



Molecular Spectroscopy

Lect 1: General Introduction

Prof. Tarek A. Fayed

Spectroscopy and Electromagnetic Radiations

Spectroscopy is the technique that involves study of the interactions between electromagnetic radiations (light) and matter (whatever atoms or molecules) and explanation of the obtained spectral pattern.

Spectra is the output which shows how the magnitude of the interaction between electromagnetic radiations and the matter varies with the frequency (or Energy) of the electromagnetic radiations.

Aims of spectroscopy

Molecular spectra can be used to make:

- 1- Qualitative analysis of a new substance or a mixture (to identify the present molecular species).
2. Quantitative determination of a known substance (using Beer-Lambert law).
3. Structural characterization of a substance (from the energy levels and various transitions, the physical and chemical properties of the substance can be established). This is done by using; IR, UV-Vis, NMR, Mass and x-rays techniques.

Fields of Applications of Spectroscopy



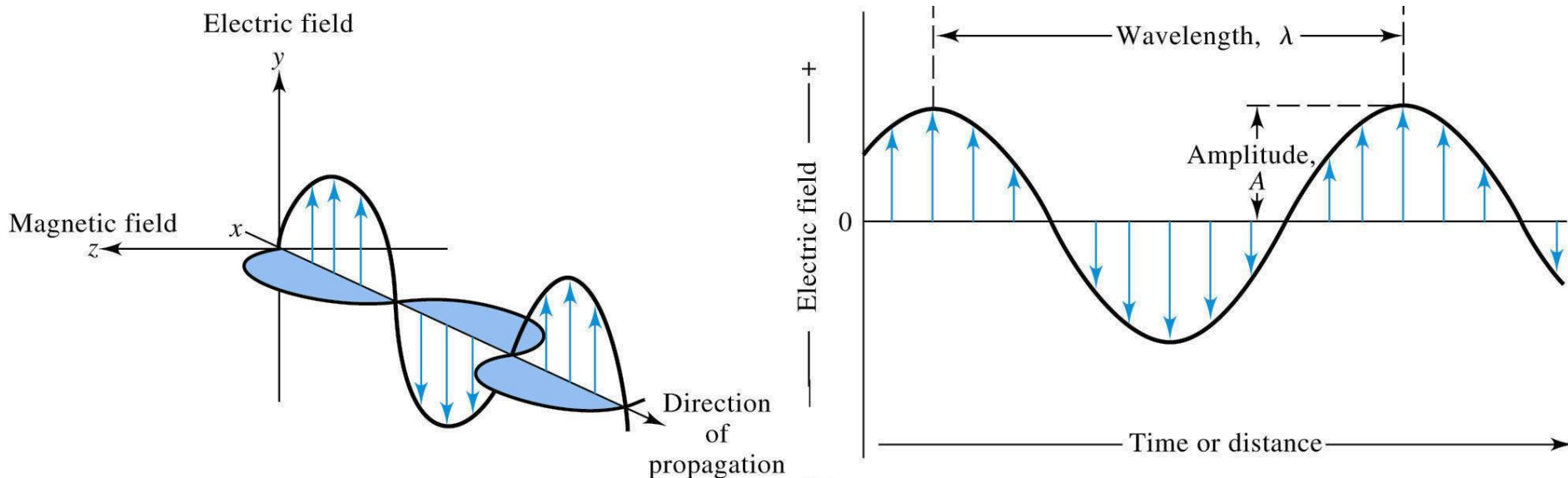
To study the following;



Nature of electromagnetic radiations, EMR

It is a kind of electromagnetic energy that is characterized by dual nature (Wave, Particle Nature).

As waves; EMR can be characterized by wavelength (λ), frequency (ν), velocity and amplitude. Electromagnetic radiation requires no supporting medium for its transmission and passes readily through a vacuum.



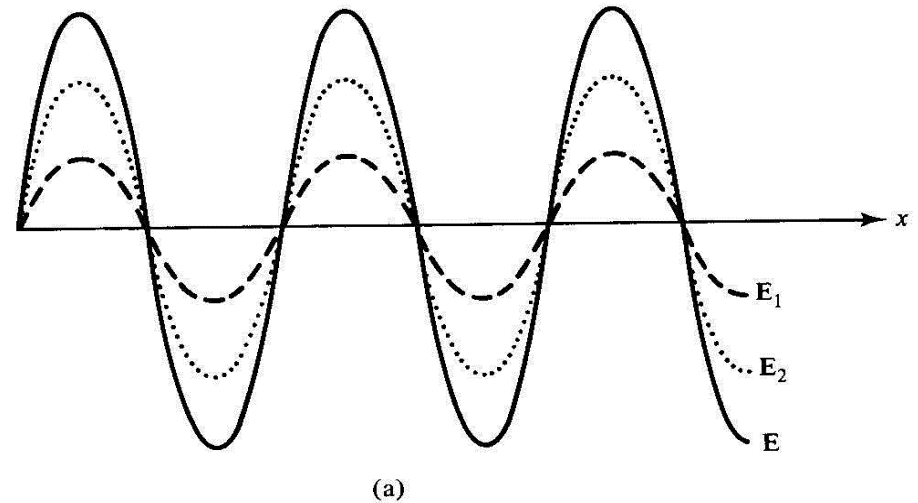
Wave parameters

- **Amplitude (A):** Length of the electric vector at a maximum in the wave.
- **Period (P):** The time in seconds required for the passage successive maxima or minima through a fixed point in space.
- **Frequency (ν):** The number of oscillations of the field that occur per second and is equal to $1/P$. (ν ; in s^{-1} or Hz).
- **Wavelength (λ):** The linear distance between any two equivalent points on successive waves (successive maxima or minima). (λ ; in A, nm, etc.).

Optical Interference

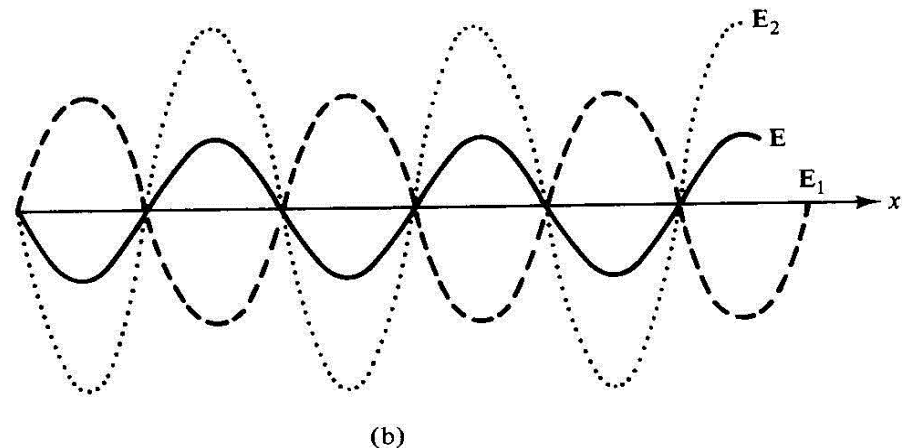
Constructive Interference

1) Two waves have identical frequency and are in phase



Destructive Interference

1) Two waves have identical frequency but are out of phase



The particle Nature of Light: Photons

In many radiation-matter interactions, it is useful to consider **EMR** as stream of discrete particles or wave-packets of energy called **photons**.

