Molecular Spectroscopy

Lect 1: General Introduction

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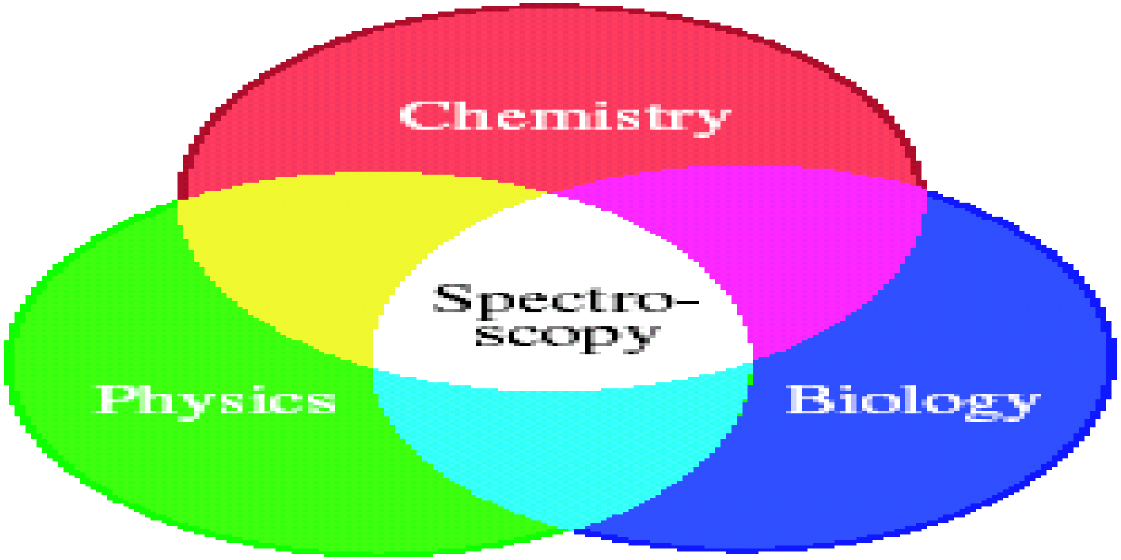
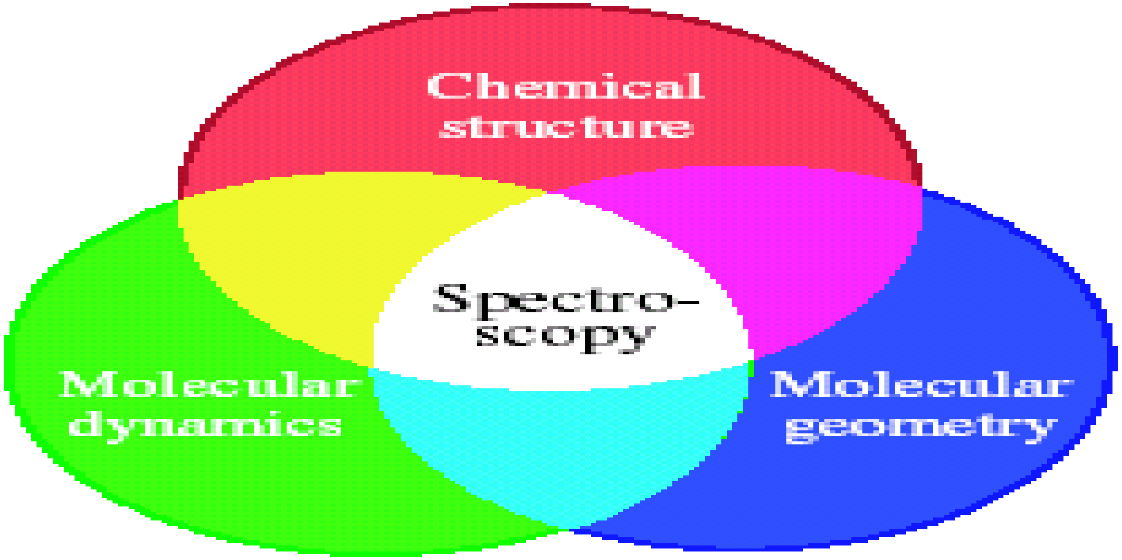
Spectroscopy and Electromagnetic Radiations

Spectroscopy: It involves the investigation of the interactions of electromagnetic radiations ***(light)*** with matter (atoms or molecules) and explanation of the spectral pattern.

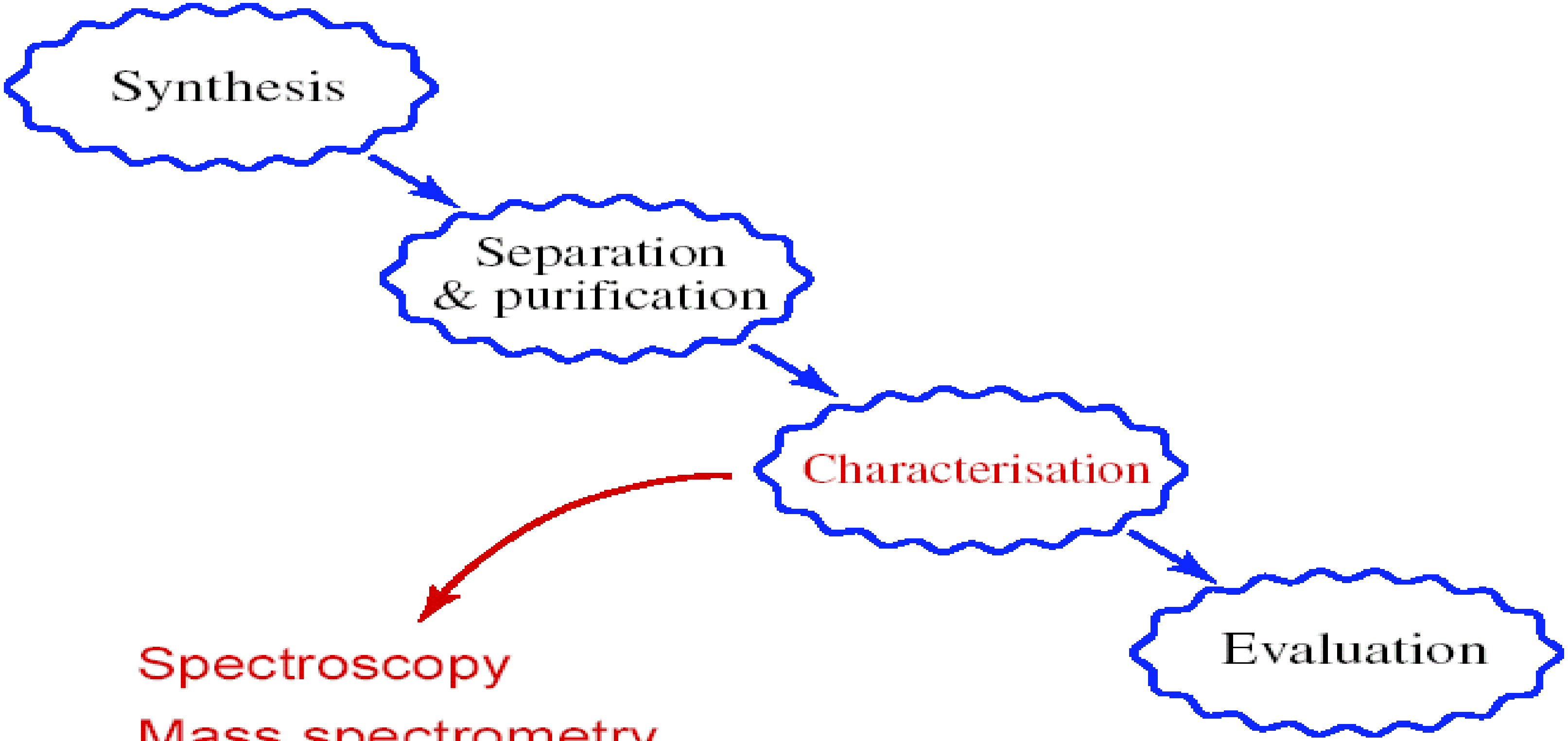
Spectra: It show how the interaction between electromagnetic radiation and the matter varies with the frequency of the electromagnetic radiation ***(Energy)***.

