MOLECULAR ENERGY LEVELS

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OUTLINE

- ❑ MOLECULE
- ❑ MOLECULAR ORBITAL THEORY
- ❑ MOLECULAR TRANSITIONS
- ❑ INTERACTION OF RADIATION WITH MATTER
- ❑ TYPES OF MOLECULAR ENERGY LEVELS

MOLECULE

- In nature there exist 92 different elements that correspond to stable atoms.
- These atoms can form larger entities- called molecules.
- The number of atoms in a molecule vary from two - as in N_2 - to many thousand as in DNA, protiens etc.
- Molecules form when the total energy of the electrons is lower in the molecule than in individual atoms.
- The reason comes from the **Aufbau principle** - to put electrons into the lowest energy configuration in atoms.
- The same principle goes for molecules.

❑ MOLECULE

❑ 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 which are stable single atom molecules are the noble gases : helium, neon, argon, krypton, xenon and radon.

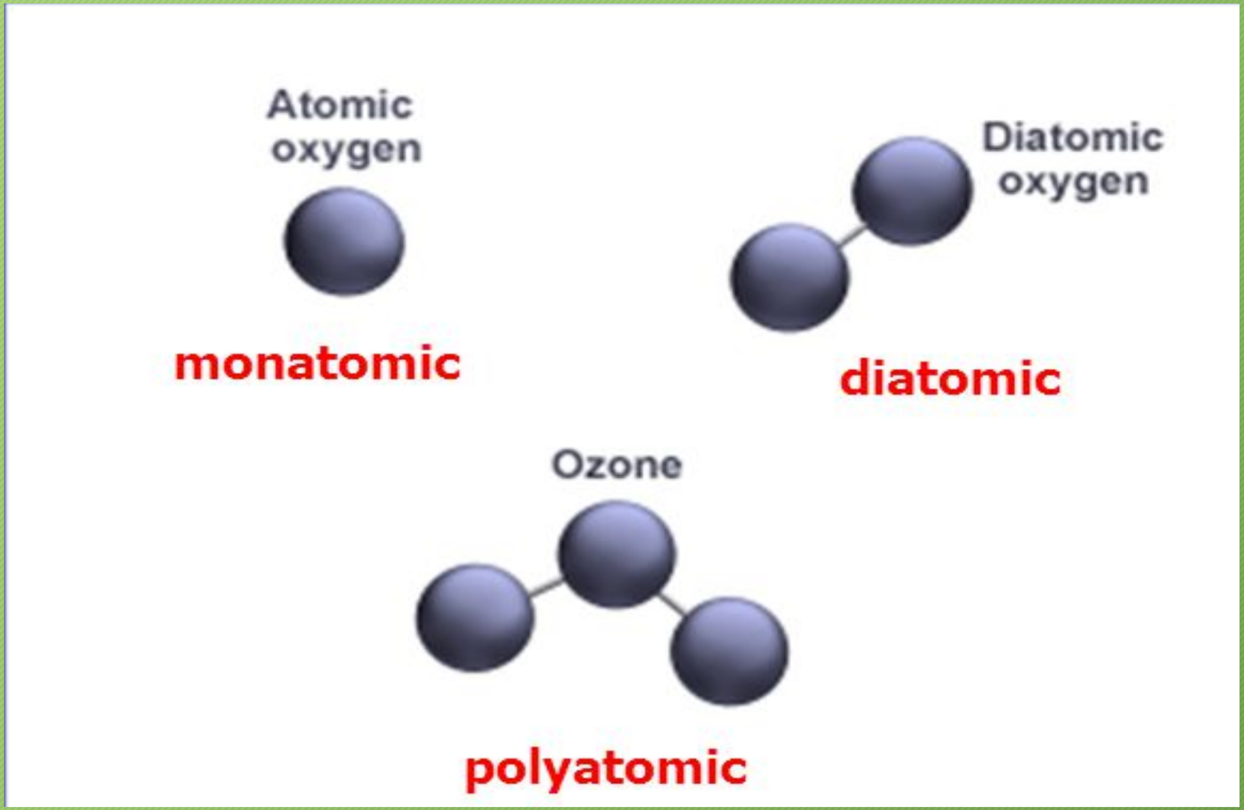
DIATOMIC MOLECULES

- Diatomic molecules are composed of only two atoms - of the same or different elements.
- Examples: hydrogen (H_2), oxygen (O_2), carbon monoxide (CO), nitric oxide (NO)

POLYATOMIC MOLECULES

- Polyatomic molecules consist of a stable system comprising three or more atoms.

TYPES OF MOLECULES



❑ Empirical, Molecular And Structural Formulas

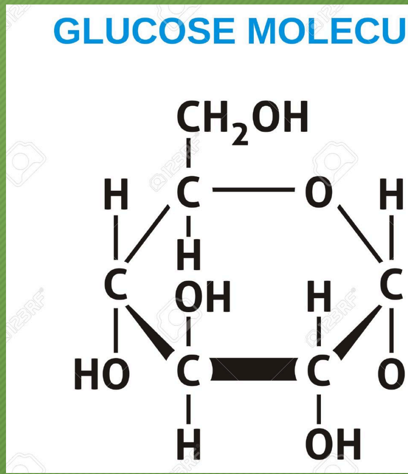
❑ Empirical formula: Indicates the simplest whole number ratio of all the atoms in a molecule.

The empirical formula of glucose is CH_2O.

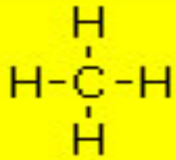
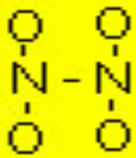
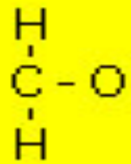
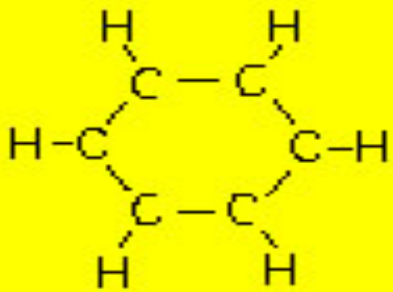
❑ Molecular formula: Describes the exact number and type of atoms in a single molecule of a compound.

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

❑ Structural formula: Indicates not only the number of atoms but also their arrangement in space.



Formulas

Name	Formulas: Empirical	Molecular	Structural
Methane	CH_4	CH_4	
dinitrogen monoxide	NO	N_2O_4	
formal-dehyde	CH_2O	CH_2O	
benzene	CH	C_6H_6	

Difference between Isomers and Allotrope

ISOTOPE

Atoms with the same number of protons but different number of neutrons are called isotopes. By changing the number of neutrons, isotopes still maintain the same overall neutrality and hence the chemical behavior remains unchanged.

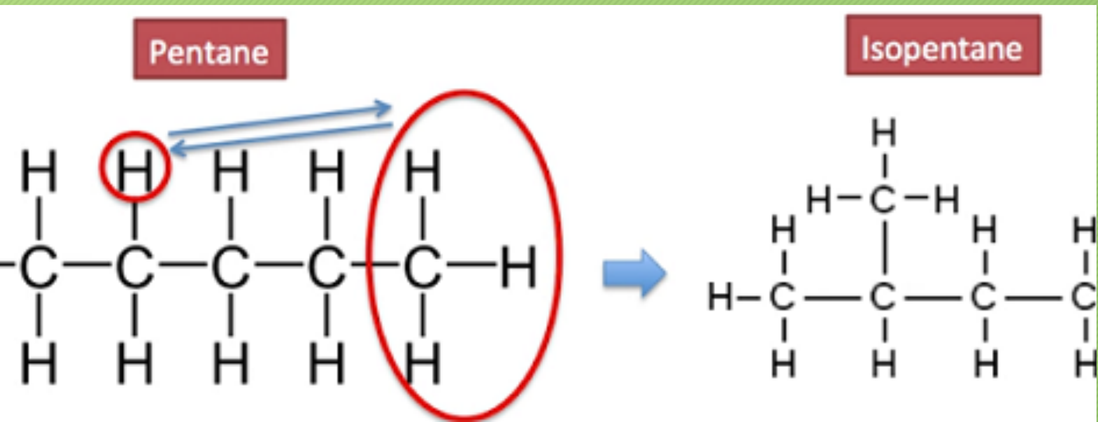
ISOMERS

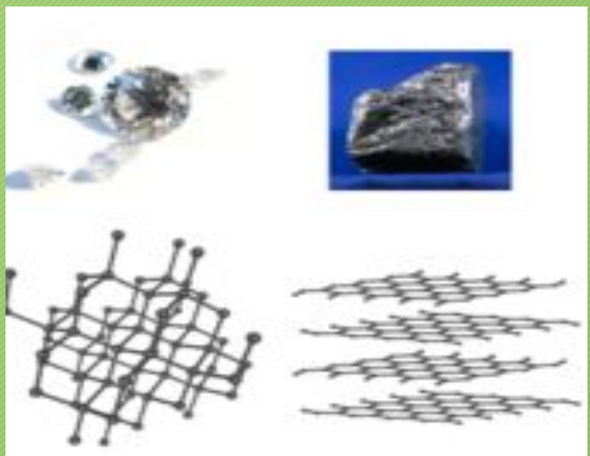
Isomers are two molecules with the same atoms joined together in a different shape. They have same molecular formula but different chemical structure. For example : Butane and isobutane

ALLOTROPE

They are different structural forms of the same element but can exhibit quite different physical and chemical properties. For example, carbon, diamond, graphite…

Examples of isomers and allotrope





Structural Isomers:
same molecular formula but different structural formula

Allotropes of carbon:
Diamond and graphite are two **allotropes** of **carbon**: pure forms of the same element that differ in structure.