The energy of the photon can be related to its wavelength, frequency, and wavenumber by;

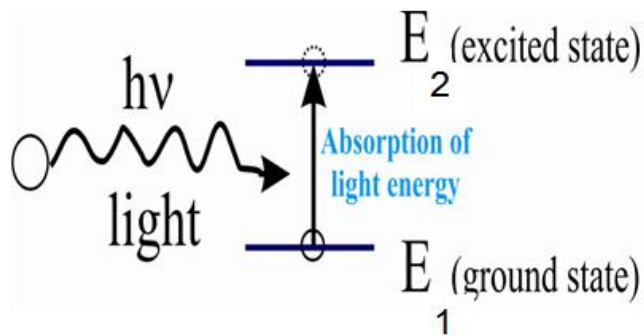
$$E = h\nu = hc/\lambda = hc\bar{\nu}$$

where, h is Planck's constant (6.63×10^{-34} J s). The wavenumber $\bar{\nu}$ and frequency ν , in contrast to the wavelength λ , are directly proportional to the photon energy E . The radiant power of a beam of radiation is directly proportional to the number of photons per second. $c =$ velocity of radiation $= 2.998 \times 10^8$ m s⁻¹ through a vacuum

Theoretically, $\bar{\nu}$ (in cm⁻¹) = $10^7 / \lambda$ (in nm)

Quantization of Energy

When a substance absorbs light, it goes from a low energy state (ground state) to a higher energy state (excited state)



Bohr frequency condition

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

h - Planck constant, $6.626 \cdot 10^{-34}$ J·sec

E_2 and E_1 - energy levels

1 and 2 - quantum numbers

units: J

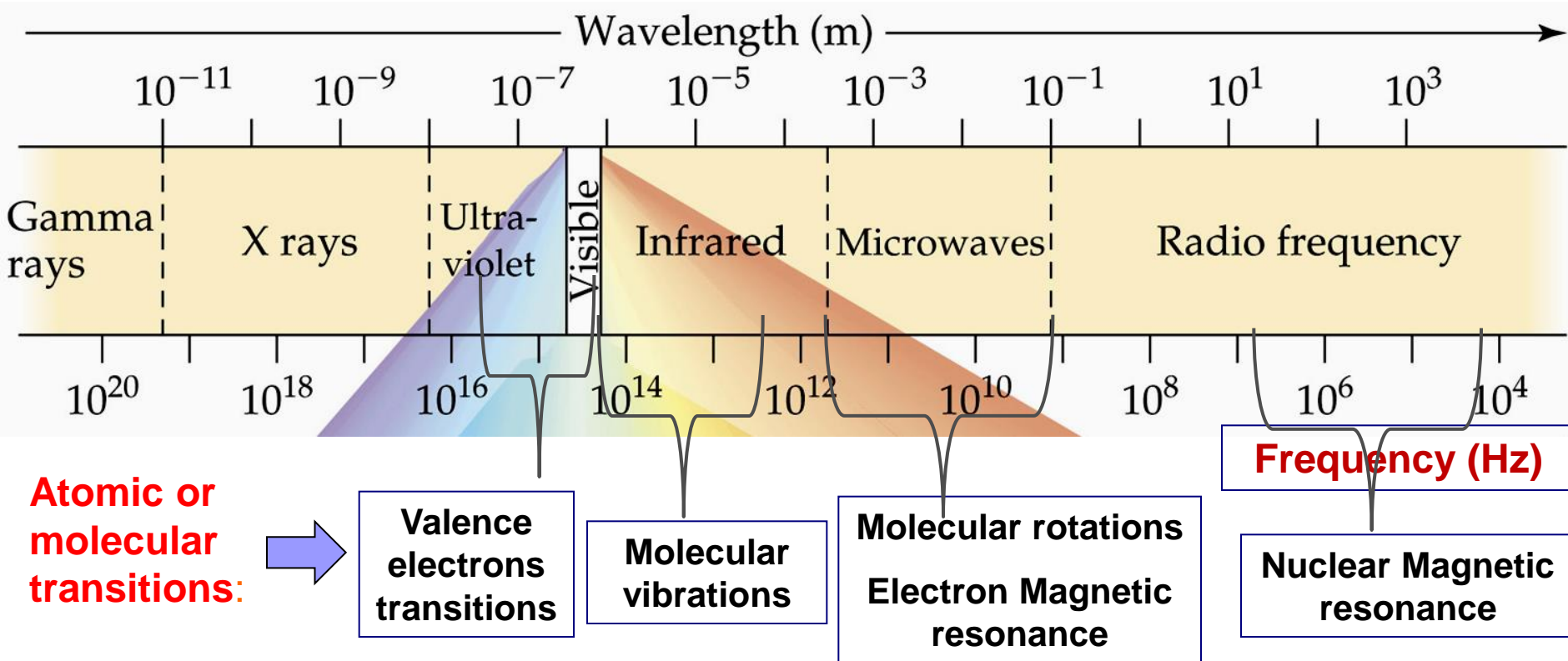
in molar units, J/mol

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

- ❖ Only photons with energies exactly equal to the energy difference between the two electron states will be absorbed
- ❖ Since different chemicals have different electronic shells which are filled, they will each absorb their own particular type of light

The electromagnetic Spectrum

The interactions of radiations with chemical systems follow different mechanism and provide different kinds of information. So, many analytical methods are based on the interaction of radiant energy with matter.

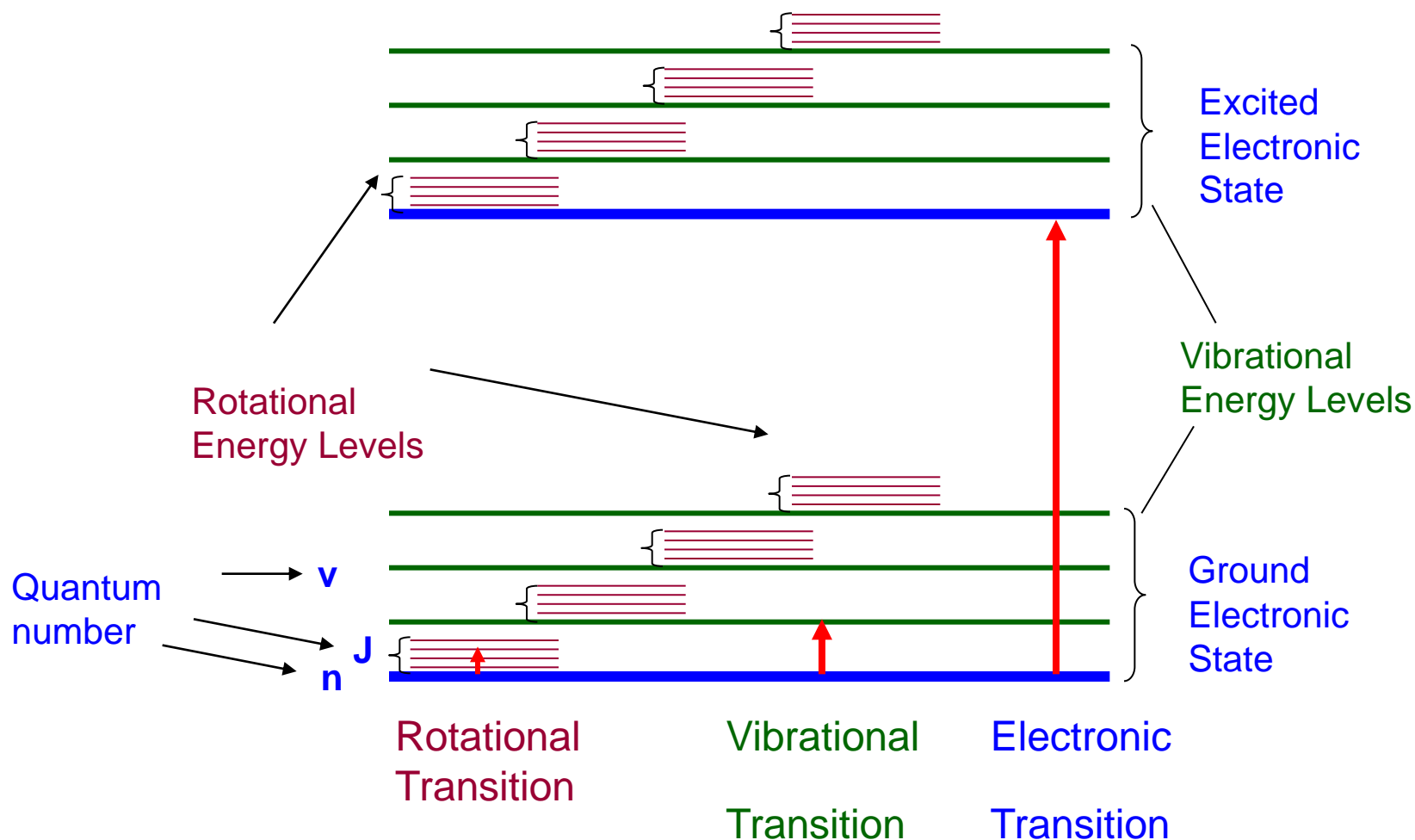


All electromagnetic radiation travels at the same speed, c

Spectral range	λ (nm)	ν (Hz)	(cm^{-1})	Energy (kJ/mol)	Spectroscopy
Radio	$\sim 1 \times 10^9$	$\sim 10^8$	~ 0.03 \checkmark	$\sim 10^{-8}$	NMR/ESR
Microwave	$\sim 100,000$	$\sim 10^{12}$	~ 30	$\sim 10^{-2}$	Rotational
Infrared	~ 1000	$\sim 10^{14}$	$\sim 3,000$	$\sim 10^3$	Vibrational
Visible	400-750	$4-6 \times 10^{14}$	14,000-25,000	$1 - 3 \times 10^5$	Electronic
Ultraviolet	100-400	$\sim 10^{15}$	$\sim 40,000$	$\sim 5 \times 10^5$	Electronic
X ray	< 100	$> 10^{16}$	$> 100,000$	$> 10^6$	Core electronic

