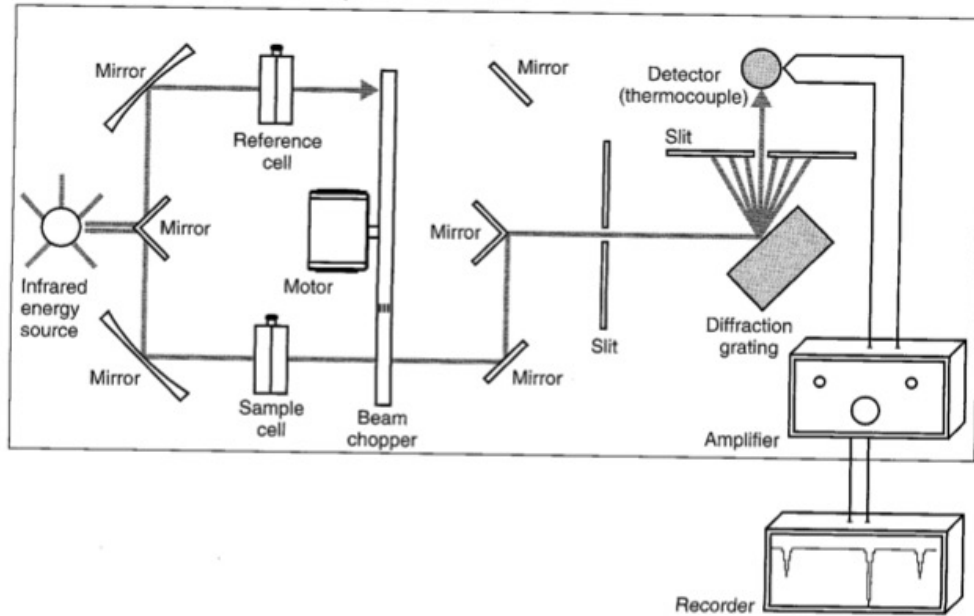
A typical measured intensity as a function of the path delay obtained from the interferometer
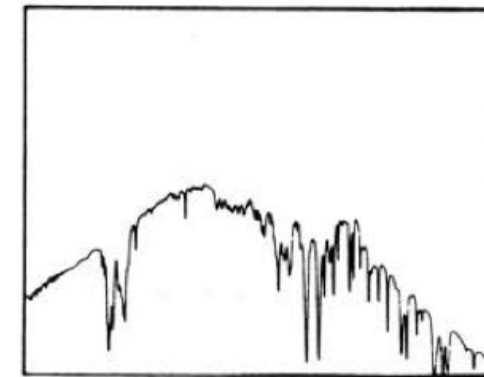

The spectrum (intensity vs wavelength/frequency/energy) gives a typical distribution of energy in a radiation from a black body. In case the path of the light has some absorbents like moisture in the atmosphere and other gaseous absorbents like CO_2
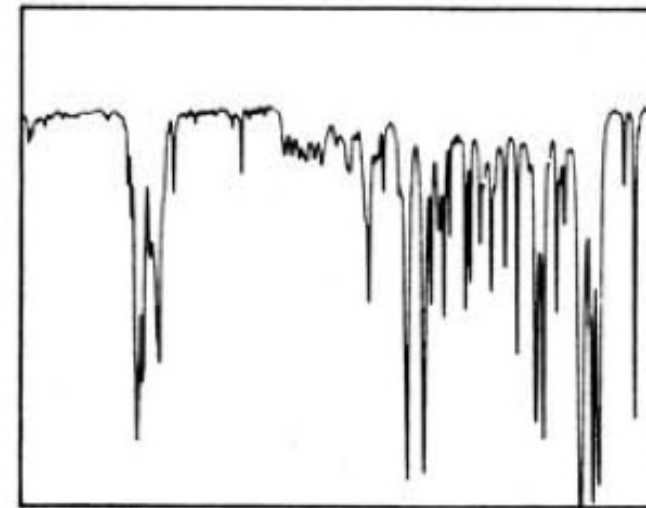
Measurement from a sample:

Final a percentage transmission $\%T(\bar{v}) = \dfrac{T(\bar{v})}{T^B(\bar{v})}$

INDENE

— FFT —

INDENE
(SINGLE BEAM)

% T

v

A single scan of the mirror path is enough to record the complete spectral response.

The FT-IR does a complete spectral scan in a matter of seconds that other dispersive techniques will take several minutes.

Instrumentation

Source: The source is mostly a heated element. Most spectroscopes operate at temperatures close to 1000 – 1500K.