Molecular Spectroscopy

Molecular spectroscopy : is the study of the interaction of electromagnetic (EM) 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 lengths, angles, strengths, energy levels, etc...)

Energy Levels

- A quantum mechanical system or particle that is bound—that is, confined spatially —can only take on certain discrete values of energy- called **energy levels.**

- The term is commonly used for the energy levels of electrons in atoms, ions or molecules- which are bound by the electric field of the nucleus.

- Can also refer to energy levels of nuclei or vibrational or rotational energy levels in molecules.

Ground and excited states

- If an atom, ion, or molecule is at the lowest possible energy level, it and its electrons are said to be in the ground state.
- If it is at a higher energy level, it is said to be excited, or any electrons that have higher energy than the ground state are excited.
- If more than one quantum mechanical state is at the same energy, the energy levels are called degenerate energy levels.

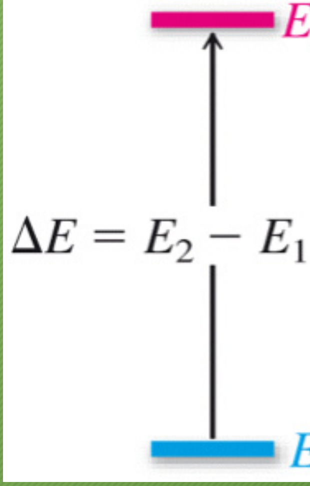
Chemical Bonds

- Chemical bonds between atoms in a molecule form because they make the situation more stable for the involved atoms.
- **Covalent bond:**, involves the sharing of electron pairs between atom.
- As atoms approach each other to covalently bond -their orbitals affect each other's energy levels to form bonding and anti-bonding molecular orbitals.
- The energy level of the bonding orbitals is lower, and the energy level of the anti-bonding orbitals is higher.
- For the bond in the molecule to be stable - the covalent bonding electrons occupy the lower energy bonding orbital - which may be signified by such symbols as σ or π.

❑ Molecular Orbital Theory

❑ Orbitals of individual atoms interact to produce new orbitals - called molecular orbitals

$$\Phi = \sum_{i=1}^{N} a_i \varphi_i$$



Φ is the molecular orbital, φ is an atomic orbital and a is a coefficient

Molecules have discrete energy levels - no continuum between levels.

Absorbs electromagnetic radiation when the energy of photon corresponds to the difference in energy between two states.

❑ Molecular Energy Levles

Energy can be stored either as potential energy or kinetic energy, in a variety of ways including

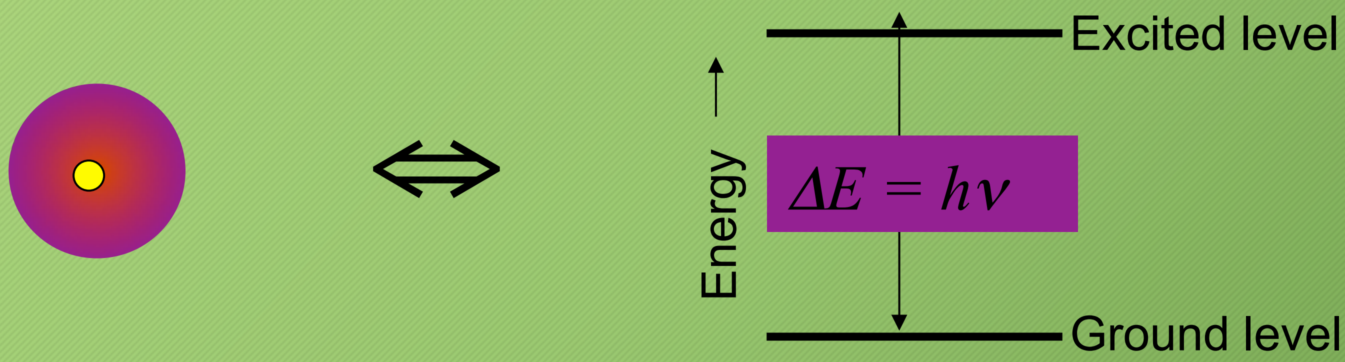
- **Translational energy**: small amounts of energy stored as kinetic energy.
- **Rotational energy:** kinetic energy associated with the rotational motion of molecules.
- **Vibrational energy:** the oscillatory motion of atoms or groups of atoms within a molecule (potential energy ↔ kinetic energy exchange).
- **Electronic energy:** energy stored as potential energy in excited electronic configurations.

All except the Translational energy are quantized

$$E_{molecule} = E_{rotational} + E_{vibrational} + E_{electronic}$$

❑ Molecular Transitions

tomic and molecular vibrations correspond to excited energy levels in quantum mechanics



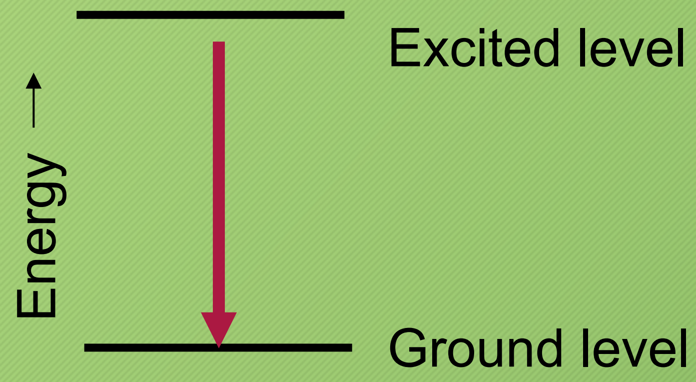
The atom is vibrating at frequency, v.

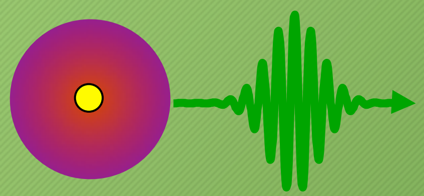
The atom is at least partially in an excited state.

- ❑ For a given frequency only one value of quantum energy for the photon is possible
- ❑ Transitions between energy levels occur by absorption, emission and stimulated emission of photons

❑ Spontaneous Emission

- When an atom/ molecule in an excited state falls to a lower energy level - it emits a photon