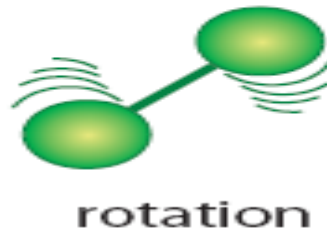
Molecular Energy Levels and interactions between light and matter

Radiations can be absorbed or emitted if the molecule changes any of its energy states (**be excited or relaxed**)



Molecular Energies

Molecules can have many different types of energy



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

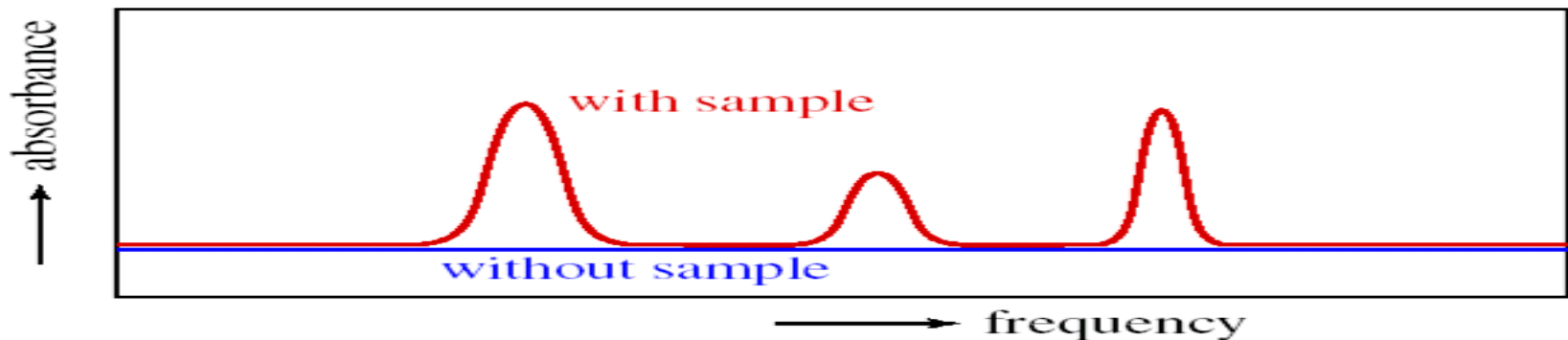
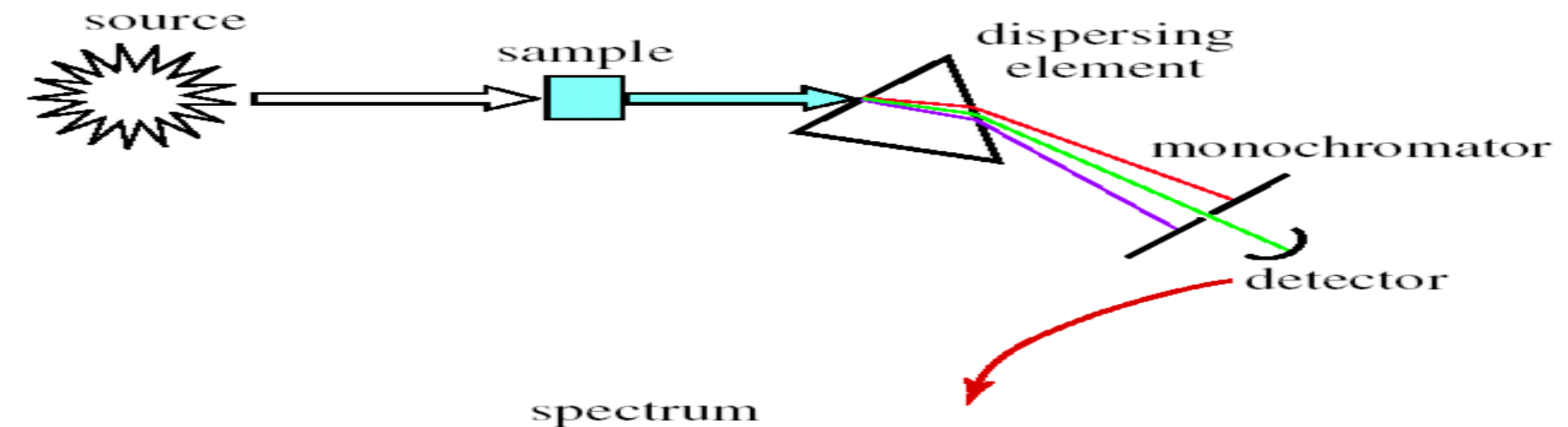


Basic components of Spectrometer

How the spectra are measured?

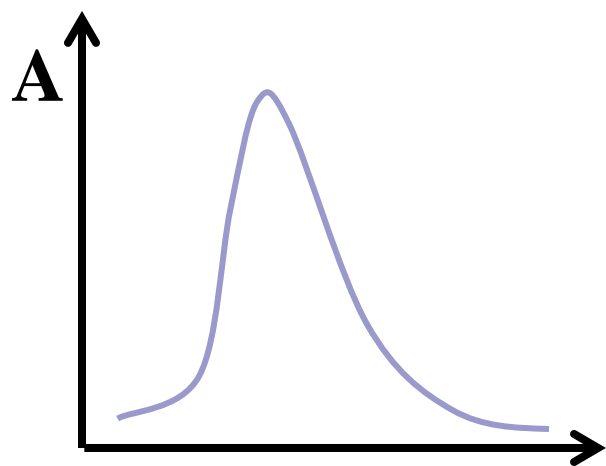
What is Spectroscopy?

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

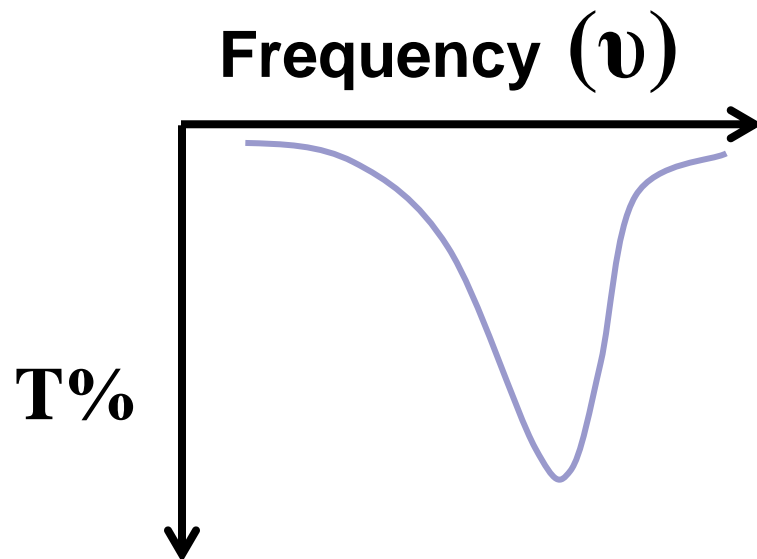


Spectra recorded by the Spectrometer

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.



