# Molecular Energy levels

## and

# Interaction of Electromagnetic Radiation with Matter.

→ There exist 92 elements → stable atoms

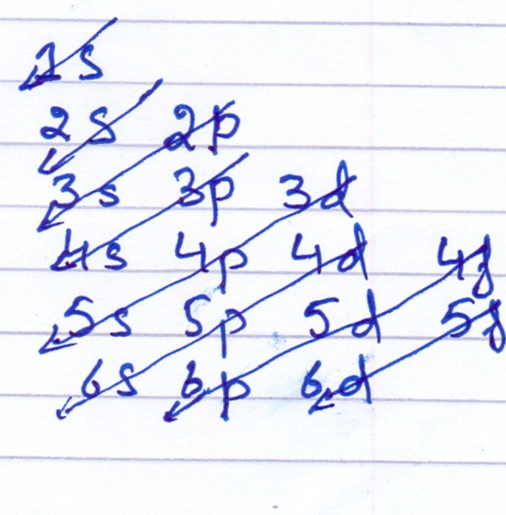
→ Atoms can form molecules

→ The number of atoms in a molecule vary from two → as in $N_2$, to many thousands as in DNA

⇒ Molecules form when the total energy of the ēs is lower in the molecule than in individual atoms

⇒ According to Aufbau principle states: to put ēs into the lowest energy configuration in atom.

⇒ The same principle goes for molecules.



Properties of molecules depend on:

→ The specific kind of atoms they are composed of

→ The spatial structure of the molecules – the way in which the atoms are arranged within the molecule.

→ The binding energy of atoms or atomic groups in the molecule.

Types of molecules

⇒ Monoatomic molecules

→ The elements that do not have tendency to form molecules.

→ Elements are stable single atom molecules

Examples are: helium, neon, argon, krypton xenon and radon.

## ⇒ Diatomic Molecules:

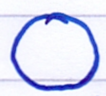
→ Are composed of only two atoms – – of same or different elements.

Examples: hydrogen ($H_2$), oxygen ($O_2$), Cabon monoxide (CO), nitric oxide (NO)

## ⇒ Polyatomic Molecules

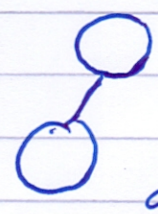
Consist of a stable system comprising three or more atoms.

Atomic oxygen



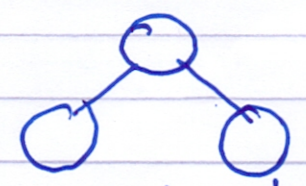
monotomic

Diatomic oxygen



diatomic

Ozone



polyatomic

# Formulas.

⇒ Empirical formula: gives the simplest whole number ratio of all the atoms in a molecule.

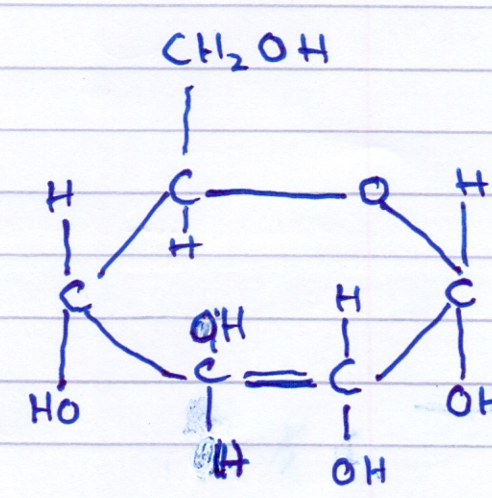
→ Example: The empirical formula of glucose is $CH_2O$

Molecular formula: Describes the exact number and type of atoms in a single molecule of a compound

- Ex: The molecular formula for glucose is $C_6H_{12}O_6$

Structural formula.

Indicates the number of atoms and their arrangement in space



# Difference between Isomers and Allotrope

## ISOTOPE:

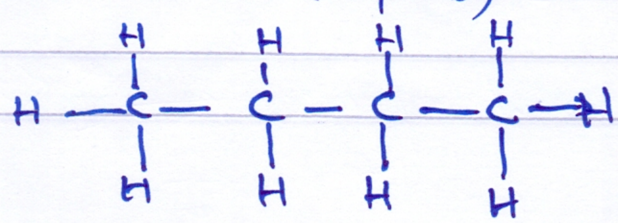
Atoms with the same number of protons but different number of neutrons are called isotopes = chemical behaviour remains unchanged

## ISOMERS:

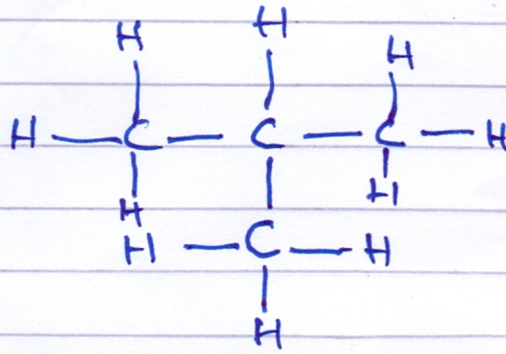
Two molecules with the same atoms joined together in a different shape.