The radiant power falls of accord to Plank's law of black body radiation:

Intensity of radiation at frequency v is given by $B(v) = \dfrac{8\pi v^2}{C^3} \dfrac{hv}{e^{\frac{hv}{KT}} - 1}$

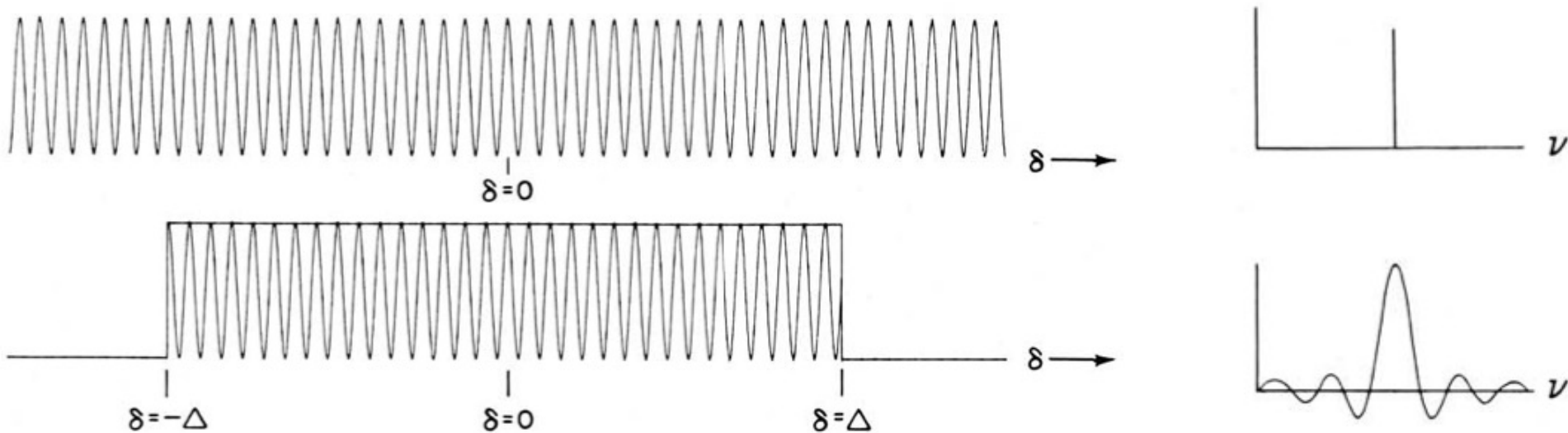B - power per unit solid angle per unit area normal to the propagation of light

Biggest problem in IR instrumentation is every component absorbs IR. Glass has strong absorption in IR (HW: get glass IR spectrum)

So, specialized components have to be used which have negligible absorption in the IR range used to measure samples. s
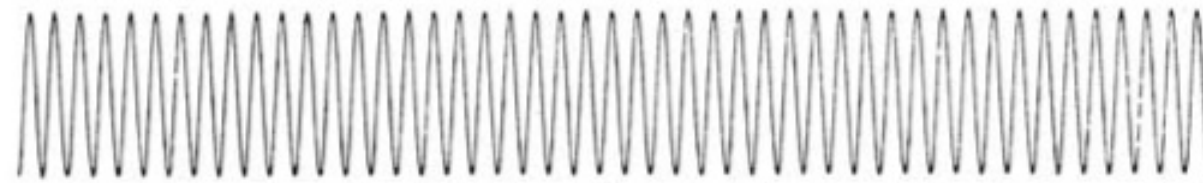
Ideal materials for usage:

1. KBr – has almost 100% transmittance in the range of 4000 – 400 cm^{-1}.
2. Even smaller energies can be observed by switching to CsI or Mylar films.
3. Thermopiles/pyro-electric detectors are typically used
        Most common detector is Deuterated triglycine sulphate (DLGS)
        Alternate detectors are mercury cadmium telluride (MCD) which requires lower operational temperatures
4. The beam splitter is typically a thin Ge film deposited on KBr bulk crystals.
5.   An important aspect of extracting the intensity in each frequency is the inverse Fourier transform

        (i) However, true inverse transform requires intensity record for infinite δ
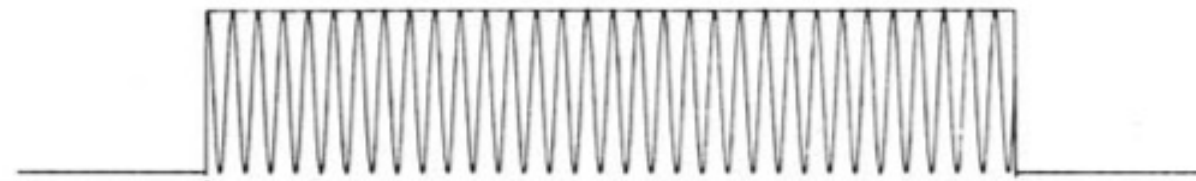   (ii) Practical considerations the path difference obtainable in experiments are limited.