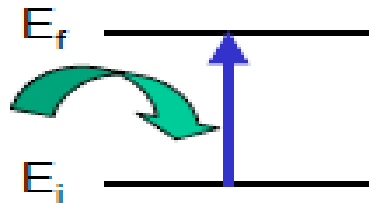
$\lambda = \text{Wavelength.}$



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

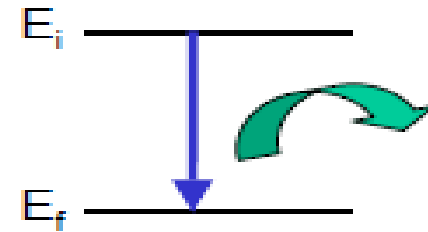
- electronic transitions
- rotational states change
- vibrational states change

Absorption spectroscopy:



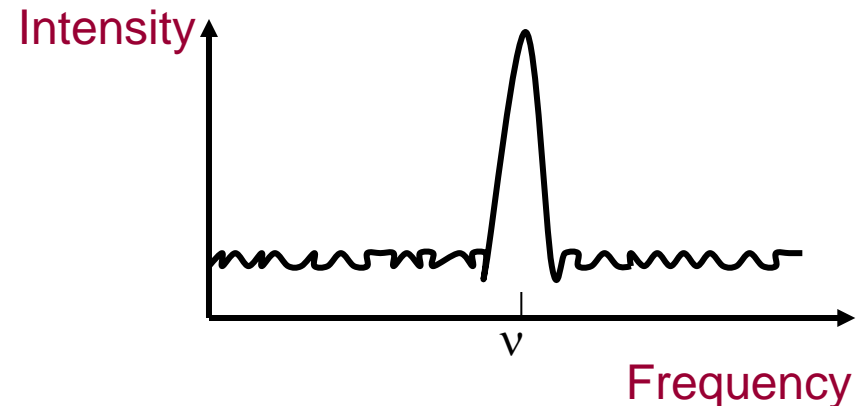
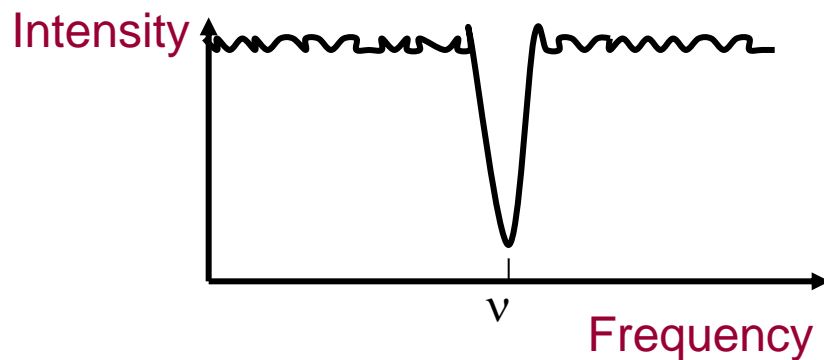
$$\Delta E = h\nu \quad (4.1)$$

Emission spectroscopy

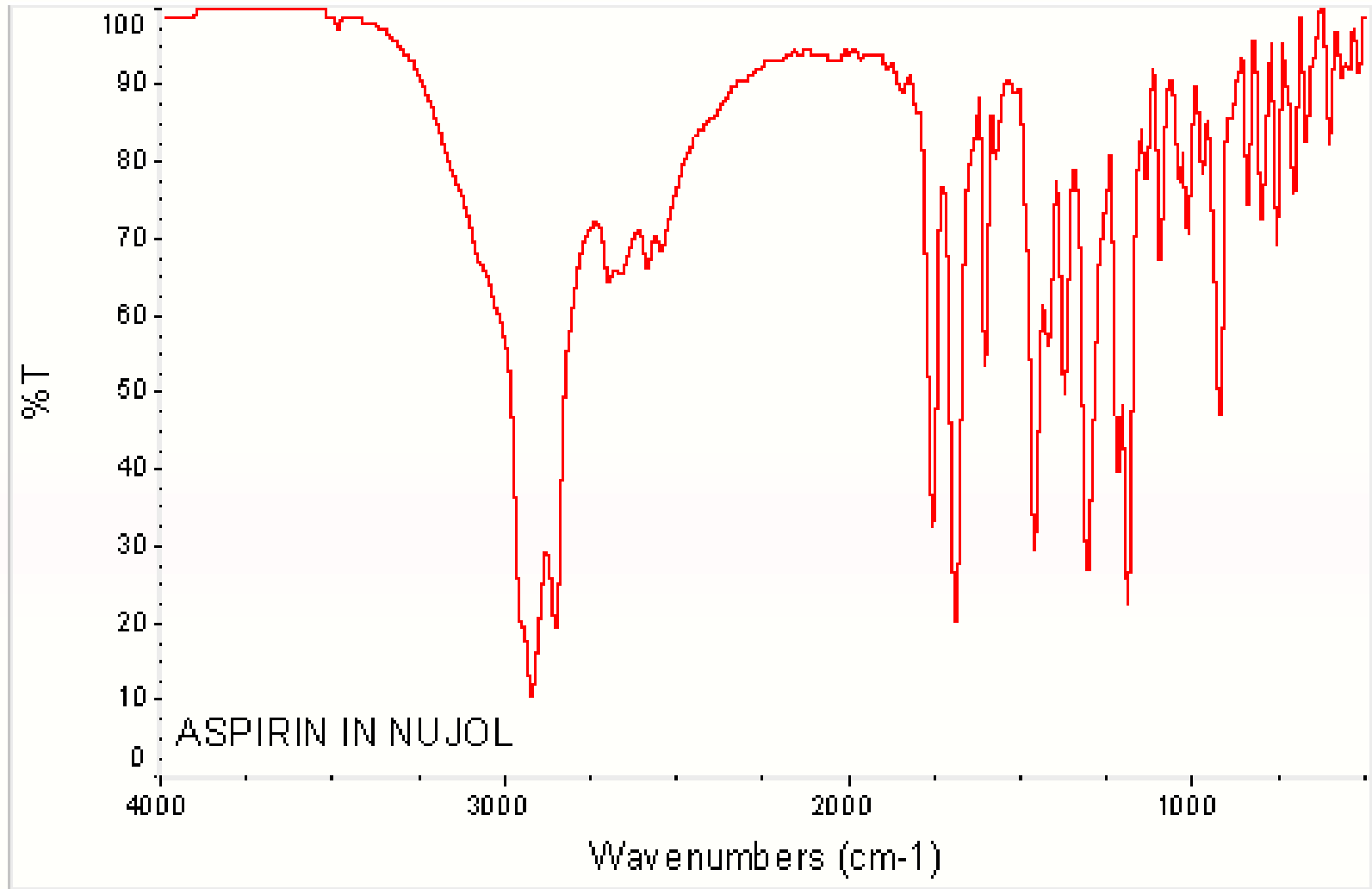


Emission or absorption spectroscopy:

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



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.