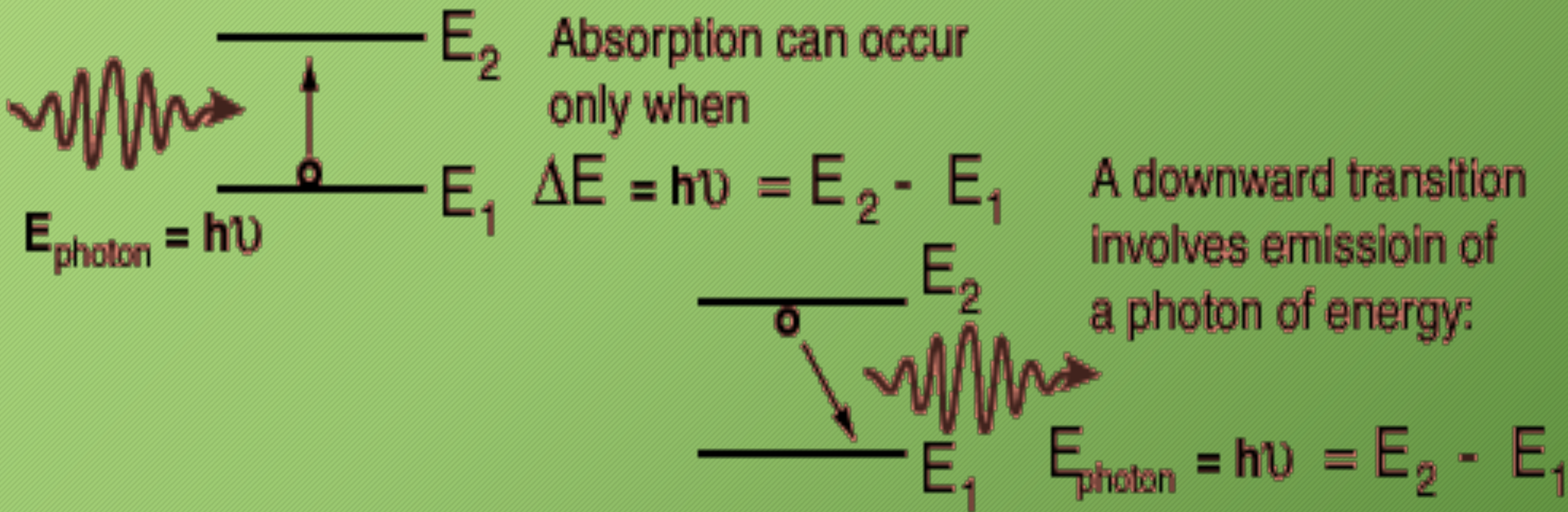




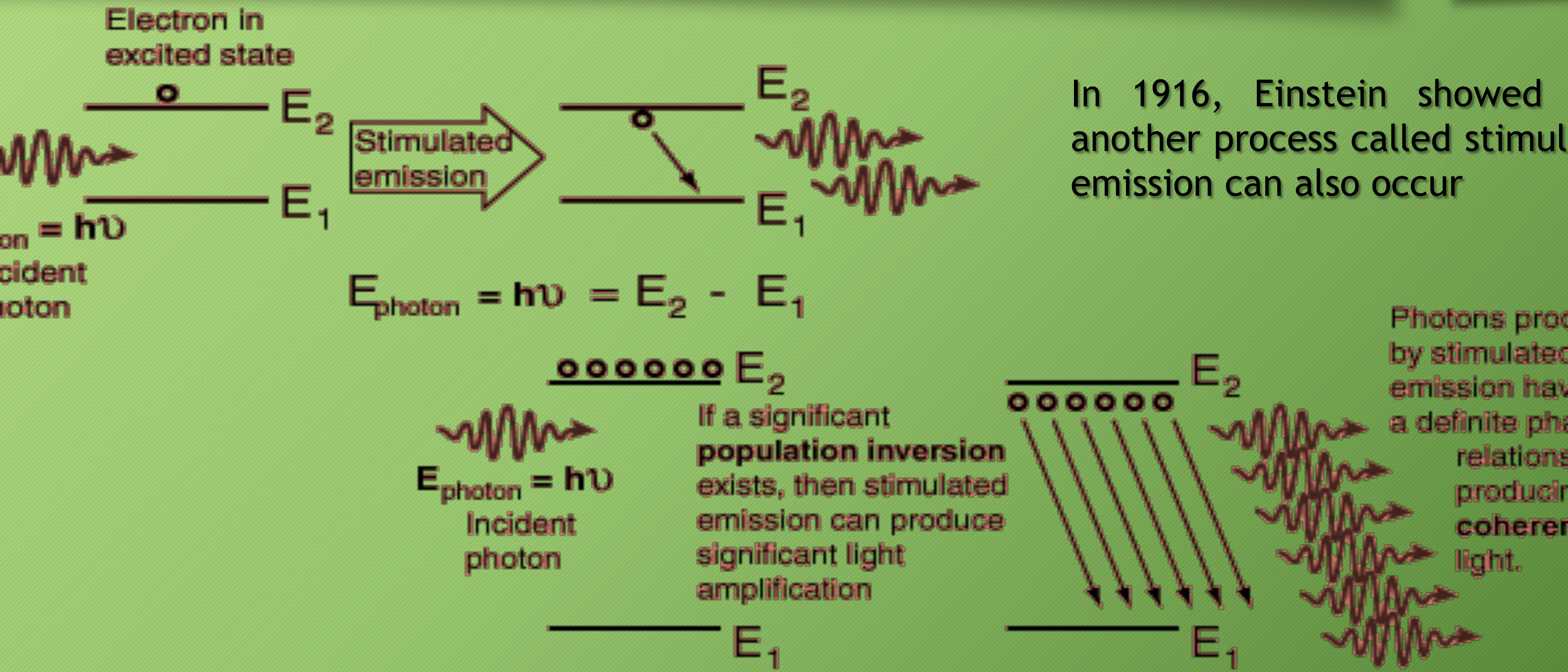
- Molecules typically remain excited for a few nanoseconds- upon de-excitation emit a photon of light.
- This process is called fluorescence .

Stimulated Absorption

- Atoms and molecules can also absorb photons, making a transition from a lower level to a more excited one