→ Same molecular formula but different chemical structure.

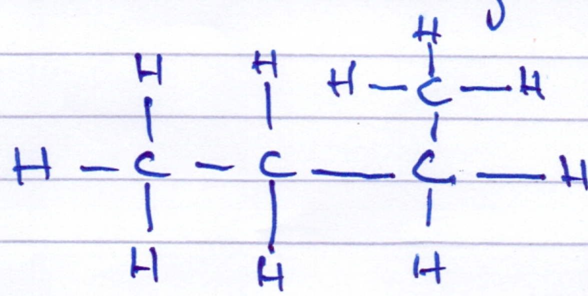
Examples: Butane $(C_4H_{10}) = CH_3CH_2CH_2CH_3$



⇒ n-butane or isobutane



Same molecular formula by different structural arrangment.



Another shape.

## ALLTROPE

Different structural forms of the same element but exhibit quite different physical and chemical properties.

Example: Diamond, graphite, ...

# Chemical Bonds

→ Chemical bonds between atoms in a molecule make the situation more stable for the involved atoms.

Ionic Bonding: is the complete transfer of valence electron(s) between atoms.

→ It generates two oppositely charged ion.

→ In ionic bonds, the metal loses ēs to become a +ively charged ion (cation) whereas the non-metal accepts those ēs to become a -ively charged anion.

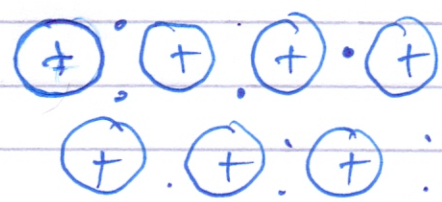
→ Two opposite ions attract each other and form the ionic bond.

Covalent Bonds: is a form of chemical bonding between two non-metal atoms which is characterized by the sharing of pairs of electrons between atoms

→ The only pure covalent bonds occur between identical atoms.

<u>Metallic bonds:</u> occur between the ionized atoms of metal and the sea of $\bar{e}$s around them.

→ is a type of chemical bonding that rises from the electrostatic attractive force between conduction $\bar{e}$s (in the form of an electron cloud) and positively charged metal ions



## Energy levels

A quantum mechanical system or particle that is bound - can take discrete values of energy. - Energy levels

-> It is used for energy levels of ēs in atoms, ions or molecules - bound by the Electric field of the nucleus.

-> Energy levels of nuclei or vibrational or rotational energy levels in molecules, are also refered as this.

-> If an atom, ion and molecule is at the lowest possible energy level, and its ēs are said to be in the <u>ground state</u>.

-> Any electrons that have higher energy than the ground state are <u>excited state</u>

- Quantized energy levels result from the relation b/w a particle's energy and its wavelength.

- For a confined particle, such as an electron in an atom, the wave function has the form of standing waves.

- Stationary states with energies corresponding to integral numbers of wavelengths can exist.

- Examples that show how energy levels come about mathematically are the
  - Particle in a box
  - Quantum harmonic oscillator.

- 

# Molecular Energy Levels

⇒ Energy can be stored as potential and kinetic energy in different ways.

1, Translational energy: small amount of energy stored as kinetic energy.