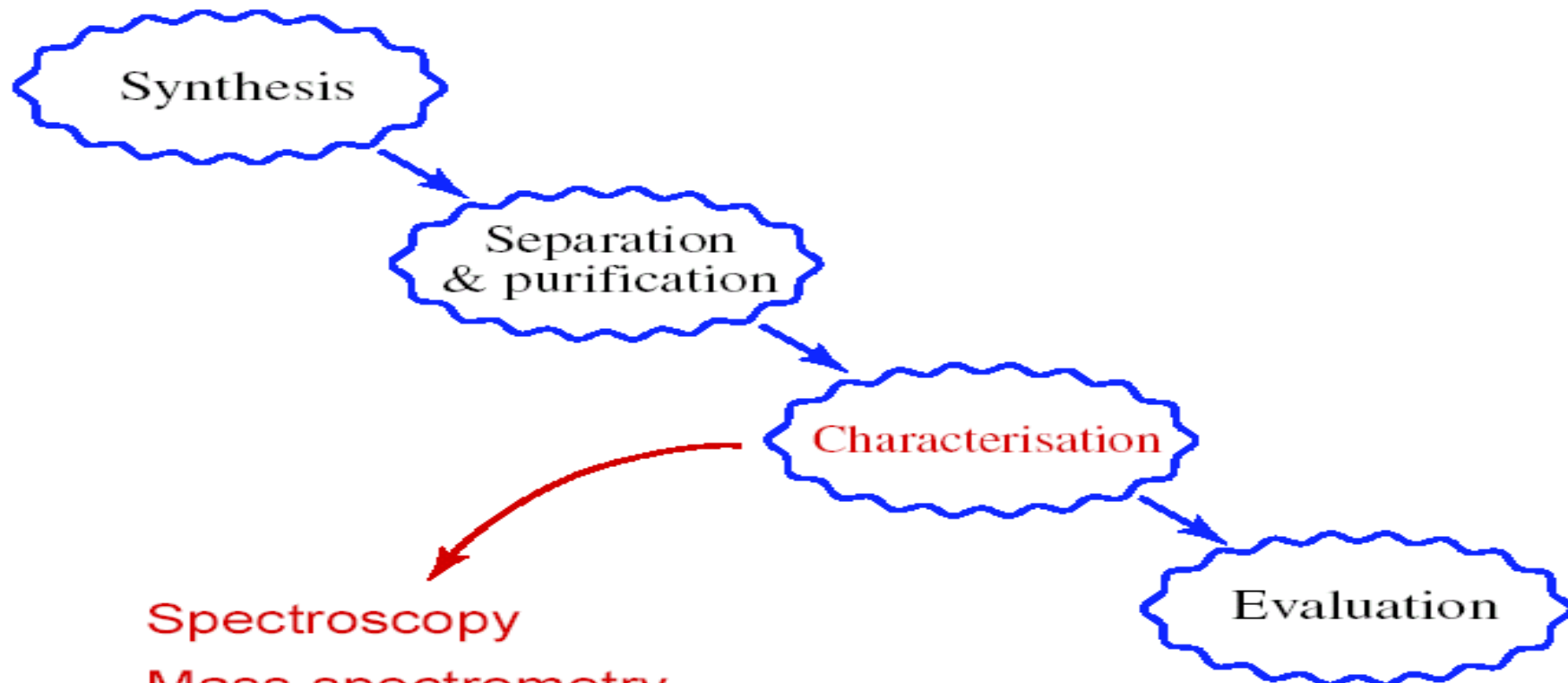
2. Width of spectral line: broadening of band is caused by;

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

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

- Transition probability (transition is allowed or forbidden).
- Population of states (how many molecule may interact).
- Path-length of the sample or conc. ($-\log (I/I_0) = A = \epsilon l c$)

The Role of Spectroscopy



Spectroscopy

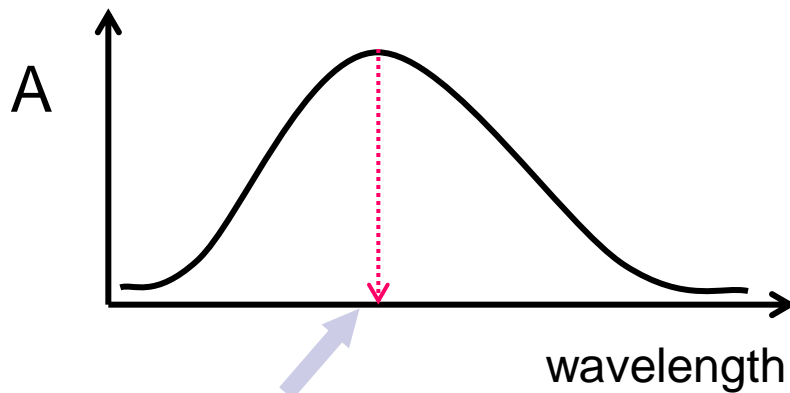
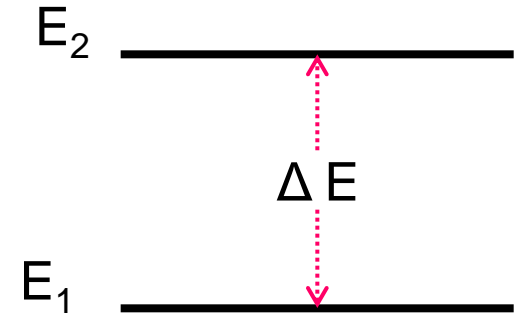
Mass spectrometry

Diffraction & scattering (X-rays, neutrons)

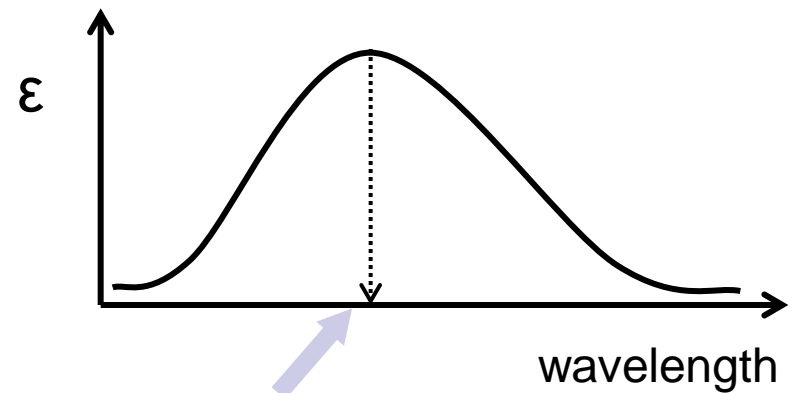
1. Bands Position

$$\Delta E = E_2 - E_1$$

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

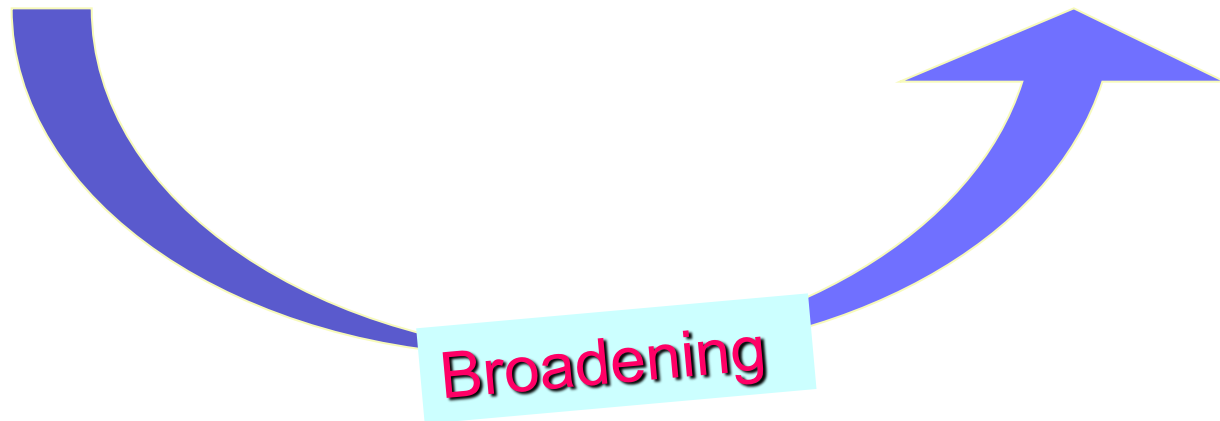
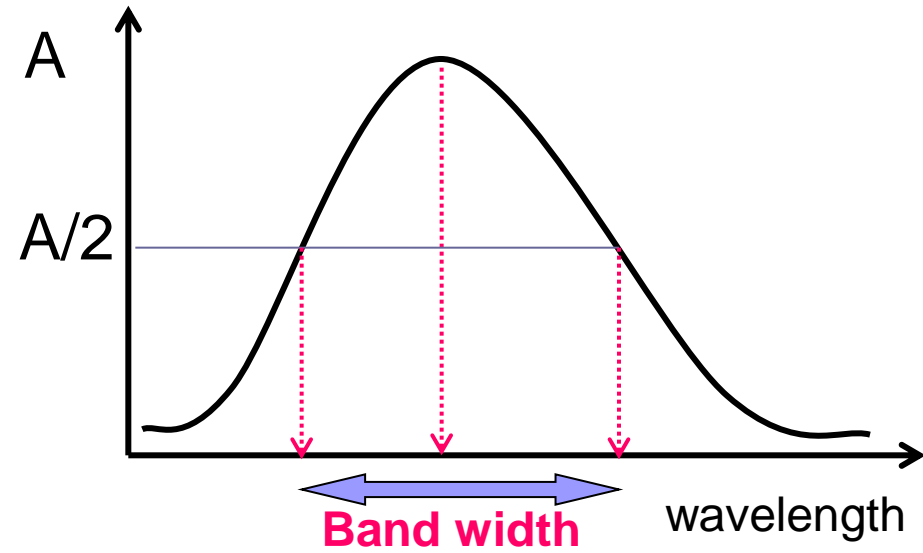
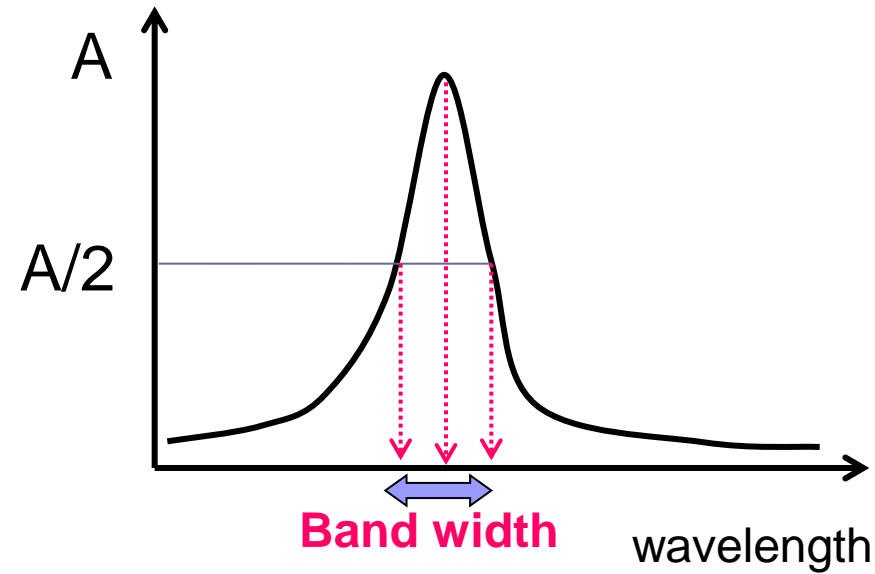