Apodization

Meaning in Greek to remove the feets, ie the ripples in the Fourier transform,
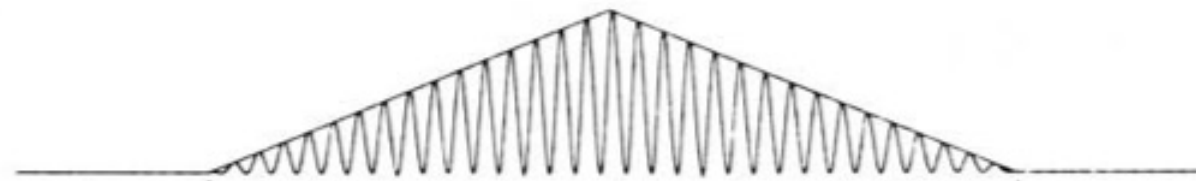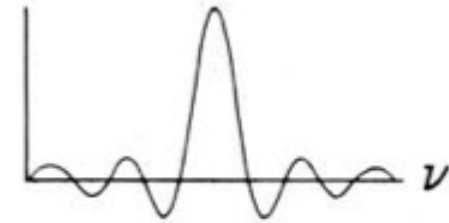

INFINITELY LONG
COSINE WAVE

$\delta=0$

BOXCAR TRUNCATION

$\delta=-\Delta$ $\delta=0$ $\delta=\Delta$
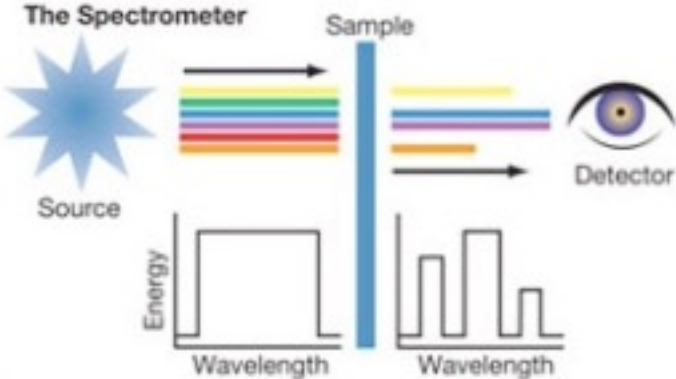
$\delta=-\Delta$ $\delta=0$ $\delta=\Delta$