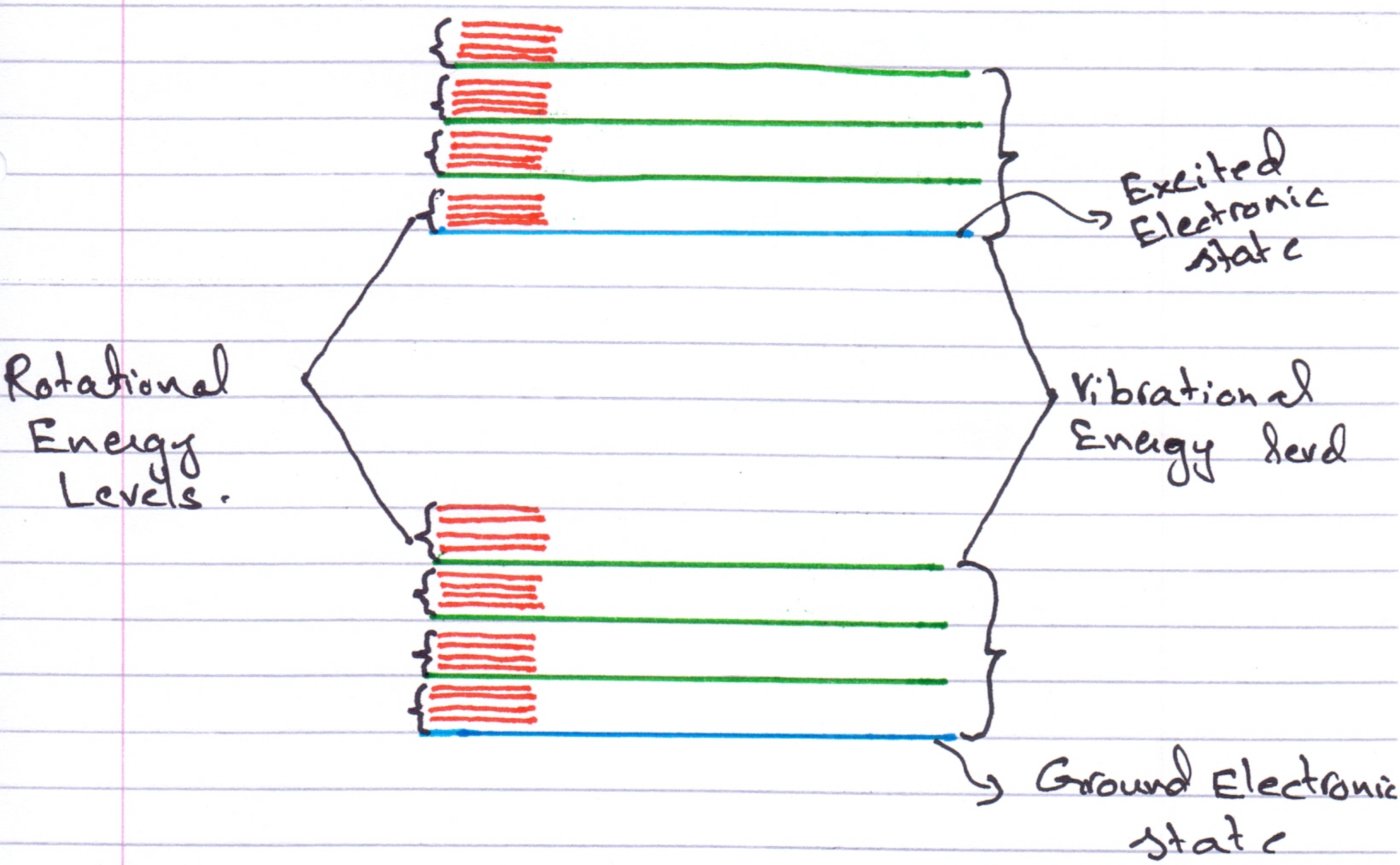
2, Rotational energy: Kinetic energy associated with the rotational motion of molecules.

3, Vibrational energy: The oscillatory motion of atoms or group of atoms with in a molecule (potential ⟷ kinetic energy exchange)

4, Electronic Energy: energy stored as potential energy in excited electronic configurations

→ All except the Translational energy are quantized

$$E_{molecule} = E_{rot} + E_{vib} + E_{ele}$$


Excited Electronic state
Rotational Energy Levels.
Vibrational Energy level
Ground Electronic state

# Molecular Energy levels.

⇒ The relative energy of the spacing b/w energy levels for various types of transitions in a molecule are in the order.

| Rotational Transitions | ≪ | Vibrational Transition | ≪ | Electronic Transition |
|---|---|---|---|---|
| 1 - 20 $cm^{-1}$ | | 2000-4000 $cm^{-1}$ | | 10000 - 50000 $cm^{-1}$ |

⇒ The various types of energy transitions occur in different regions of the EM-Spectrum and do not overlap.

# Molecular Electronic levels

→ In molecules we have two opposing forces – the repelling force of the nuclei and the binding force of the electrons.

→ If the orbit of the electrons change then binding force will change ⇒ The net potential energy of the molecule will change.

⇒ This leads to the change in inter-atomic distance.

⇒ Different electronic levels will have different rotational and vibrational constant.