Band position



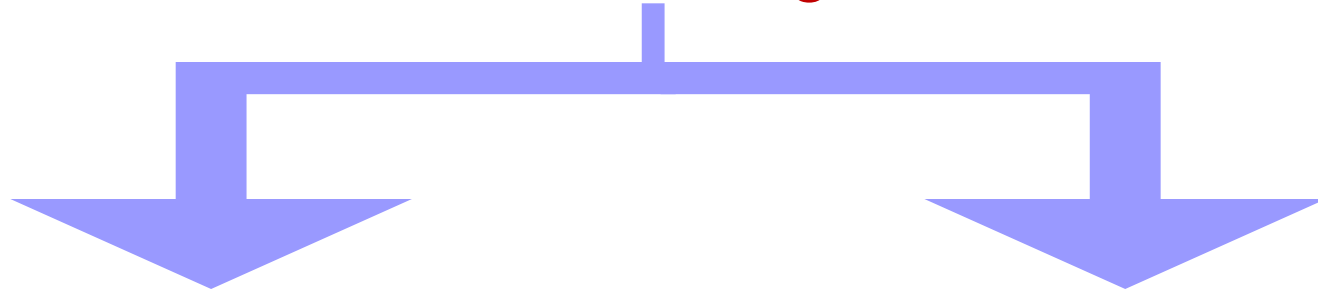
Band position

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 the 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 ν_0 , the molecule is moving toward or away from the stationary observer (**detector**) with velocity ($\pm v$), then the observer measure the frequency not as ν_0 but as ν where;

$$\bar{\nu} = \nu_0 \left(1 \pm \frac{v}{c} \right)$$

iii. Life-time broadening

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

According to Heisenberg Uncertainty Principle;

$$\delta(E) \times \delta(t) \approx \frac{h}{2\pi} = \hbar$$

$$\delta(t) = \text{uncertainty in time} = \tau$$

Lifetime broadening in frequency $= \frac{1}{2\pi c \tau}$
Where τ is the lifetime

example

- Calculate the lifetime broadening in cm^{-1} for an excited state with lifetime ($\tau = 1\text{p.s.}$).

Note: $1\text{p.s} = 10^{-12}\text{ s}$.

$$\begin{aligned} \text{Lifetime broadening in wavenumber} &= \frac{1}{2\pi c \tau} \\ &= \frac{1}{2 \times 3.14 \times 2.998 \times 10^{10} \times 1 \times 10^{-12}} \end{aligned}$$

The intensity of the spectral line

It is governed by;

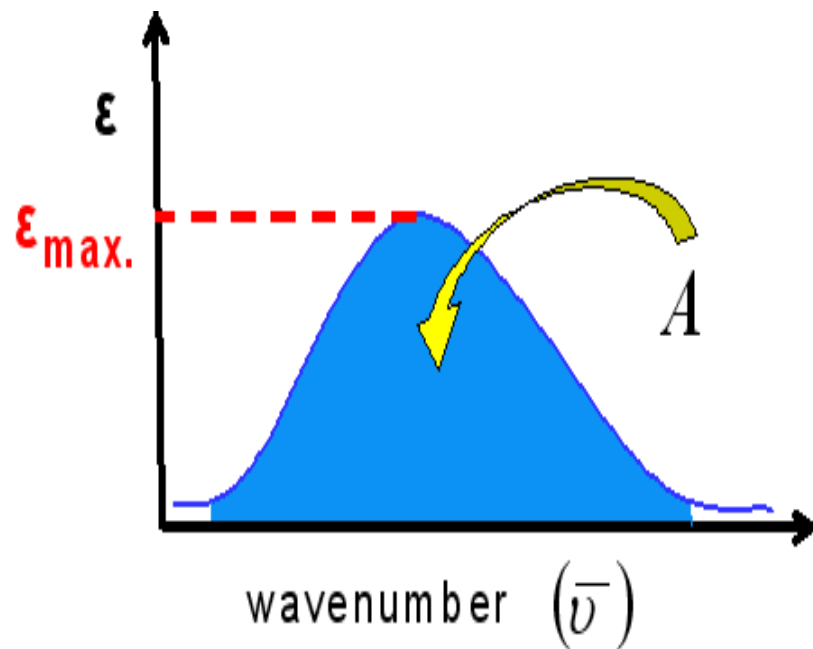
1. Transition probability from which selection rules can be obtained.
2. Population of the energy levels.
3. Path length of the sample.