Applications of Spectroscopy





The Role of Spectroscopy



Synthesis

Separation & purification

Characterisation

Evaluation

Spectroscopy

Mass spectrometry

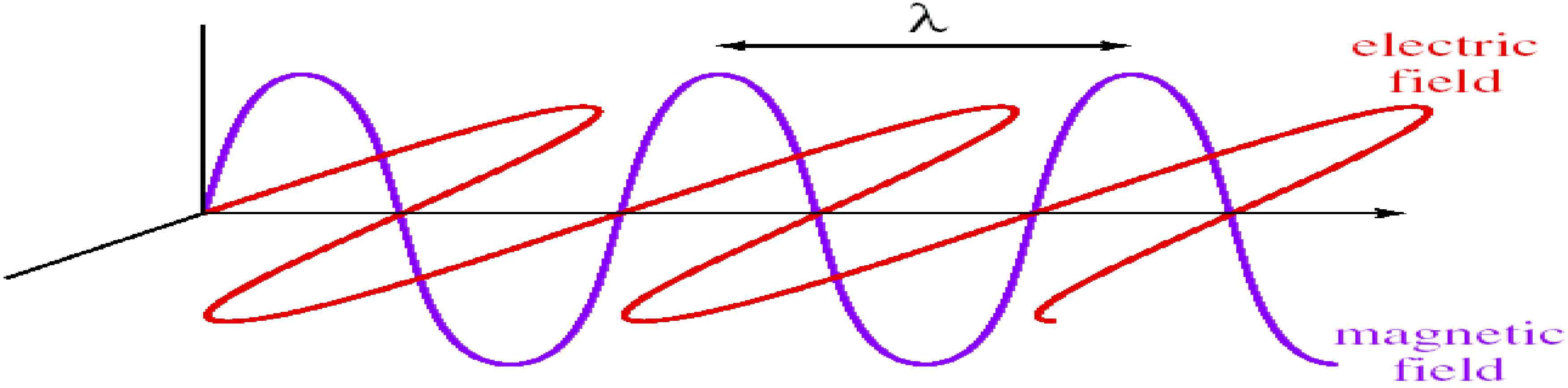
Diffraction & scattering (X-rays, neutrons)

Electromagnetic Radiation (e.m.r.)

Light can be described in two complementary ways...

Wave picture:

Consists of oscillating electric and magnetic fields



$$c = \lambda \nu$$

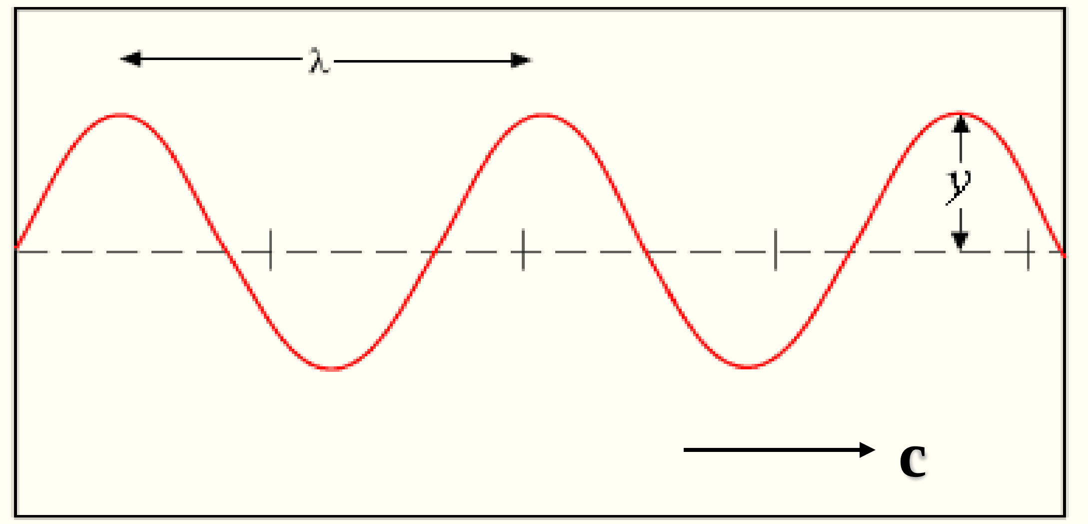
c – velocity ($m\ s^{-1}$)
λ – wavelength (m)
ν – frequency ($Hz \equiv s^{-1}$)

c_0 (vacuum) = $2.99776 \times 10^{8}\ m\ s^{-1}$

Particle picture: consists of “packets” of light, photons, each with energy $E = h\nu$

h – Planck's constant

Properties of electromagnetic radiations



As waves, electromagnetic radiations are characterized by:

λ = wavelength (length of single wave), y = amplitude

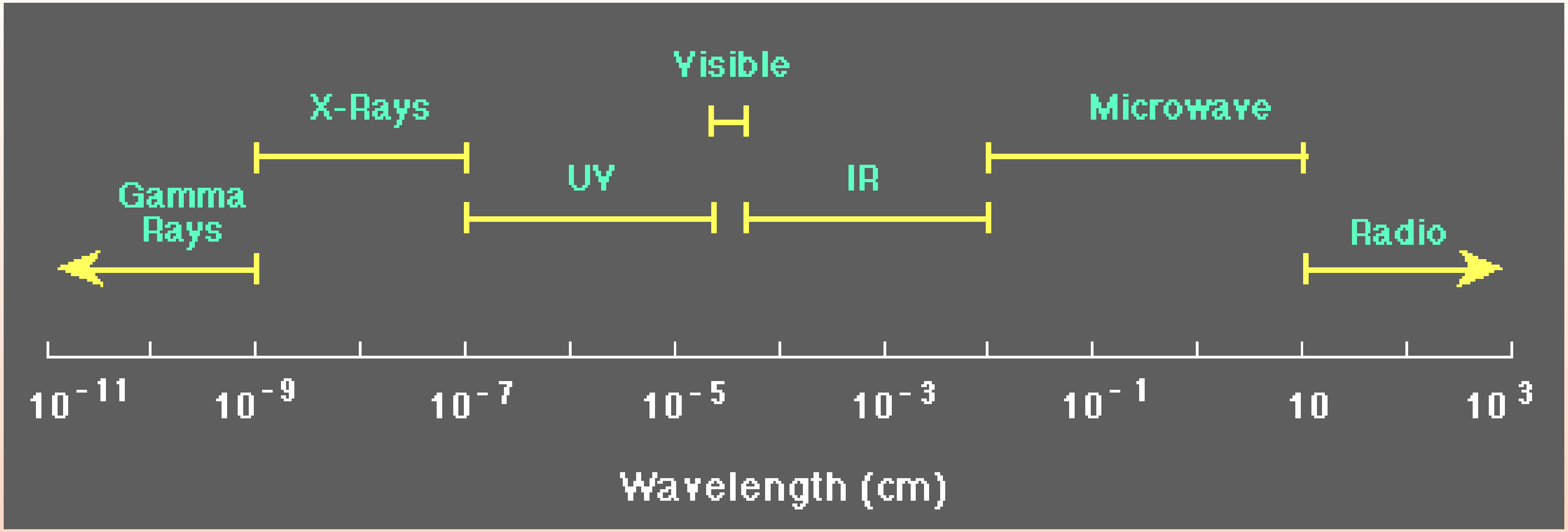
C = speed of light in a vacuum

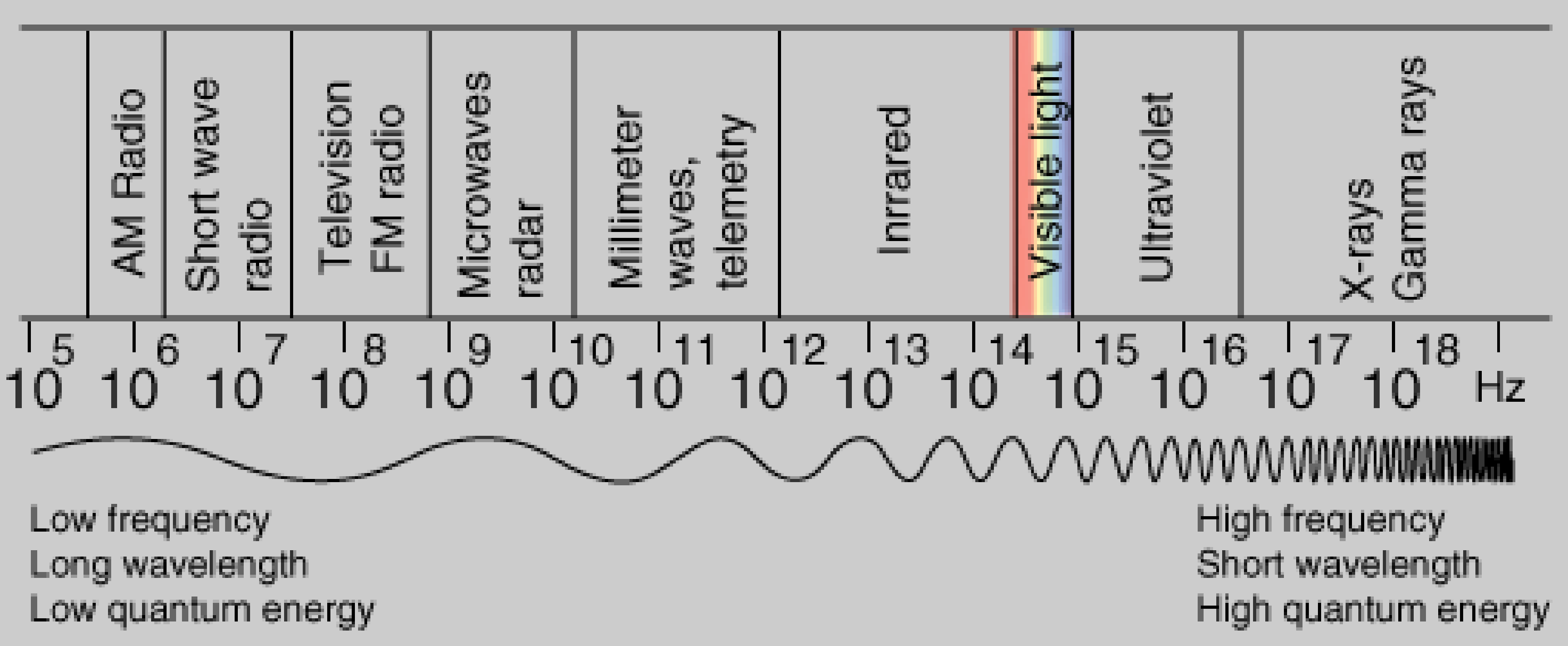
ν = frequency (number of cycles passing a certain point per second)