Sample Collection techniques

Examples
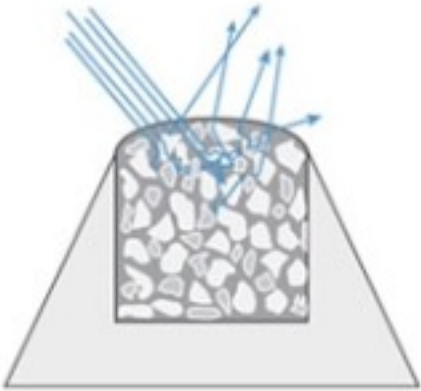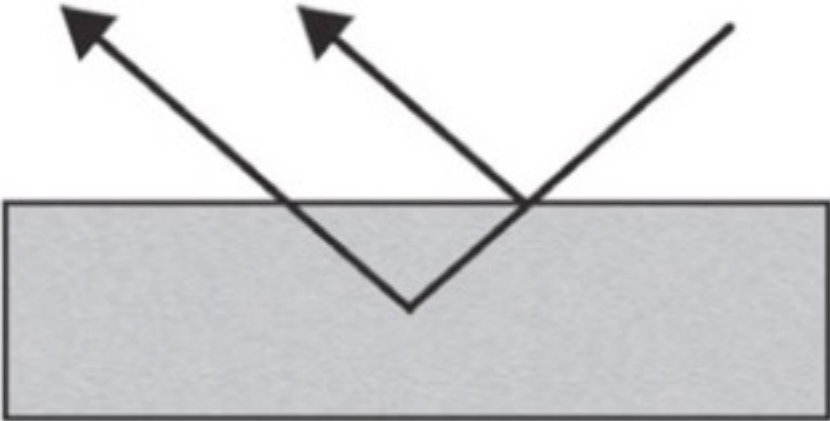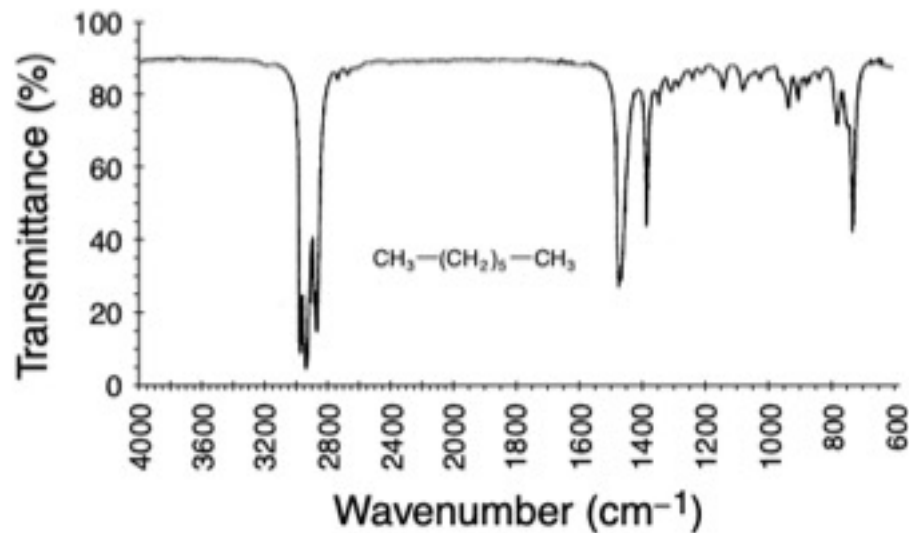

Figure 3 Attenuated total reflectance (ATR) spectrum of *n*-heptane. Copyright Coates Consulting.

Table 1 Saturated aliphatic (alkane/alkyl) group frequencies

Group frequency (cm^{-1})	Functional group/assignment
Methyl ($-CH_3$)	
2970–2950/2880–2860	Methyl C–H asym./sym. stretch
1470–1430/1380–1370	Methyl C–H asym./sym. bend
1385–1380/1370–1365	*gem*-Dimethyl or "iso"- (doublet)
1395–1385/1365	Trimethyl or "*tert*-butyl" (multiplet)
Methylene ($>CH_2$)	
2935–2915/2865–2845	Methylene C–H asym./sym. stretch
1485–1445	Methylene C–H bend
750–720	Methylene $-(CH_2)_n-$ rocking $(n \geq 3)$
1055–1000/1005–925	Cyclohexane ring vibrations
Methyne ($>CH-$)	
2900–2880	Methyne C–H stretch
1350–1330	Methyne C–H bend
1300–700	Skeletal C–C vibrations
Special methyl ($-CH_3$) frequencies	
2850–2815	Methoxy, methyl ether O–CH_3, C–H stretch
2820–2780	Methylamino, N–CH_3, C–H stretch