⇒ $E_{n,v,J} = E_n + E_v + E_j$

## Vibrational Molecular Levels

→ Like atoms – molecular motion is governed by quantum mechanics.

→ Energies due to rotation and vibration are quantized.

## Molecular Vibrations

→ Chemical bond acts like a spring and can display SHM

→ with an effective spring constant $k$ for the bond involved and effective mass $m_{eff}$

→ Angular freq. $\omega = \sqrt{\frac{k}{m_{eff}}}$

→ Energy of vibration

$$E_v = \left(v + \frac{1}{2}\right)\hbar\omega = \left(v + \frac{1}{2}\right)hf$$

→ $\frac{1}{2}\hbar\omega$ — zero-point energy that implies that molecule never stops vibrating – even in the $v=0$ state

→ $v$ — vibrational quantum number

$v = 0, 1, 2, 3, \ldots$

→ zero-point energy exists at absolute zero

→ Energy levels are equally spaced with separation $\hbar\omega$

→ Follows selection rule $\Delta V = \pm 1$, if no accompanying electronic transition otherwise can be anything.

→ For diatomic molecule with mass $M_1$ & $M_2$

$$m_{eff} = \frac{M_1 M_2}{M_1 + M_2}$$

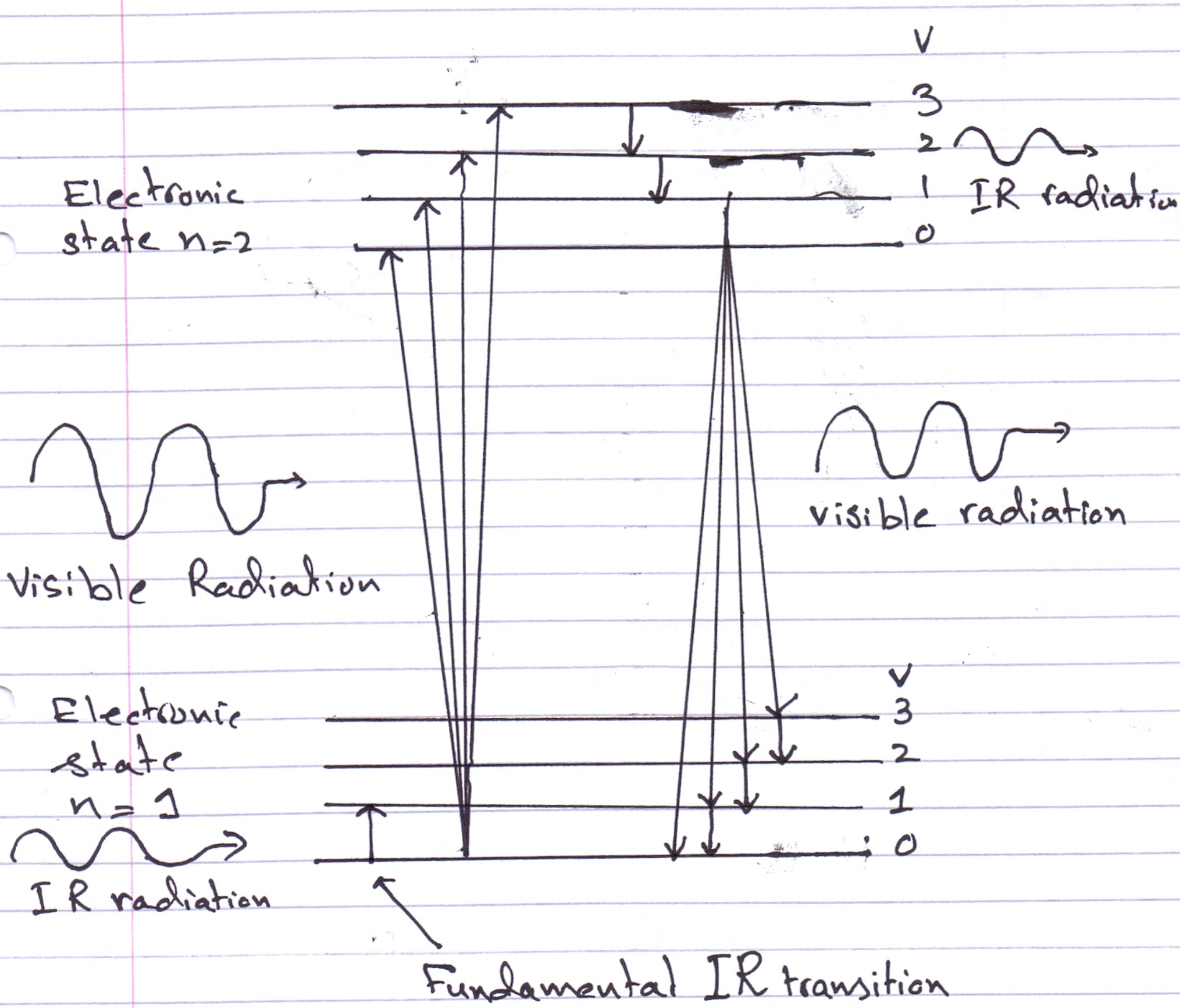
→ Energy scale for molecular vibrations is much less than for electronic excitations