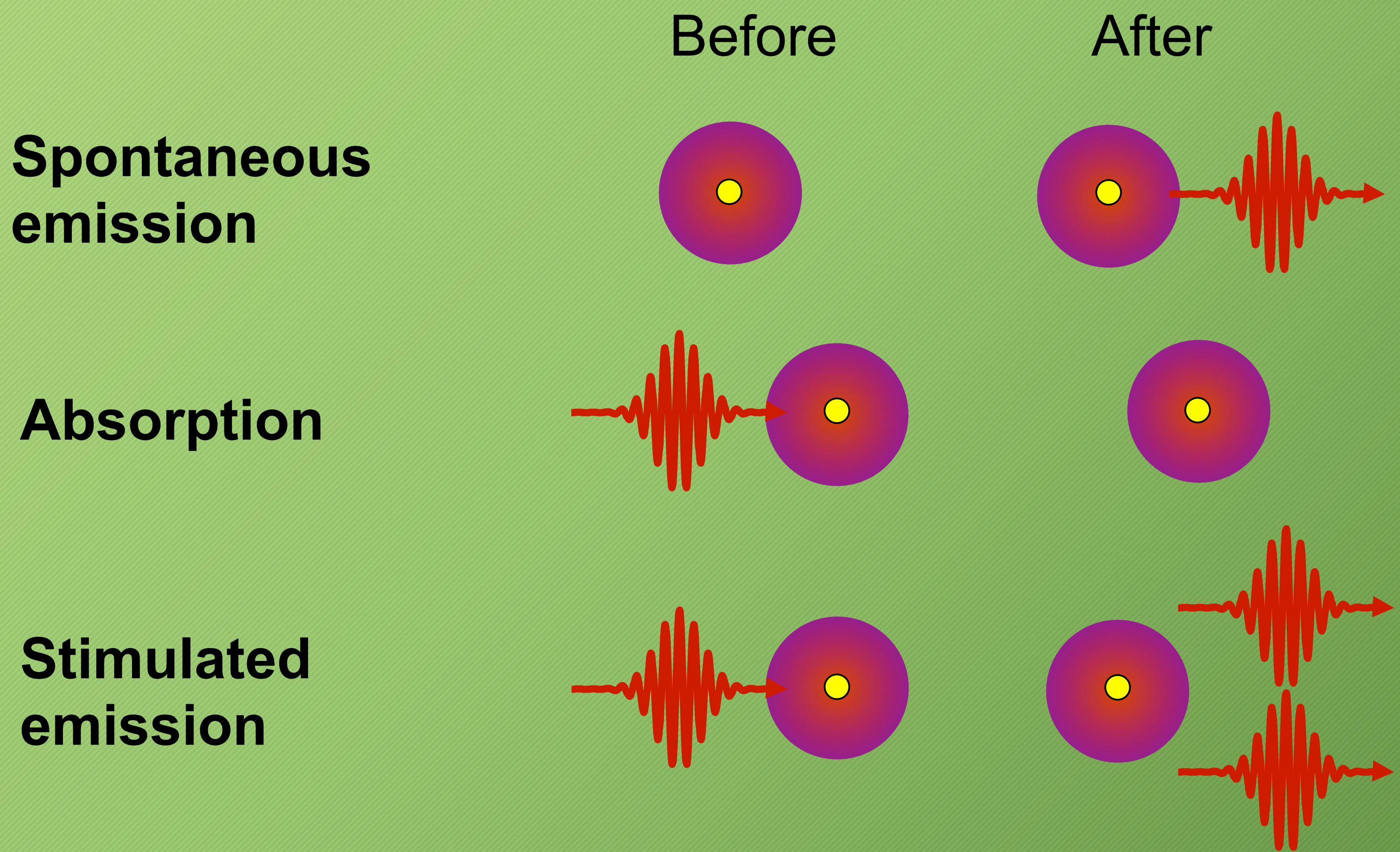


❑ Stimulated Emission



In 1916, Einstein showed another process called stimul emission can also occur

❑ Molecular Trnasitions



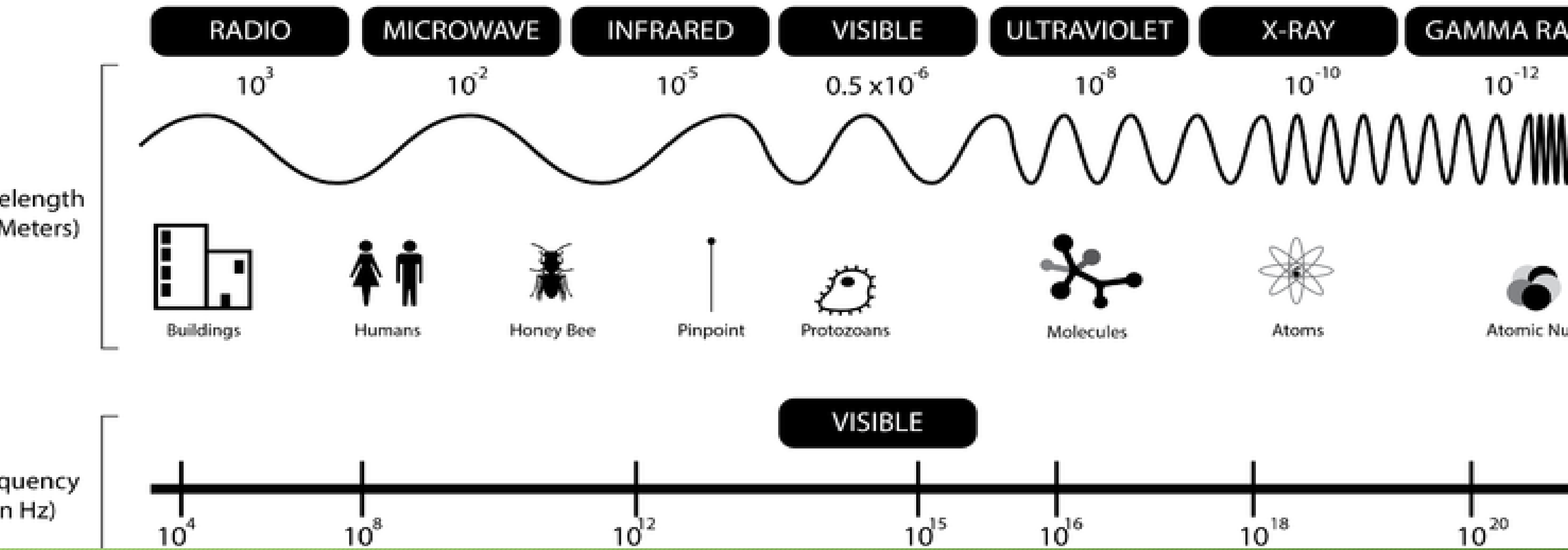
Electromagnetic radiation

- Electromagnetic (EM) radiation consists of photons which behave as both particles and waves.

$\nu = \dfrac{c}{\lambda}$	$\bar{\nu} = \dfrac{1}{\lambda}$

c = speed of light (2.998x108 ms-1)
λ = wavelength (m)
v = frequency (s-1)
= wavenumber (m-1)

Electromagnetic spectrum



INTERACTION OF RADIATION WITH MATTER

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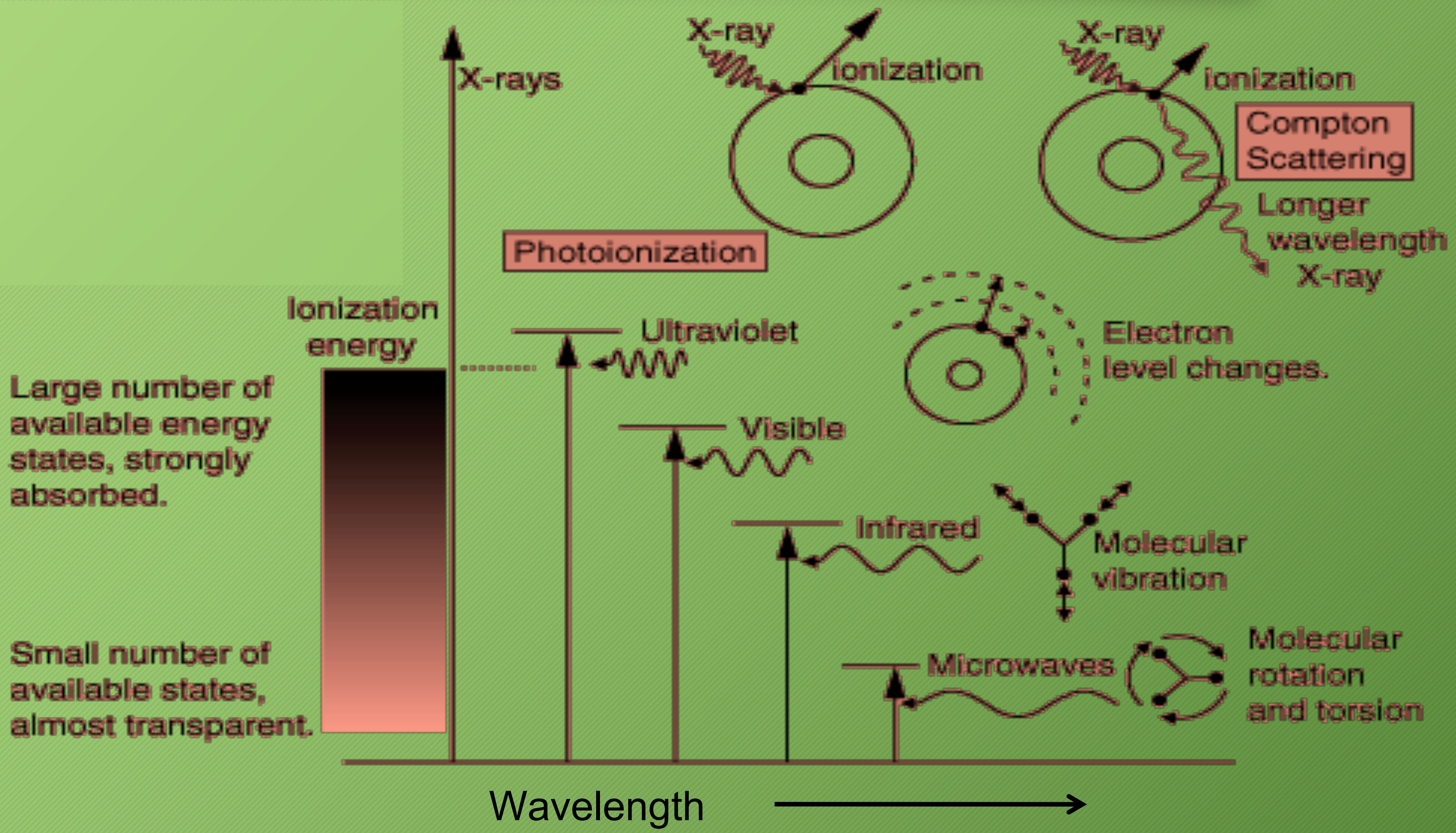
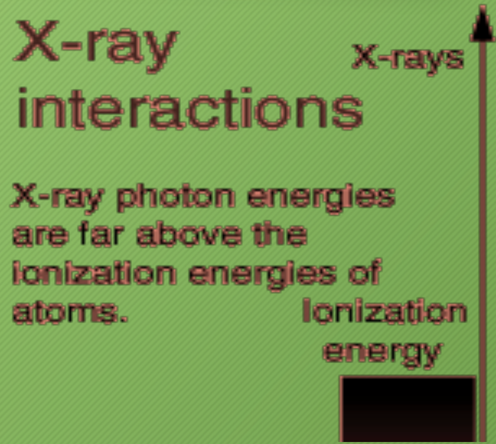