in Hertz

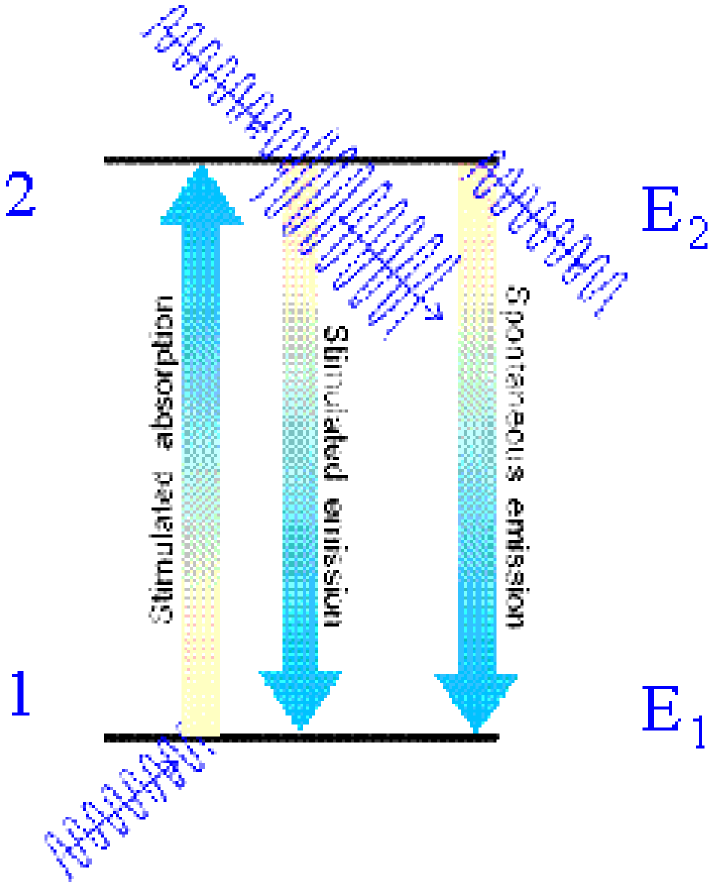
$\tilde{\nu} = 1/\lambda$ (in cm) wavenumber = a number of waves that fit a centimetre, units = cm^{-1}

The Electromagnetic Spectrum





Quantization of Energy



Bohr frequency condition

$$\Delta E = E_2 - E_1 = h\cdot\nu = h\cdot c\cdot\tilde{\nu}$$

h - Planck constant, $6.626\cdot10^{-34}$ J·sec

E_2 and E_1 - energy levels

1 and *2* - quantum numbers

units: J

in molar units, J/mol

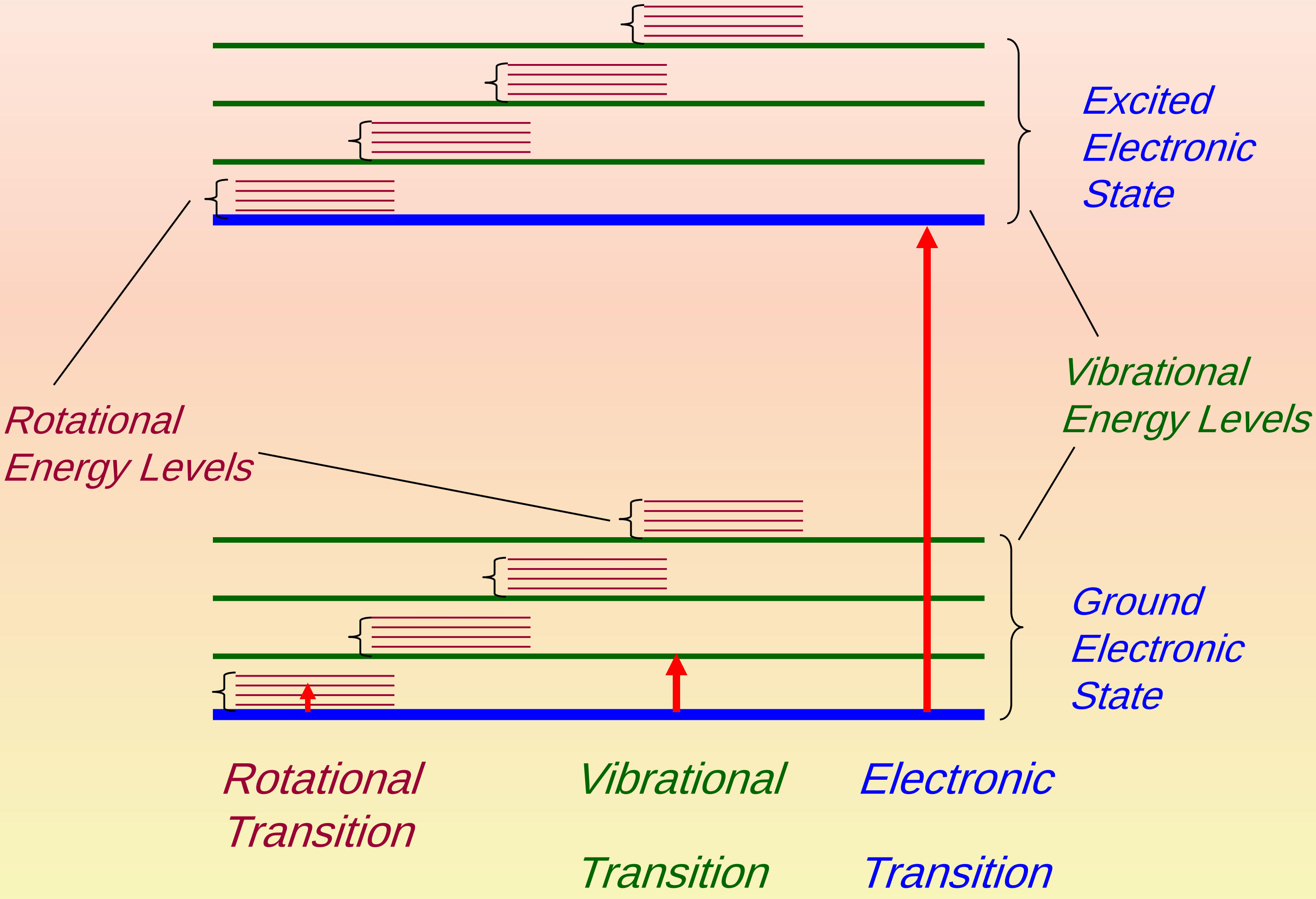
$$\Delta E = N_A\cdot h\cdot\nu$$

Energy 'units': *J, cal, Hz,* cm^{-1}*, eV*

Which units do we use in NMR, UV, IR spectroscopy?