Interpretation of Infrared Spectra, A Practical Approach

John Coates
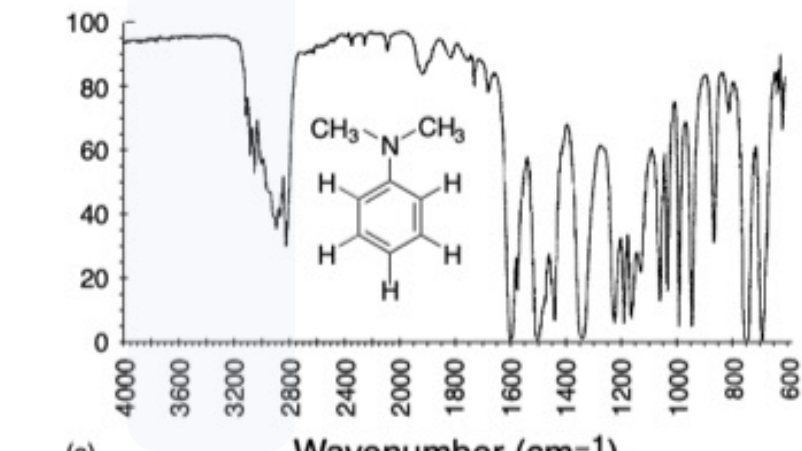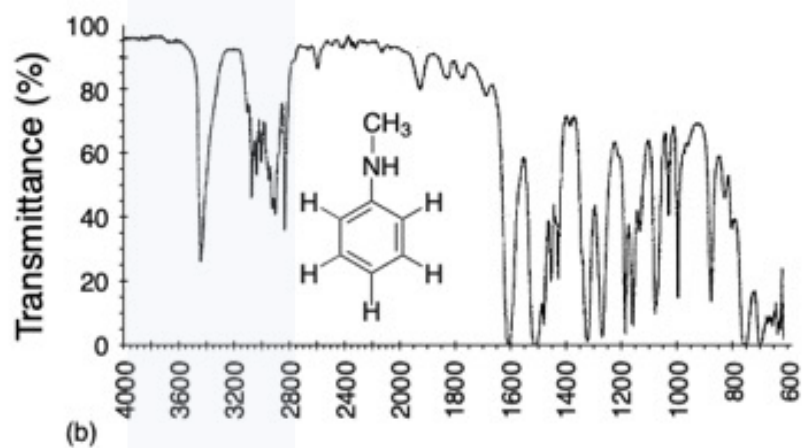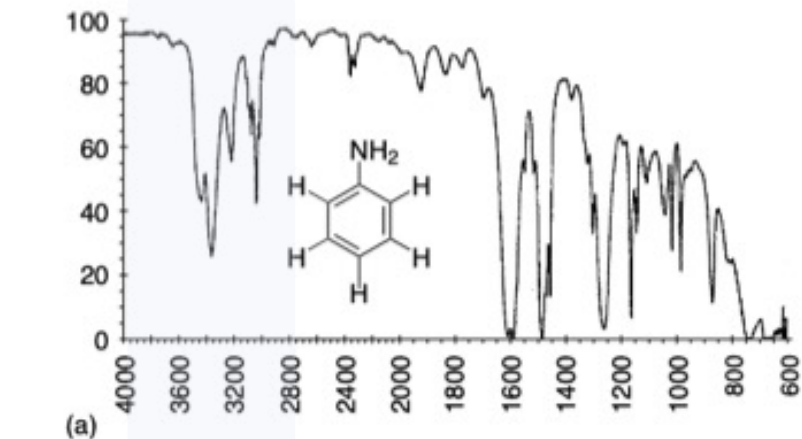*Coates Consulting, Newtown, USA*

Examples - II

Table 8 Amine and amino compound group frequencies

Origin	Group frequency, wavenumber (cm^{-1})	Assignment
Primary amino		
N–H	3400–3380 +3345–3325	Aliphatic primary amine, NH stretch
N–H	3510–3460 +3415–3380	Aromatic primary amine, NH stretch
N–H	1650–1590	Primary amine, NH bend
C–N	1090–1020	Primary amine, CN stretch
Secondary amino		
>N–H	3360–3310	Aliphatic secondary amine, NH stretch
>N–H	~3450	Aromatic secondary amine, NH stretch
>N–H	3490–3430	Heterocyclic amine, NH stretch
=N–H	3350–3320	Imino compounds, NH stretch
>N–H	1650–1550	Secondary amine, NH bend
C–N	1190–1130	Secondary amine, CN stretch
Tertiary amino		
C–N	1210–1150	Tertiary amine, CN stretch
Aromatic amino		
C–N	1340–1250	Aromatic primary amine, CN stretch
C–N	1350–1280	Aromatic secondary amine, CN stretch
C–N	1360–1310	Aromatic tertiary amine, CN stretch

Table 3 Aromatic ring (aryl) group frequencies

Origin	Group frequency, wavenumber (cm^{-1})	Assignment
C=C–C^a	1615–1580	Aromatic ring stretch
C=C–C^a	1510–1450	Aromatic ring stretch
C–H	3130–3070	Aromatic C–H stretch
C–H	1225–950 (several)	Aromatic C–H in-plane bend
C–H	900–670 (several)	Aromatic C–H out-of-plane bend
	770–730 + 710–690	Monosubstitution (phenyl)
	770–735	1,2-Disubstitution (ortho)
	810–750 + 900–860	1,3-Disubstitution (meta)
	860–800	1,4-Disubstitution (para)
"Combi"^{b}	2000–1660 (several)	Aromatic combination bands

Interpretation of Infrared Spectra, A Practical Approach

John Coates
Coates Consulting, Newtown, USA

Lastly, width of every band

- Rotational states around vibrational levels – Selection rules
- Collision broadening
- Doppler broadening
- Heisenberg uncertainity
- Detector uncertainity