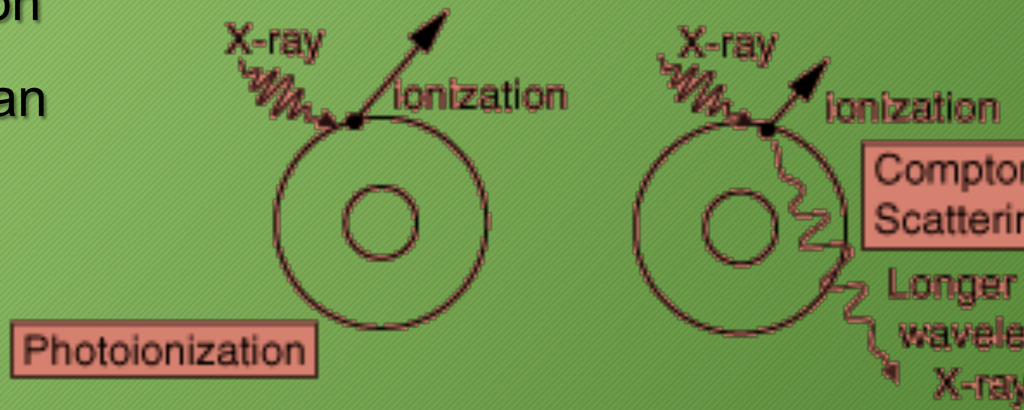
X-RAY INTERACTIONS

uantum energies of x-ray photons are too high to be bsorbed by electronic transitions in most atoms - nly possibility is complete removal of an electron rom an atom - x-rays are ionizing radiation



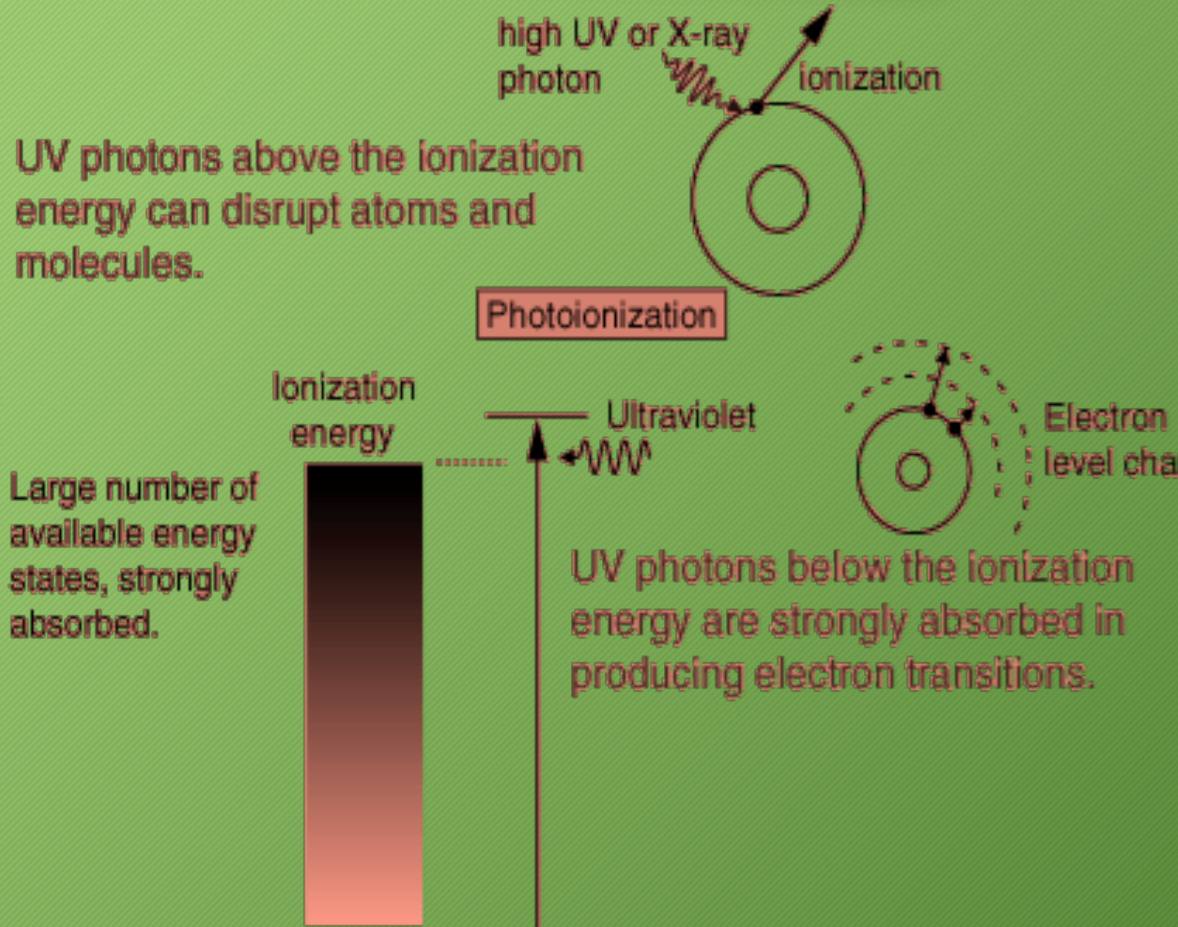
hotoionization: If all the energy is given to an electron

ompton scattering: If part of the energy is given to an lectron and the rest to a lower energy photon



UlTRAVIOLET INTERACTIONS

- Near UV radiation is absorbed very strongly in the surface layer of the skin by electron transitions
- At higher energies, ionization limit for many molecules are reached and the more dangerous photoionization processes occur.
- Sunburn is primarily an effect of UV radiation, and ionization produces the risk of skin cancer

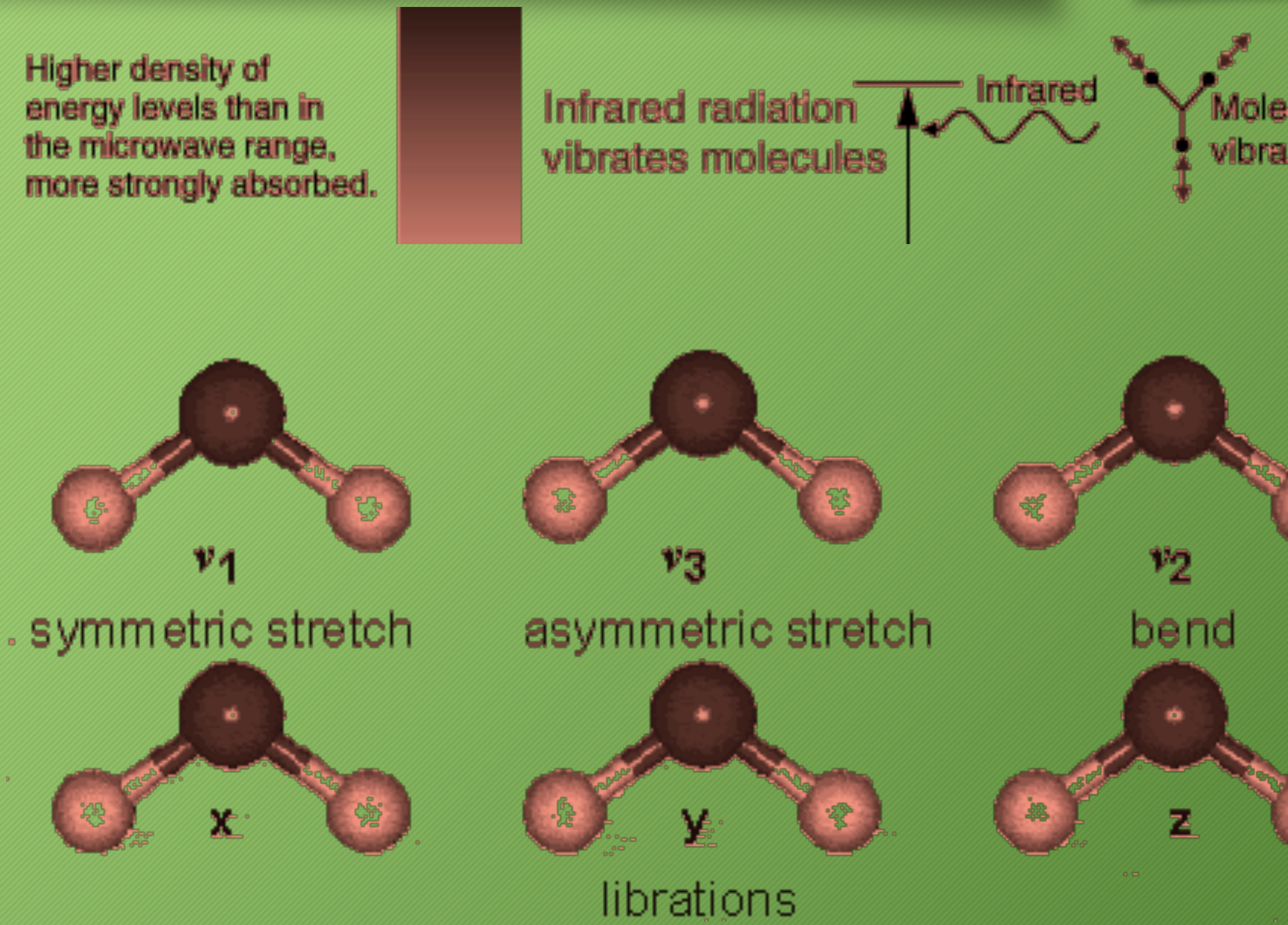


❑ VISIBLE LIGHT INTERACTIONS

- ❑ Visible light is also 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 causes heating, but not ionization
- ❑ Car windshields transmit visible light but absorb higher UV frequencies