→ Excitation energies corresponds to IR region of the spectrum.

→ Vibrational levels are built on electronic states - each electronic state will host the whole range of vibrational states.

→ At normal temperature most of molecules will be in state $V=0$

# Vibrational excitation and de-excitation



# Rotational Molecular Levels

→ In quantum machanics – the rigid rotor has energy levels

$$E_J = \frac{\hbar^2}{2I} J(J+1)$$

where I – is the moment of inertia of the rigid rotor relative to the axis of rotation.

→ $J = 0, 1, 2, \ldots$ Angular momentum

→ Excitation energies correspond to the microwave region

→ Energy scale for rotations << vibration

→ Each vibrational level has rotational bands built on it

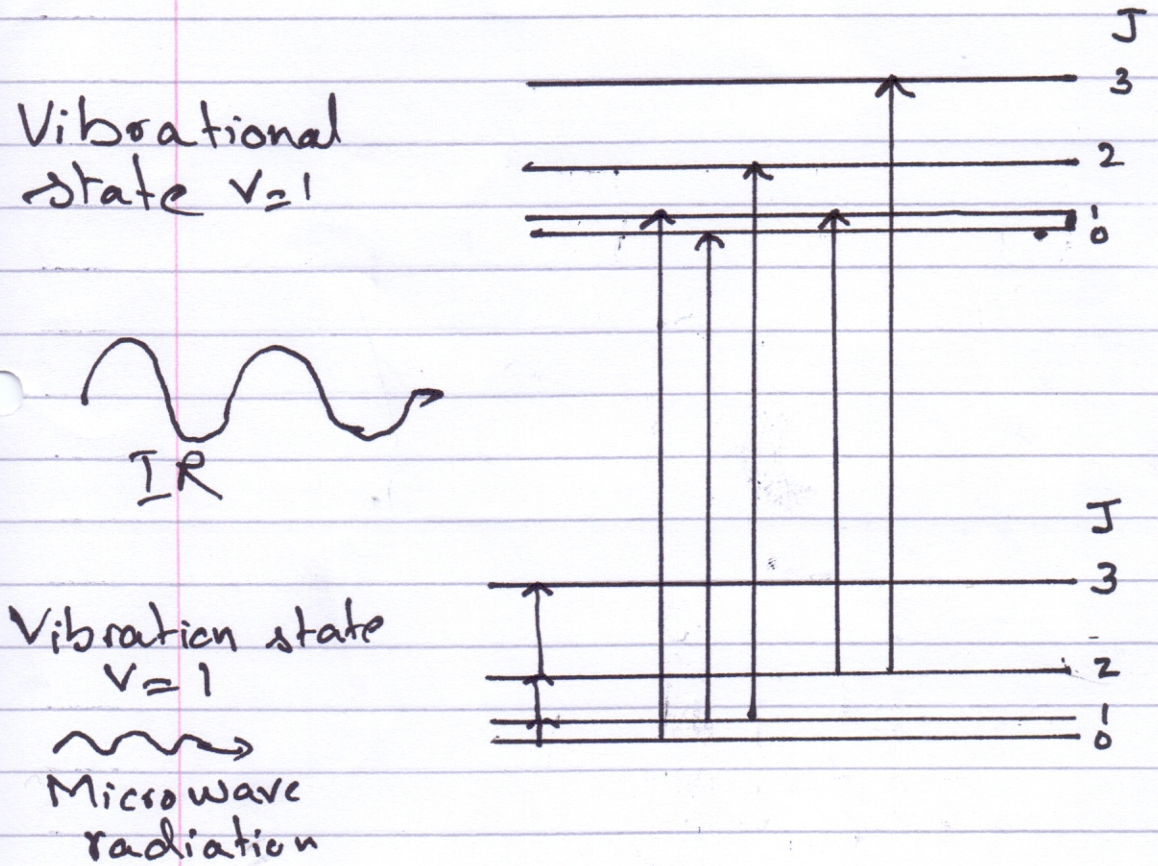
→ Selection rule ⇒ $\Delta J = \pm 1$

Rigid Rotor is a mechanical model that is used to explain rotating systems.