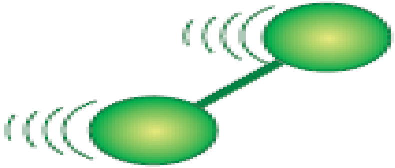
Molecular Energy Levels and interactions between light and matter

Radiations can be absorbed or emitted if the molecule changes any of its energy states

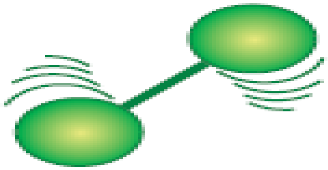


Molecular Energies

Molecules can have many different types of energy

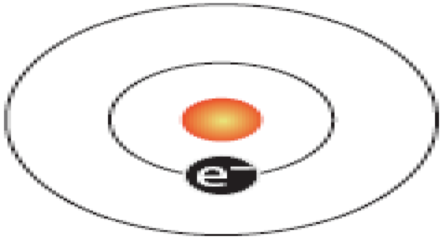


translation



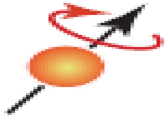
rotation

vibration



electron orbital

electron spin



nuclear spin

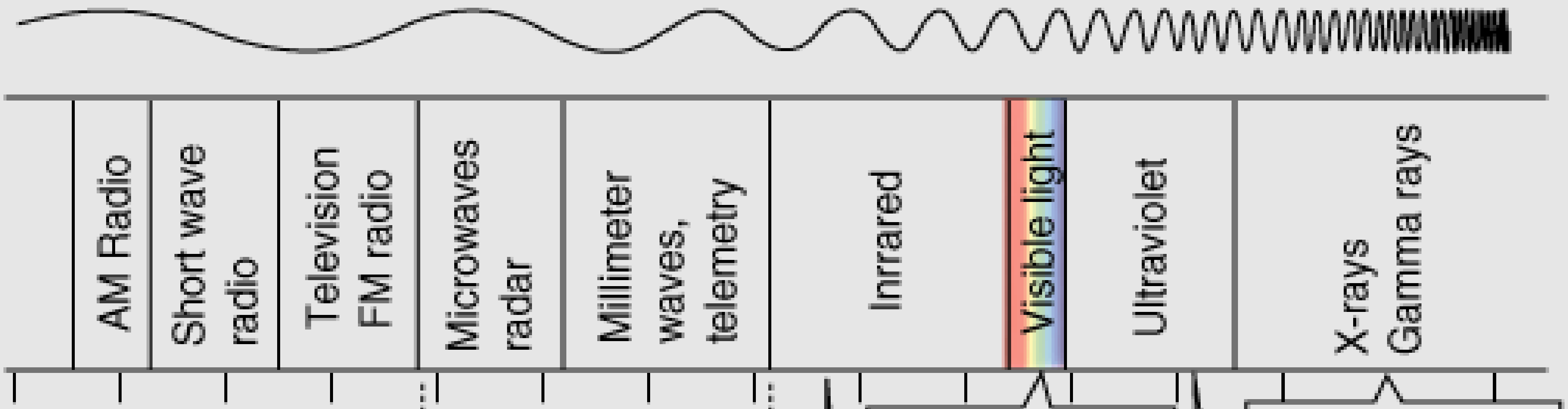
These energies are quantised, giving a set of energy levels:

Interactions with Matter

Radio-wave;	*Changes nuclear and electron spin*
Microwave;	*Changes molecular rotations*
Infrared;	*Changes molecular vibrations*
Visible;	*Causes transition of outer shell electrons*
Ultraviolet;	*Causes molecular dissociation*
X-ray;	*Causes transition of inner shell electrons*
γ-ray;	*Causes nuclear transitions*

Low frequency
Long wavelength
Low quantum energy

High frequency
Short wavelength
High quantum energy



Body is transparent. You are commonly penetrated by radiation in this range from local radio and TV stations and other forms of communication.

Almost transparent. Tiny amount of absorption rotates molecules and contributes heating, but no effects distinguishable from heating.

Strongly absorbed because it causes electron jumps to higher levels. Not enough energy to ionize.

Almost transparent since quantum energies so high that atoms can't absorb and remain intact. Ionizes.

Stronger absorption vibrates molecules. Physiological effect is heating since it is putting molecules into vibrational motion.

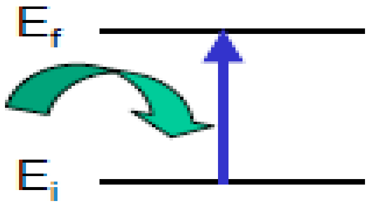
Very strongly absorbed by electron jumps. Doesn't penetrate skin. Upper end can ionize.

To have a physiological effect, the energy of the radiation must be absorbed. To be absorbed, there must be quantum energy level pairs which match the photon energy of the radiation. If these energy level pairs are not available in a given frequency range, then the material will be transparent to that radiation.

Origin of spectral lines in molecular spectroscopy: absorption or emission of a photon when the energy of the molecule changes:

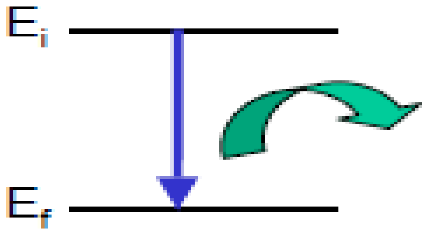
- electronic transitions
- rotational states change
- vibrational states change

Absorption spectroscopy:



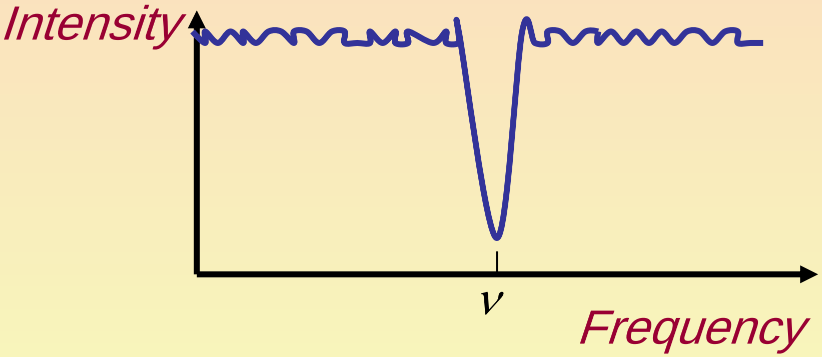
$$\Delta E = h\nu \qquad (4.1)$$

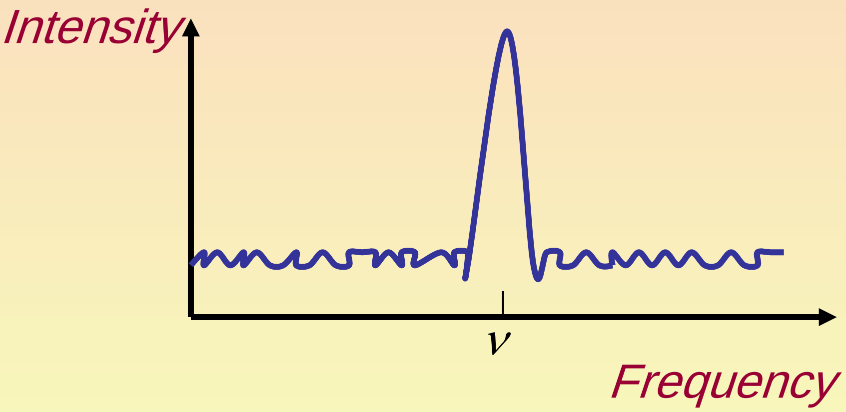
Emission spectroscopy



Emission or absorption spectroscopy:

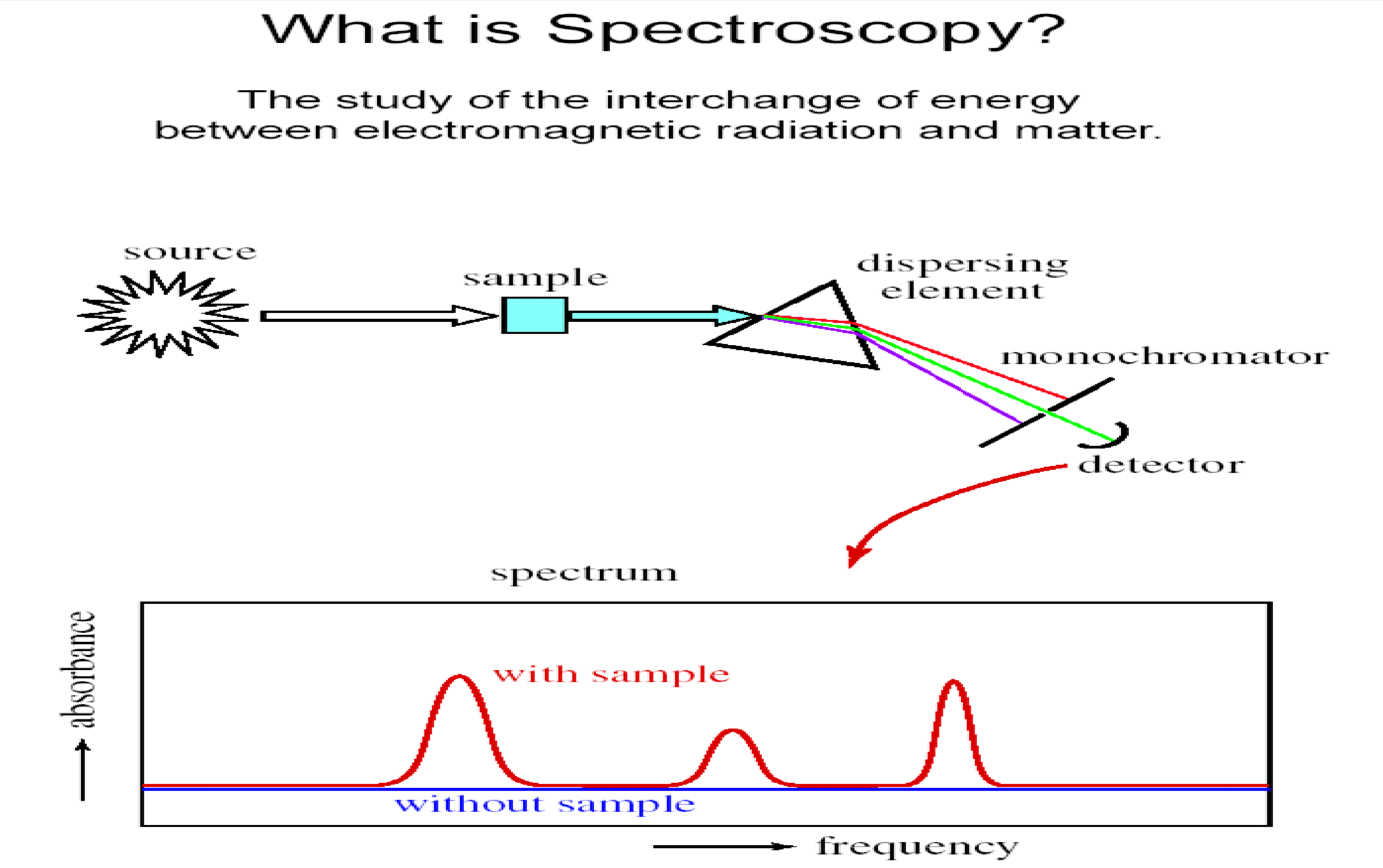
- give the same information about the energy levels
- practical considerations determine which technique is better to use.





Basic components of Spectrometer

How the spectra are measured?

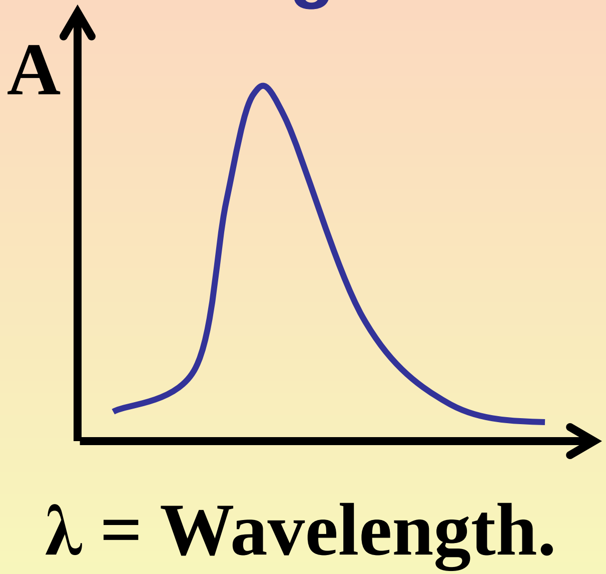


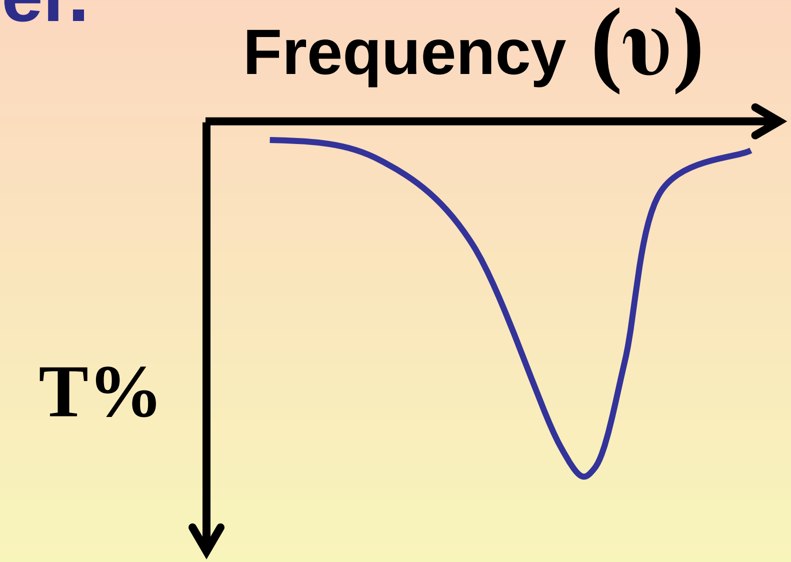
What is Spectroscopy?

The study of the interchange of energy between electromagnetic radiation and matter.

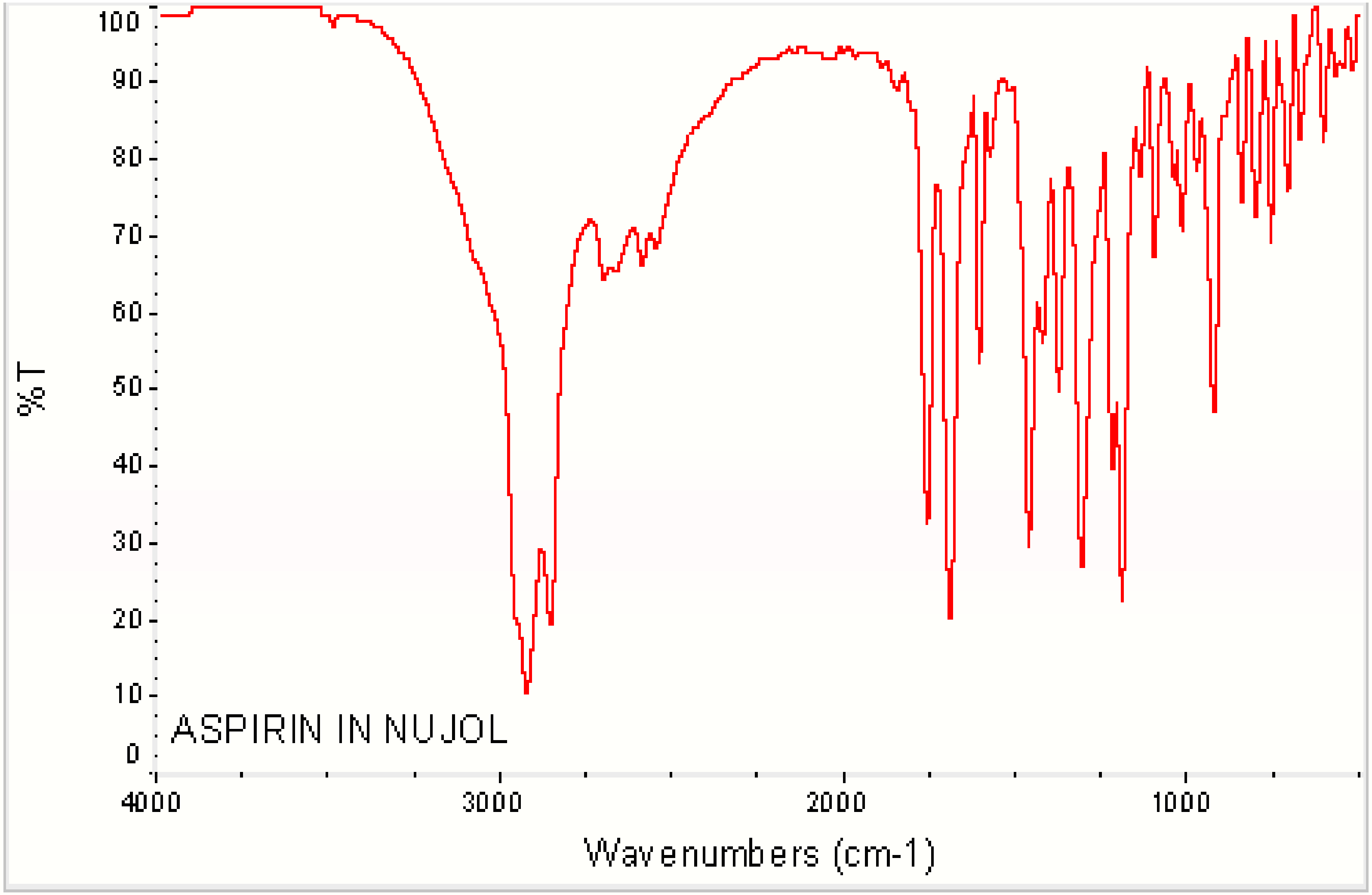
Spectra recorded by the Spectrometer

White-light covering a wide range of frequencies is passed through a sample cell and then to a monochromator (a prism or grating). Detector (photodiode array) records the intensity of transmitted light as a function of frequency or records the absorbance as a function of wavelength or wavenumber.