INFRARED (IR) INTERACTIONS

- he energy level of infrared light orresponds to the energy equired to cause **molecular brations**
- ibrations arise as molecular onds are not rigid but behave ke springs



❑ INFRARED (IR) INTERACTIONS _ CONT'D

Vibrational transitions are Sub-divided into two classes:

Stretching : symmetric and asymmetric

Bending: scissoring, rocking, wagging and twisting

Stretching frequencies are higher than corresponding bending frequencies - it i
asier to bend a bond than to stretch or compress it

Bonds to hydrogen have higher stretching frequencies than those to heavier
toms.

Triple bonds have higher stretching frequencies than corresponding double bon
which in turn have higher frequencies than single bonds

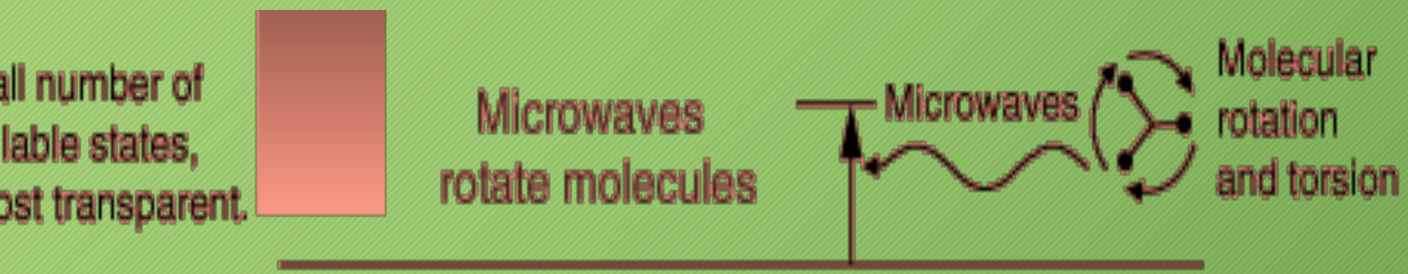
MICROWAVE INTERACTIONS

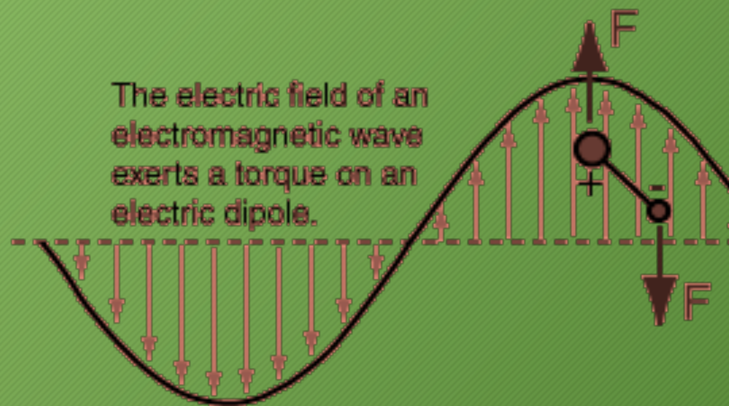
Quantum energy of microwave photons (10^{-5}-10^{-3} eV) matches the ranges of energies separating quantum states of molecular rotations.

Like electronic and vibrational transitions *rotational motion of molecules is quantized*

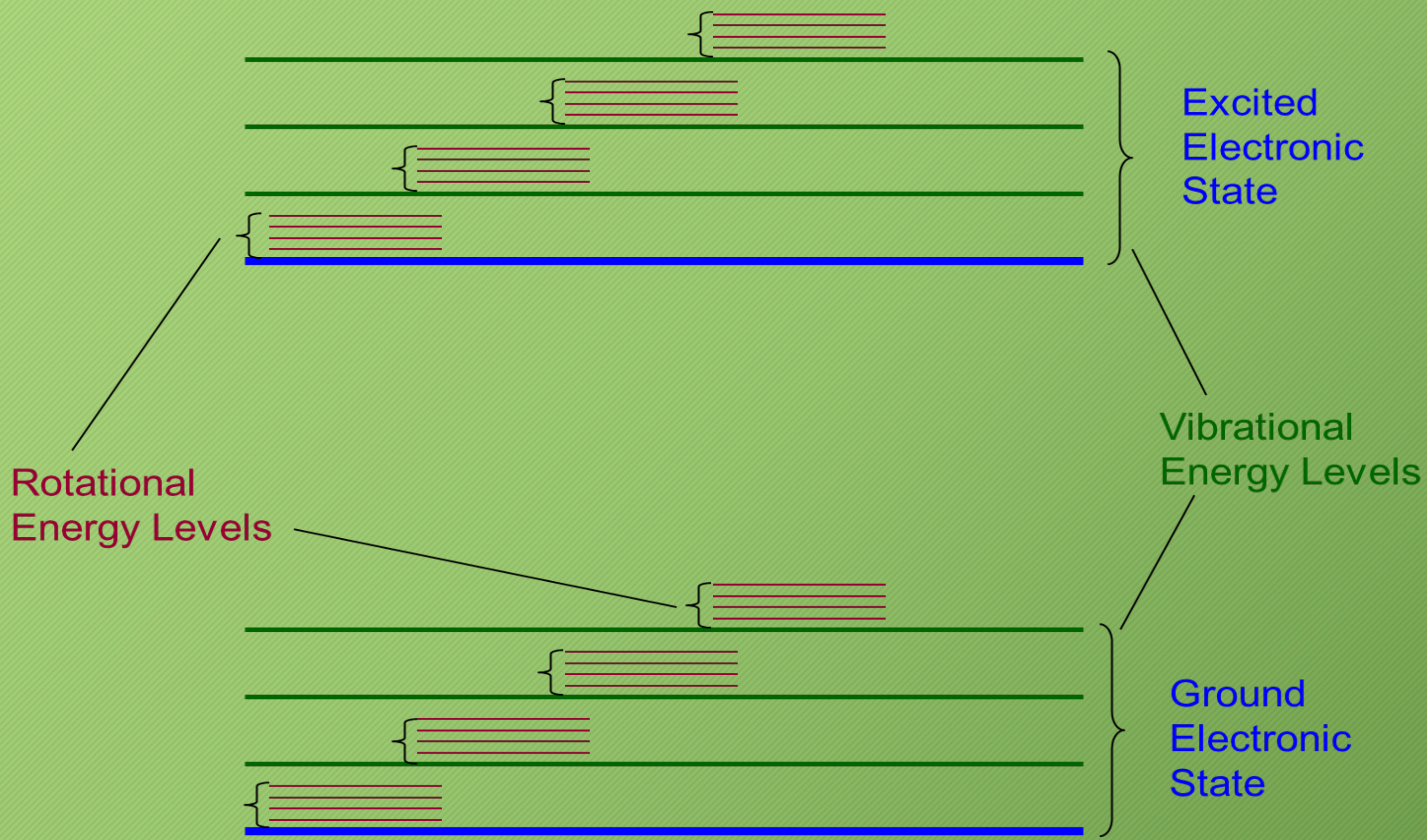
Absorption of microwave radiation causes heating due to increased molecular rotational activity

Most matter transparent to μ-waves, microwave ovens use high intensity μ-waves to heat material