→ The linear rigid rotor model consists of two point masses at fixed distances from their center of mass. For many diatomics ~~this~~ the distances are not usually fixed.

$E = T + V$ as $V \to 0$ for fixed distance

# Rotational Levels




⇒ Two types of transitions

J → increasing

J → decreasing

# Molecular Spectroscopy

⇒ Is the study of the interaction of electromagnetic radiation with matter.

⇒ Based on the analysis of EM radiation that is emitted, absorbed or scattered by molecules – we can have information on

→ Chemical analysis

→ Molecular structure
  → Bond length
  → Strengths
  → angles
  → energy levels

⇒ EM radiations consists of photons which behave as both particles & waves.

$c = \nu\lambda$

$\lambda$ – wavelength

$\nu$ – freq

$c$ – speed of light.

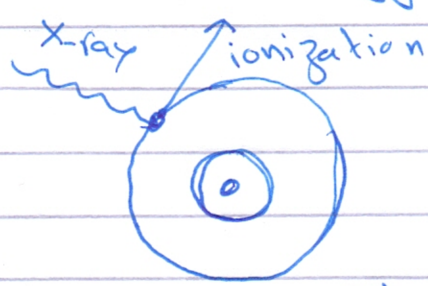
# X_Ray Interactions

⇒ Energies of X-ray photons are too high to be absorbed by electronic transitions in most atoms

⇒ Only possibility is the complete removal of an electron from atom

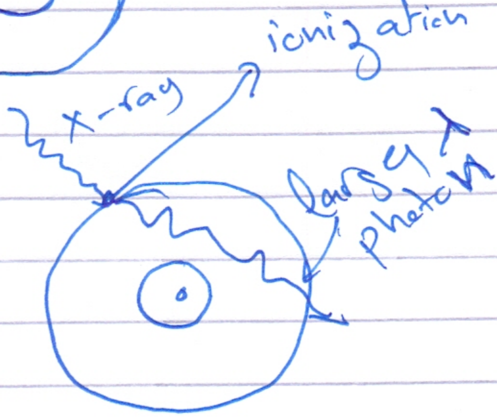
⇒ X-rays are ionizing radiation

⇒ <u>Photoionization</u>: If ~~the~~ all the energy is given to an electron



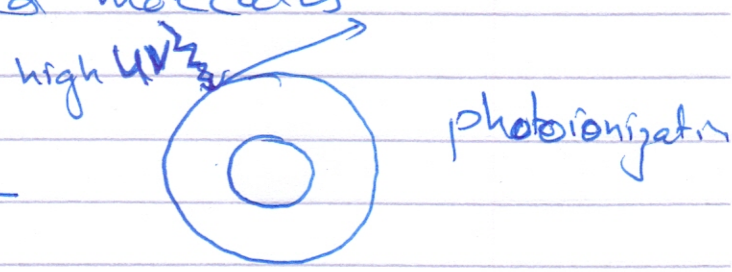

<u>Compton Scattering</u>

If part of the energy is given to an electron and the rest ~~go~~ to a lower energy photon