Transition probability is governed by transition moment $|M|$

Transition moment gives the probability of a transition between two states (1) and (2) as a result of photon resonance absorption obeying Bohr-Einstein conditions:

$$E_2 - E_1 = hc\bar{\nu}$$

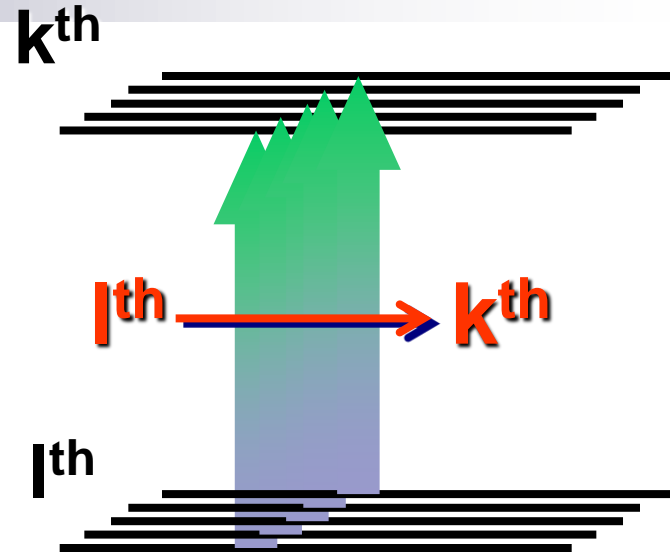
The maximum value of molar absorption coefficient ($\epsilon_{\max.}$), oscillator strength (f -number) and integrated absorption coefficient (A) are taken as indications for the intensity of transition.



$$A = \int_{band} \epsilon_{(\bar{\nu})} d\bar{\nu}$$

Oscillator strength (f):

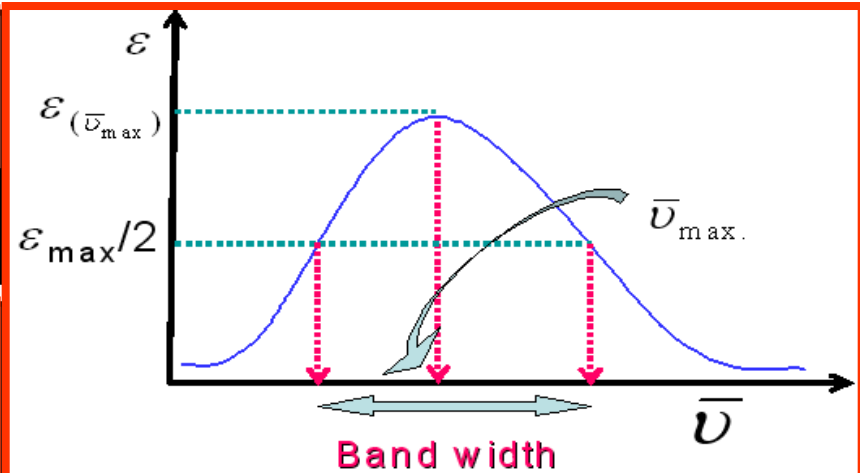
If we regard the molecule as oscillating dipole then the oscillator strength (f) is defined as the number of virtual oscillators equivalent to transitions from $l^{\text{th}} \rightarrow k^{\text{th}}$ electronic state in quantum theory.



$$f = 4.32 \times 10^{-9} \int_{band} \epsilon_{(\bar{\nu})} d\bar{\nu}$$

If the band has Gaussian shape:

$$\begin{aligned} \int_{band} \epsilon_{(\bar{\nu})} d\bar{\nu} &= \epsilon_{(\bar{\nu}_{max})} \times \Delta\bar{\nu}_{1/2} \\ &= \epsilon_{(\bar{\nu}_{max})} \times (\text{band width}) \end{aligned}$$



$$f \geq 1$$

Allowed transition

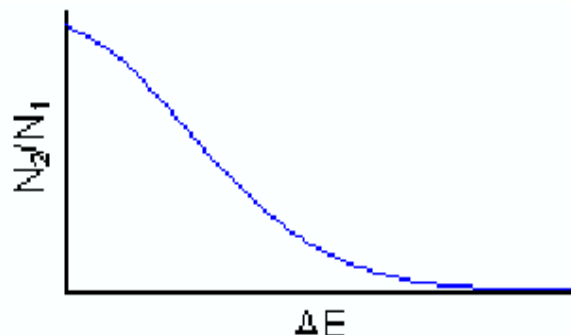
$$f \ll 1, (10^{-2} - 10^{-4})$$

forbidden transition

Population of the energy levels

1. Boltzmann distribution

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



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

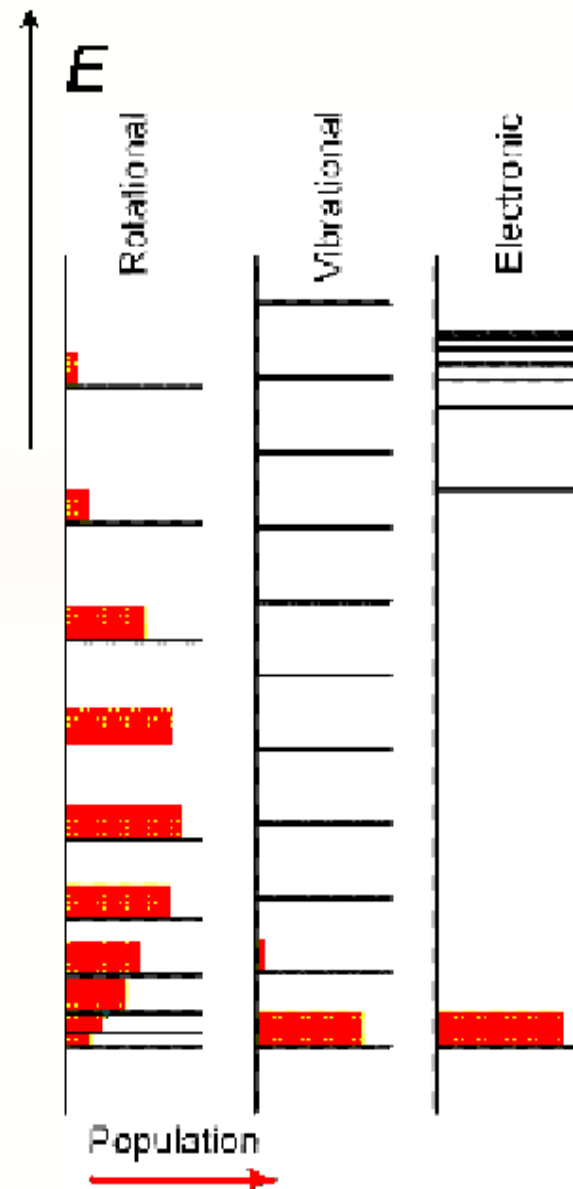
$$\frac{N_2}{N_1} = e^{-(h\nu / kT)} = e^{-(hc\tilde{\nu} / kT)} = e^{-(N_A hc\tilde{\nu} / RT)}$$