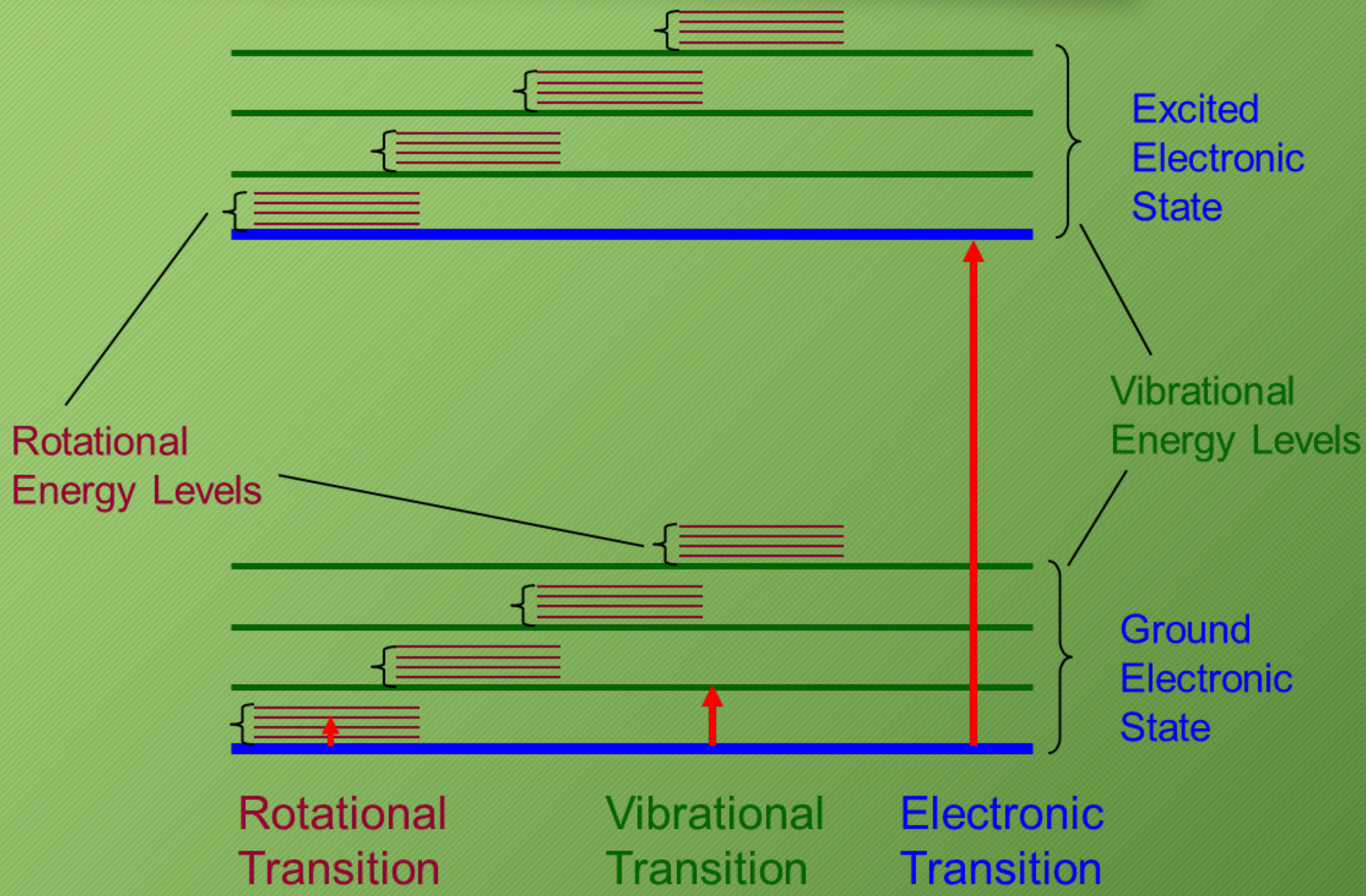


❑ MOLECULAR ENERGY LEVELS



❑ MOLECULAR ENERGY LEVELS _ CONT'D

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



❑ MOLECULAR ENERGY LEVELS _ CONT’D

e relative energy of the spacings between energy levels for various types of ansitions in a molecule are in the order:

Rotational Transition	$\ll$	Vibrational Transition	$\ll$	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

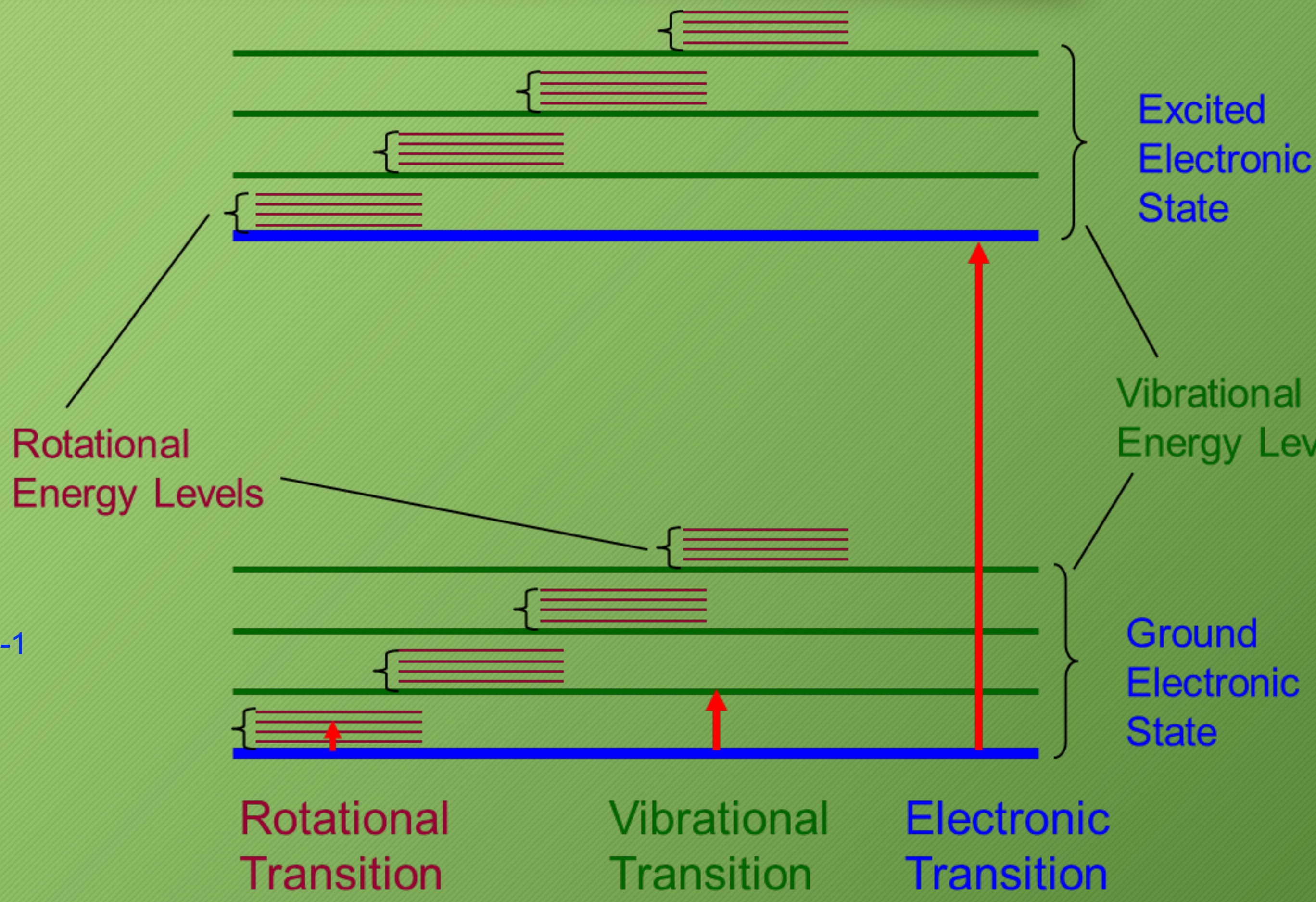
❑ MOLECULAR ENERGY LEVELS _ CONT'D

Vibrational Transition

2000-4000 cm^{-1}

Infrared

Rotational Transition	Electronic Transition
1-20 cm^{-1}	10000-50000 cm^{-1}
Microwave	UV-Visible