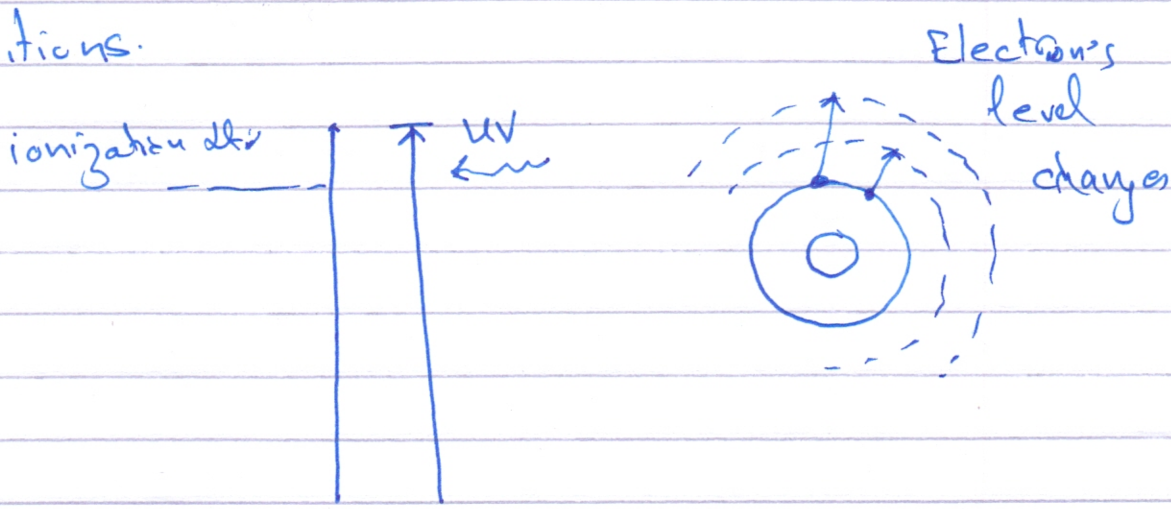
# ULTRAVIOLET INTERACTIONS

⇒ UV photons above the ionization energy can disrupt atoms and molecules




⇒ At higher energies - ionizing limit for many molecules are reached and photoionization takes place.

⇒ UV photons below the ionizing energy are strongly absorbed in producing electronic transitions.

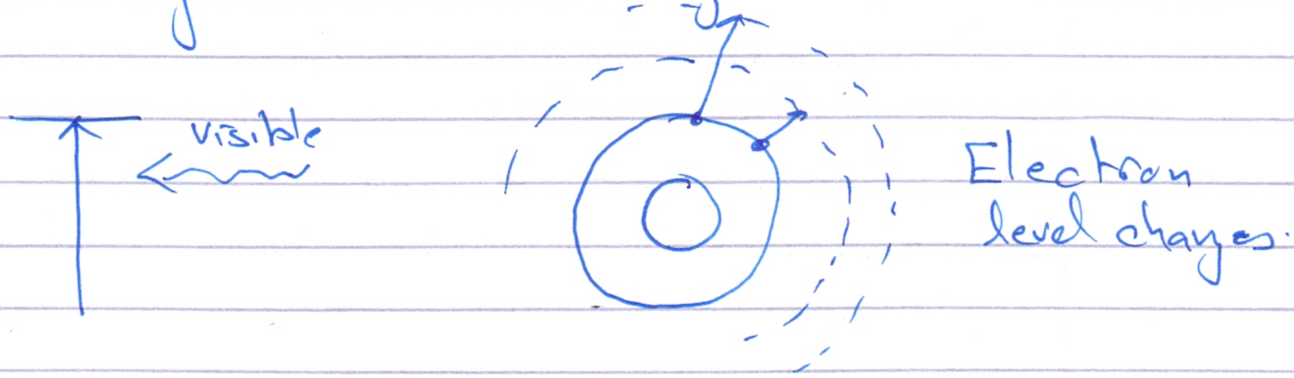


# Visible Light Interactions:

=> Visible light is absorbed by electron transitions.

=> Higher energies are absorbed more relative to low energies.— red light is less strongly absorbed than blue light.

=> Absorption of visible light can causes heating but no ionization



## UV & visible Spectroscopy.

-> An emission spectrometer is used to analyse light emitted from an excited source.

=> Radiation from an external source interacts with matter - absorption occurs.

-> Certain characteristic frequencies ~~are~~ of radiation are absorbed by each kind of matter and these frequencies are thus missing from the spectrum of radiation reflected from the object.

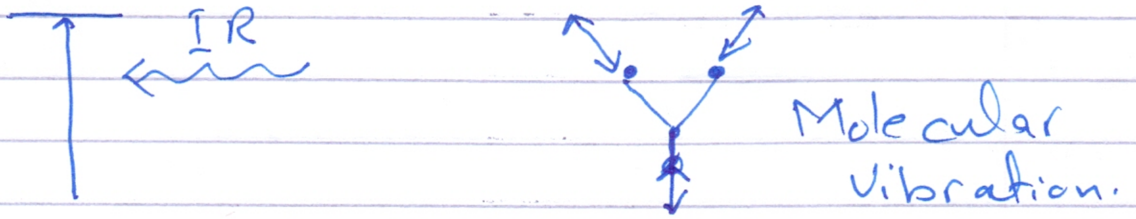
=> A red apple is absorbing white light and reflecting wavelengths of of visible light that are in the red region.

-> An absorption spectrometer is used to analyze light reflected by or transmitted through matter.

# Infrared Interactions

⇒ The energy of infrared light corresponds to the energy required to cause molecular vibration (molecule absorbs a quanta of energy E=hν)

⇒ Vibrations arise as molecular bonds are not rigid but behave like springs.