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

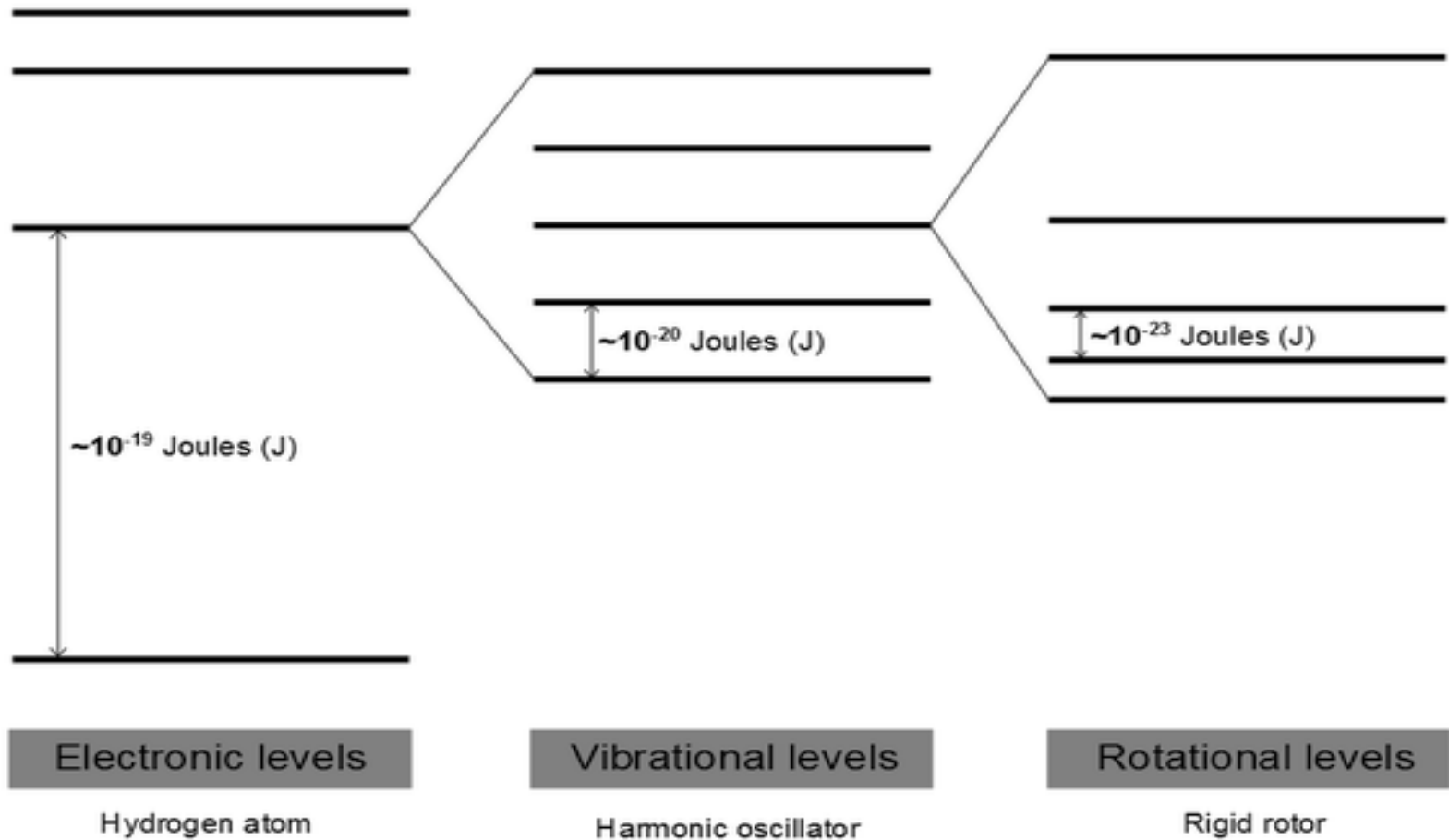
2. Number of degenerated energy levels

Number of degeneracy = $2J + 1$

Where; J is the rotational quantum number

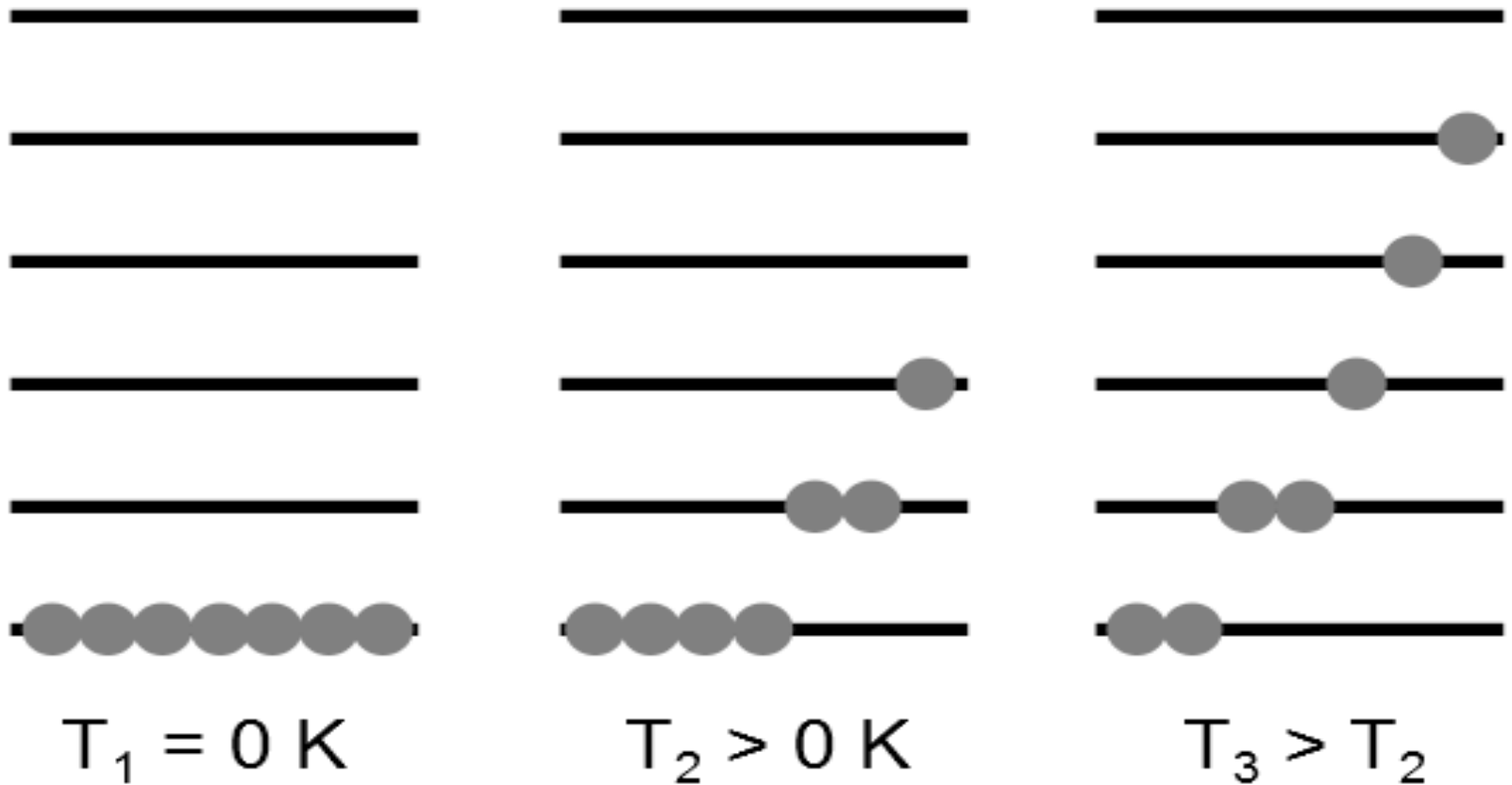


Typical values for energy level separations



Population of energy states

Population of a state is the average number of molecules in a state at any time.



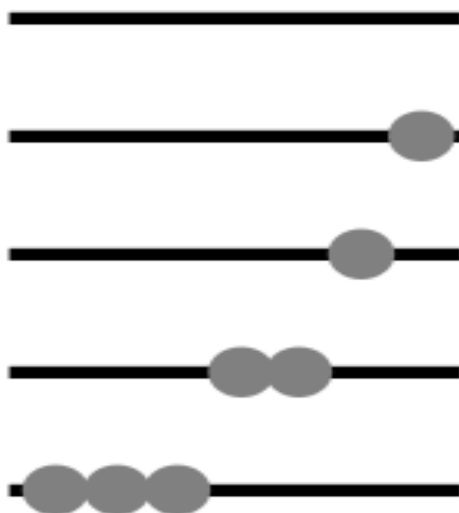
At lower temperatures, the lower energy states are more populated. At higher temperatures, more higher energy states become populated, but each with less population.

Effect of energy separation on the population of states

At 300 K $k_B T \sim 2.5 \text{ kJ mol}^{-1}$.

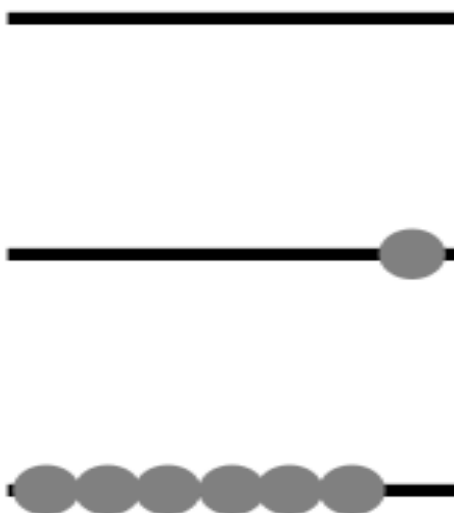
Rotational

$$\Delta E = 0.012 \text{ kJ mol}^{-1}$$



Vibrational

$$\Delta E = 12 \text{ kJ mol}^{-1}$$



Electronic

$$\Delta E = 120 \text{ kJ mol}^{-1}$$



Example

Assuming that the vibrational energy levels of HCl and I_2 are equally spaced, with energy separations of 2990.94 and 216.51 cm^{-1} respectively, calculate for each case the ratio of the number of molecules in the first two vibrational states relative to the ground state at $T = 300 \text{ K}$ and 800 K .

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} ?*