Spectral features



- Position of bands
- Width of spectral lines
- Intensity of spectral lines

Spectral features

1. Bands Position: It is determined by the wavelengths or the frequencies at which the molecule absorb, it depends on its structural features (Functional groups), as well as its environment (solvent used). It is determined by the spacing between the energy levels (i.e energy difference between energy levels involved in the transition) not by the energy of the levels themselves.

2. Width of spectral line: broadening is caused by;

- Collisional broadening (due to molecular interactions).
- Doppler broadening (molecular interactions in case of gases).
- Lifetime broadening $(\delta E.\ \delta t \sim h/2\pi)$

3. Intensity of spectral lines: It tells us about the;

- Transition probability (transition is allowed or forbidden).
- Population of states.
- Path length of the sample $(-\log (I/I_o) = A = \varepsilon\ l\ c\ )$

Aims of spectroscopy

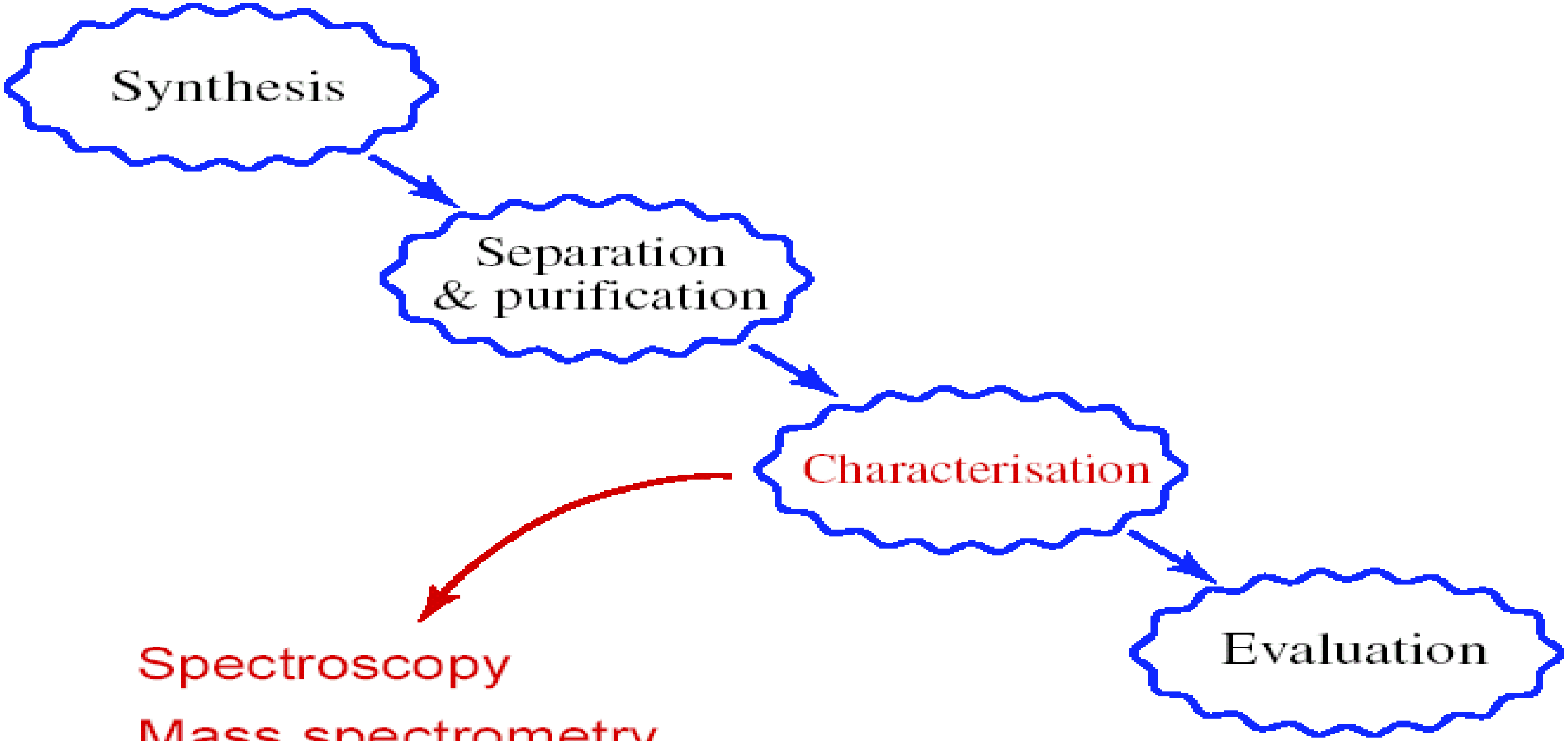
Molecular spectra can be used to make;

1- Qualitative analysis of a new substance or mixture (to identify the present molecular species).

2. Quantitative determination of a known substance (using Beer-Lamber law).

3. Structural characterization of a substance (from the energy levels and various transitions - establish the physical and chemical properties of the substance).

The Role of Spectroscopy



Synthesis

Separation & purification

Characterisation

Evaluation

Spectroscopy

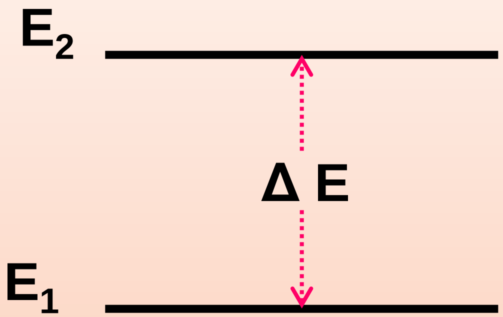
Mass spectrometry

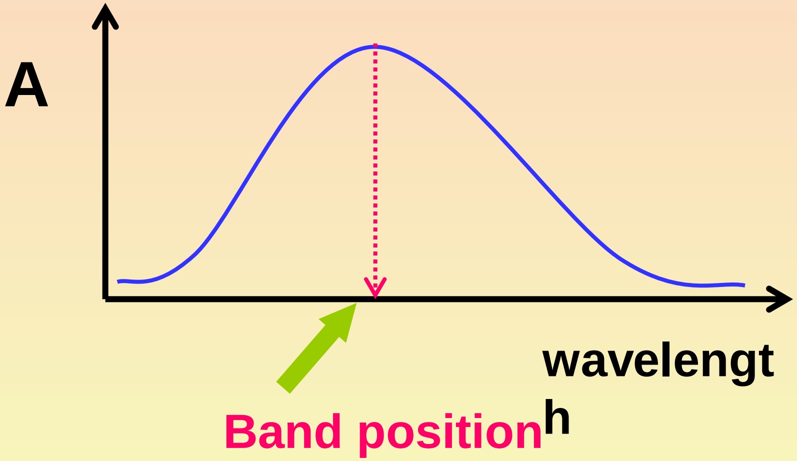
Diffraction & scattering (X-rays, neutrons)