⇒ A molecular vibration occurs when atoms in a molecule are in periodic motion.

→ while molecule as whole has constant translational and rotational motion.

⇒ A fundamental vibration is excited when one quantum of energy E=hν is absorbed by the molecule in its ground state.

⇒ For two quanta absorbed the first overtone is excited and so on.

⇒ The vibrational states of a molecule can be probed by using.

→ Infrared spectrascopy.

→ Raman "

Infrared Spectrascopy: involves the interaction of infrared radiation with matter — its is based on absorption spectrascopy.

Raman Spectroscopy: used to observe the vibrational, rotational and other low frequency modes in a system. Its is commonly used in chemistry.

⇒ It relies on inelastic scattering, or Raman scattering of monochromatic light (say laser) in visible, near infrared or near ultraviolet range.

⇒ The laser light interacts with molecular

Vibrations, phonons or other excitations in the system.

~~As~~

⇒ The energy of the laser photons being shifted up or down ⇒ gives information about the vibrational modes in the system.

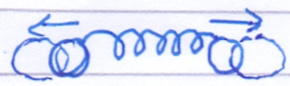
⇒ Vibrational excitation can occure in conjuction with electronic excitation in ultra-violet - visible region = called Vibronic transition.

⇒ Vibrational

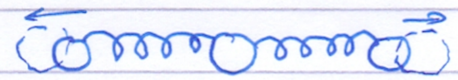
Vibrational transitions are sub-divided into two classes

→ **Stretching:**

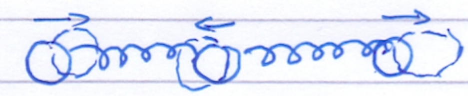
Symmetric and Asymmetric



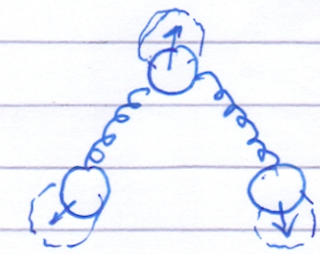
diatomic
$N_2$, $O_2$, CO



Linear triatomic ($CO_2$, $N_2O$)



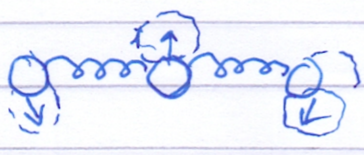
Asymmetric stretch.



→ **Bending**

Scissoring, rocking, wagging and twisting.

→ Stretching frequencies are higher than corresponding bending frequencies — it is easier to bend a bond than to stretch or compress it



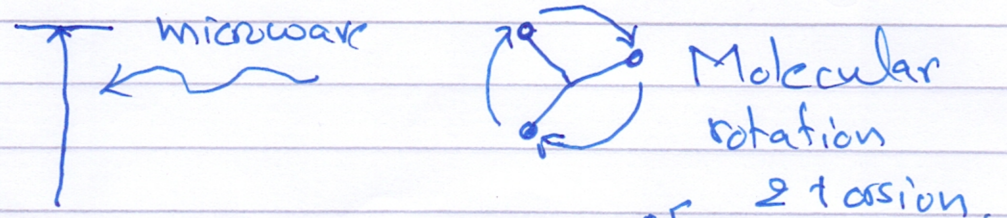
Triatomic ($H_2O$, $O_3$)

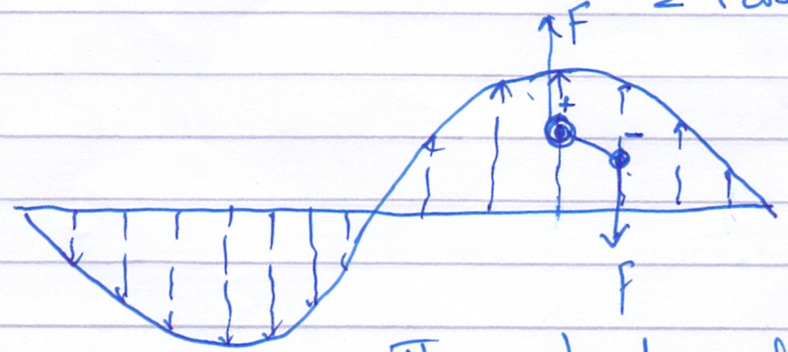
# Microwave Interactions

→ Quantum energy of microwave photons matches the ranges of energies separating quantum states of molecular rotations.

→ Rotational motion of molecules is quantized.

→ Absorption of microwave radiation causes heating due to increased molecular rotational activity.




The electric field of an electromagnetic wave exerts a torque on an electric dipole