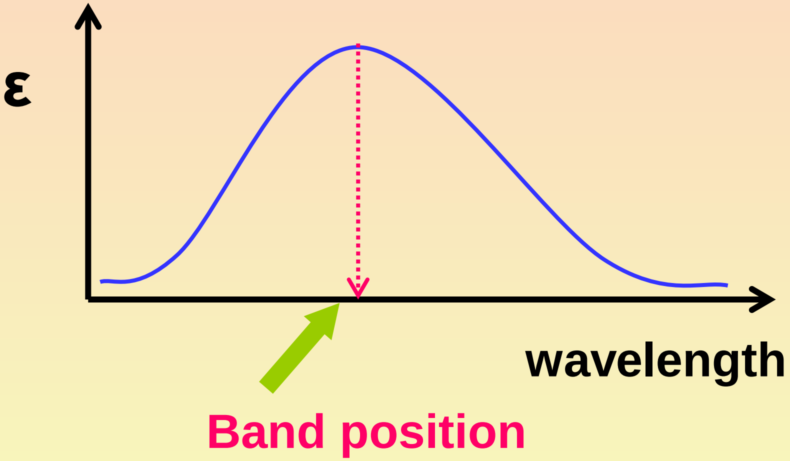
1. ***Bands Position***

$$\Delta E = E_2 - E_1$$

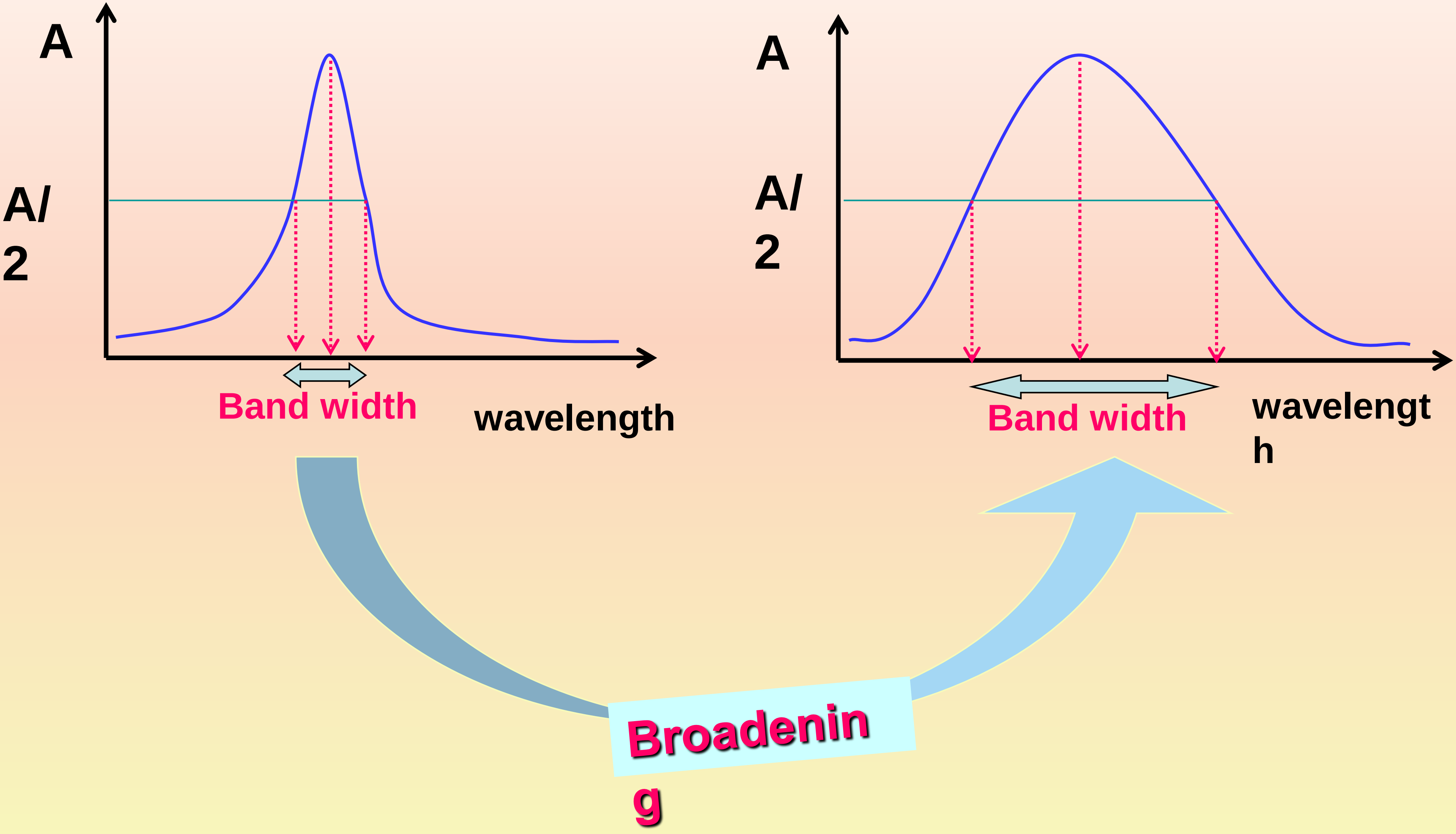
$$= h\upsilon = \frac{hc}{\lambda} = hc\bar{\upsilon}$$







2. Width of spectral lines: (half- and base band width)



Spectral band broadening is due to:

i. Collision broadening

Elastic collision:

No energy from internal degree of freedom is transferred during the collision.

Inelastic collision:

The excitation energy is transferred from the excited molecule A^* to a collision partner B

- The collision of molecules causes the excited state to revert to the ground state, shorten the lifetimes of the excited state and leads to broadening of the associated spectral lines.

ii. Doppler broadening

- Occurs in gaseous state, and increases with temperature due to increasing differences between the distribution of velocities of molecules.
- The radiation frequency is shifted when the absorbing or emitting molecule is moving towards or away from the observer (light detector).
- Light source emits light photons with frequency $\nu_\circ$, the molecule is moving toward or away from the stationary observer with velocity (± v), then the observer measure the frequency not as $\nu_\circ$ but as ν^- where;

$$\upsilon^{-} = \upsilon_0\left(1 \pm \frac{\mathbf{v}}{c}\right)$$

iii. Life-time broadening

- If a system exists in an energy state with energy (*E*) ***for a limited time*** ***(τ = lifetime of the state). The energy of that state will be uncertain to an extent (δE).***

According to Heisenberg Uncertainty Principle;

$$\delta(E)\times\delta(t)\approx\frac{h}{2\pi}=\hbar$$
$$\delta(t)=\text{uncertainty in time}=\tau$$

$$\textit{Lifetime broadening in frequency}=\frac{1}{2\pi\tau}$$

Where τ is the lifetime

example

- Calculate the lifetime broadening in cm^{-1} for an excited state with lifetime (***τ = 1p.s.)***.

Note: 1p.s = 0^{-12} s.

$$\text{Lifetime broadening in wavenumber} = \frac{1}{2\pi c\tau}$$

$$= \frac{1}{2 \times 3.14 \times 2.998 \times 10^{10} \times 1 \times 10^{-12}}$$

The intensity of the spectral line

It is governed by;

1. ***Transition probability from which selection rules can be obtained.***
2. ***Population of the energy levels.***
3. ***Path length of the sample.***

$$\textit{Transition probability is governed by}$$

$$\textit{transition dipole moment } \left|\vec{M}\right|$$

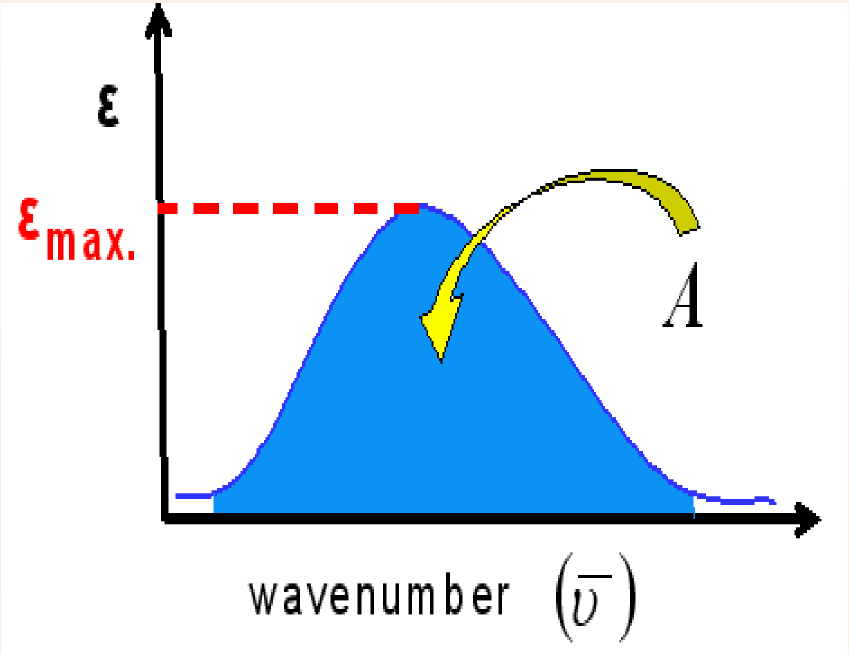
Transition dipole moment gives the probability of a transition

between two states (1) and (2) as a result of photon resonance

absorption obeying Bohr-Einstein conditions:

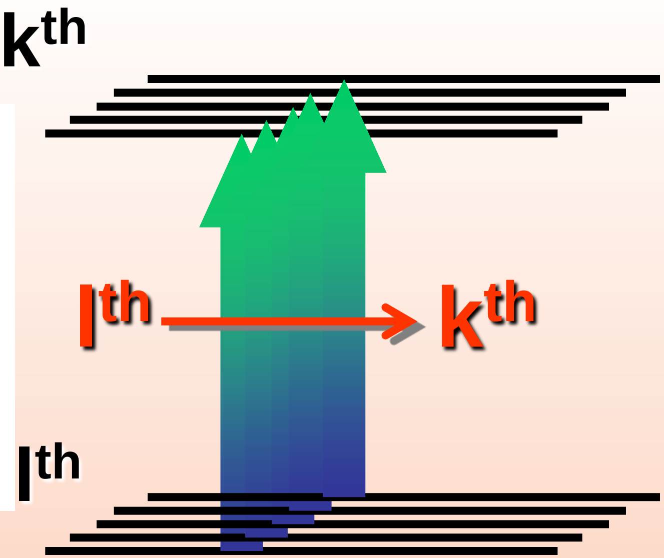
$$E_2 - E_1 = hc\overline{\upsilon}$$

The maximum value of molar absorption coefficient ($\varepsilon_{max.}$) ,oscillator strength (f -number) and integrated absorption coefficient (A) are taken as indications for the intensity of transition.



$$A = \int_{band} \varepsilon_{(\overline{\upsilon})}\, d\overline{\upsilon}$$

Oscillator strength (f):



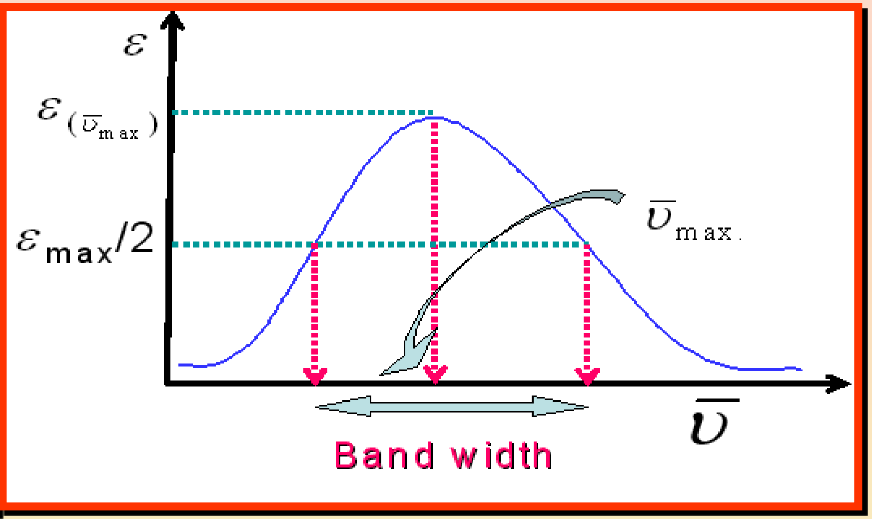
If we regard the molecule as oscillating dipole then the oscillator strength (f) is defied as the number of virtual oscillators equivalent to transitions from l^th → k^th electronic state in quantum theory.

$$f = 4.32 \times 10^{-9} \int_{band} \varepsilon_{(\bar{\upsilon})}\, d\bar{\upsilon}$$

If the band has Gaussian shape:

$$\int_{band} \varepsilon_{(\bar{\upsilon})}\, d\bar{\upsilon} = \varepsilon_{(\bar{\upsilon}_{\max})} \times \Delta\bar{\upsilon}_{1/2}$$

$$= \varepsilon_{(\bar{\upsilon}_{\max})} \times (band\ \ width)$$



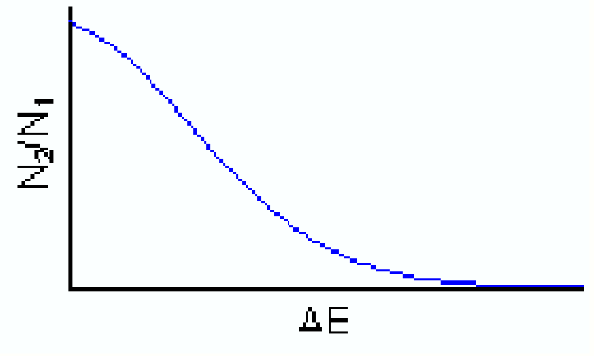
$f \geq 1$ → **Allowed transition**

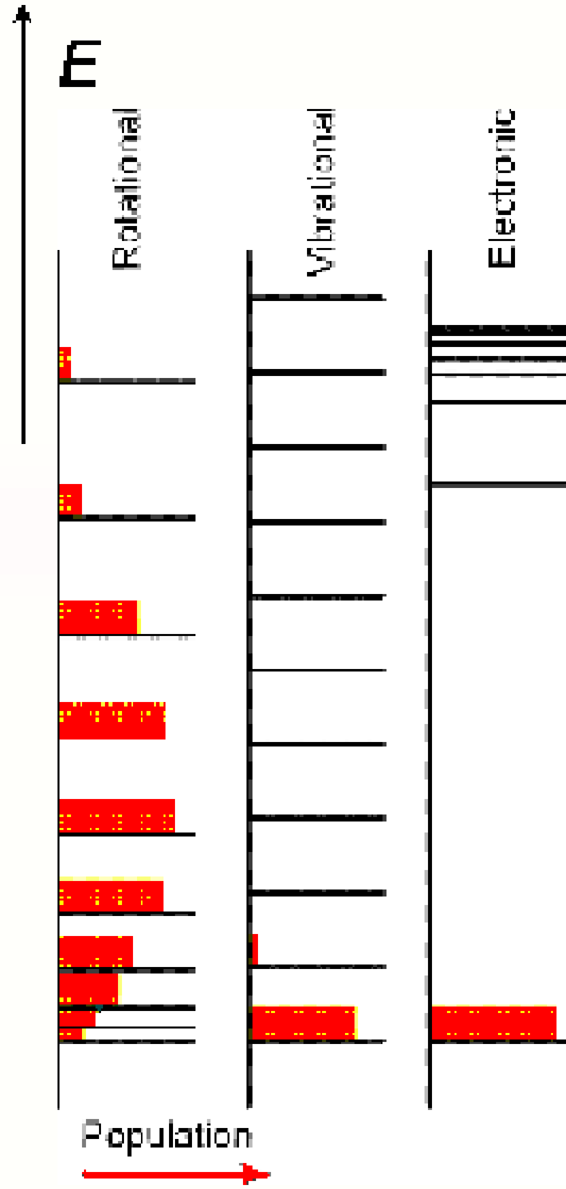
$f << 1$, **(10^{-2} – 10^{-4})** → **forbidden transition**

Population of the energy levels

1. Boltzmann distribution

$$\frac{N_2}{N_1} = e^{-(\Delta E / kT)}$$





since $E = h \cdot \nu = h \cdot c / \lambda = h \cdot c \cdot \tilde{\nu}$

$$\frac{N_2}{N_1} = e^{-(h\nu / kT)} = e^{-(hc\tilde{\nu} / kT)} = e^{-(N_A hc\tilde{\nu} / RT)}$$

k=1.381·10^{-23} J/K and R=8.314 J/(K·mol)

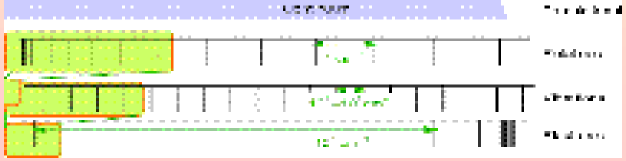
2. Number of degenerated energy levels

Summary

1. Electromagnetic spectrum
2. Quantization of energy - Bohr frequency condition

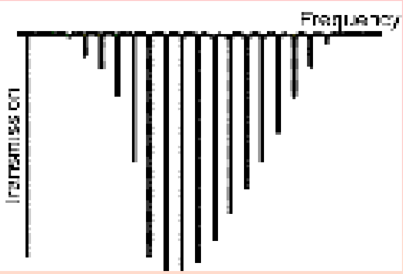
$$\Delta E = E_2 - E_1 = h \cdot \nu = h \cdot c \cdot \tilde{\nu}$$

3. Energy 'units': *J, cal, Hz, cm^{-1}, eV*
4. Energy levels in molecules



5. Spectral features

   position of bands
   width of spectral lines
   intensity of spectral lines



6. Population of the energy levels
   Boltzmann distribution

$$\frac{N_2}{N_1} = e^{-(\Delta E / kT)}$$

Which units do we use in NMR, UV, IR spectroscopy?
Can you convert 2000 cm^{-1} into m^{-1}?