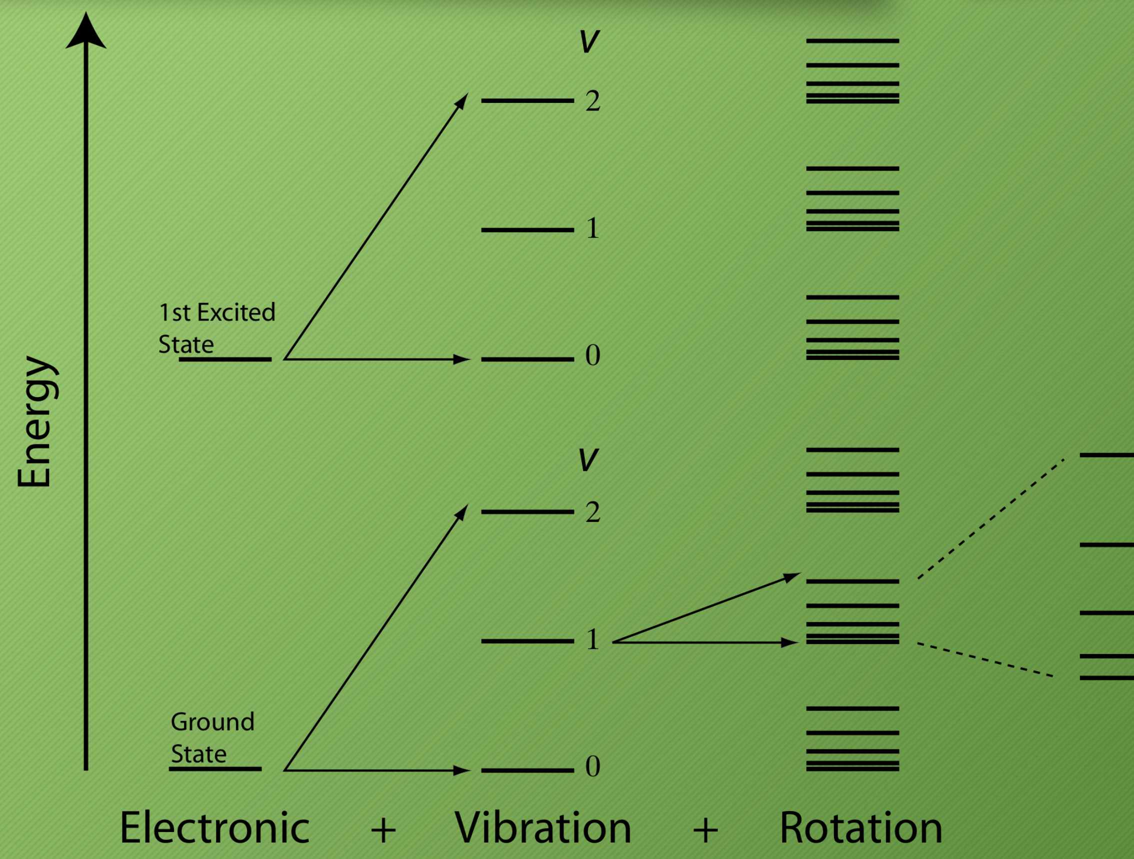


❑ ABSORPTION SPECTRA OF MOLECULES _ CONT'D

- Electronic, vibrational and rotational energy levels are superimposed
- The absorption spectrum of a molecule is determined by all allowed transitions between pairs of energy levels that interact with the radiation field

V = Vibrational quantum number

J = Rotational quantum number



VIBRATIONAL MOLECULAR LEVELS

- Like atoms - molecular motion is governed by quantum mechanics.
- Chemical bond acts like a spring and can display Simple harmonic motion
- Energies due to vibration are quantized : $E_v = \hbar\omega\ (v + ½)$
- Vibrational quantum number $v = 0,1,2,3,\ldots$
- Angular frequency $\omega = \surd k/m_{eff}$
- An effective spring constant k for the bond involved
- Effective mass m_{eff}

VIBRATIONAL MOLECULAR LEVELS _ CONT'D

- ½ℏω comes from quantum mechanics and represents zero-point energy
- The zero point energy ½ ω implies molecule never stops vibrating - eve when its in the v = 0 state
- Zero point energy cannot be harvested or extracted - Still exists at absolute zero - All molecules are then in v = 0 state
- Energy levels are equally spaced with separation ω
- Obey selection rule Δv = ±1

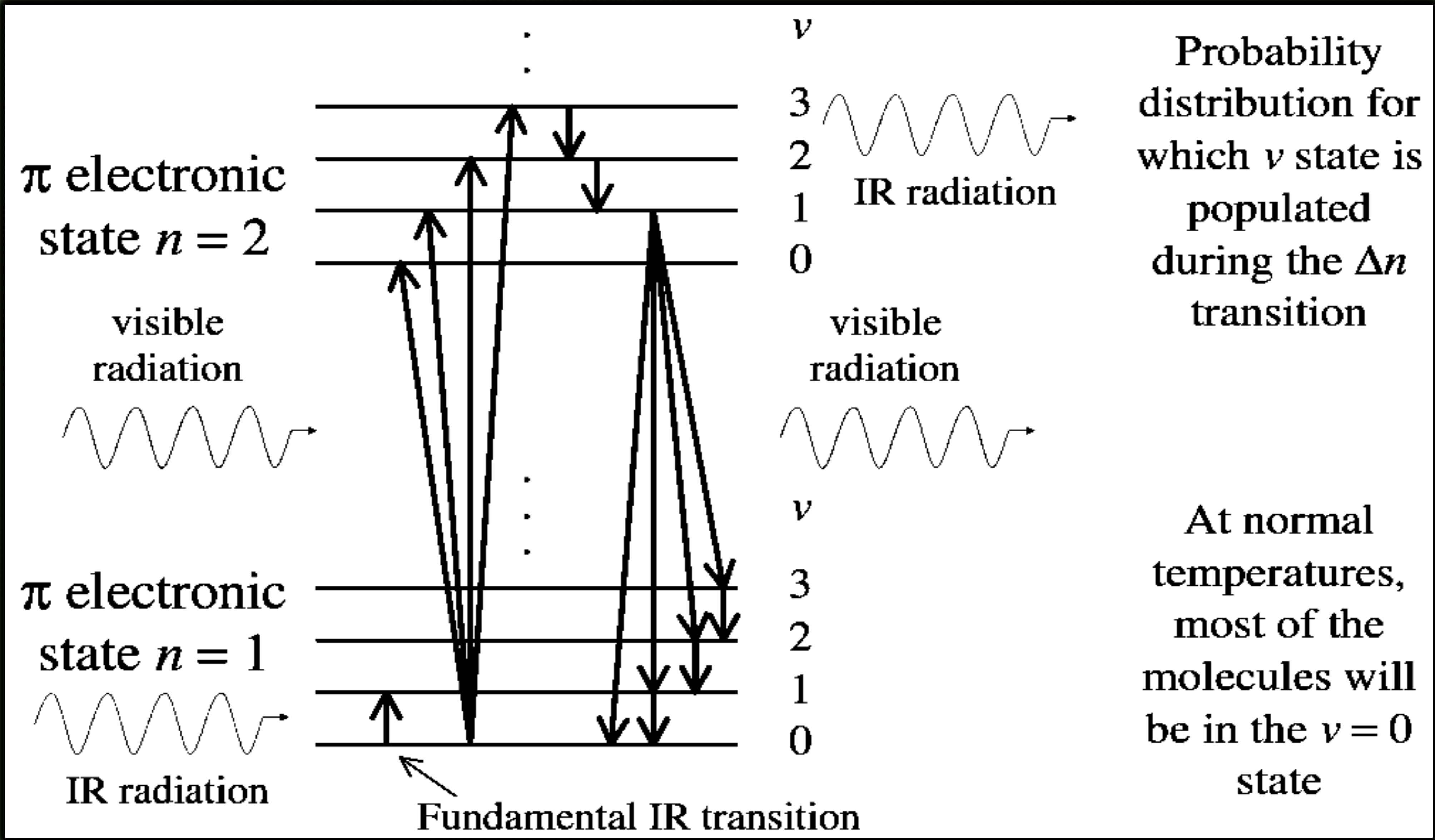
VIBRATIONAL MOLECULAR LEVELS _ CONT'D

- For diatomic molecule with mass M_1 and M_2 - the effective mass

  $m_{eff} = (M_1 M_2)/(M_1 + M_2)$

- Energy scale for molecular vibrations is much less than that for electronic excitations
- Excitation energies correspond to IR region of the spectrum
- Vibrational levels are built on electronic states – each electronic state will host the whole range of vibrational states

Vibrational excitation and de-excitation



VIBRATIONAL MOLECULAR LEVELS _ CONT'D

Fundamental or normal modes

ν_1 **Symmetric stretch**

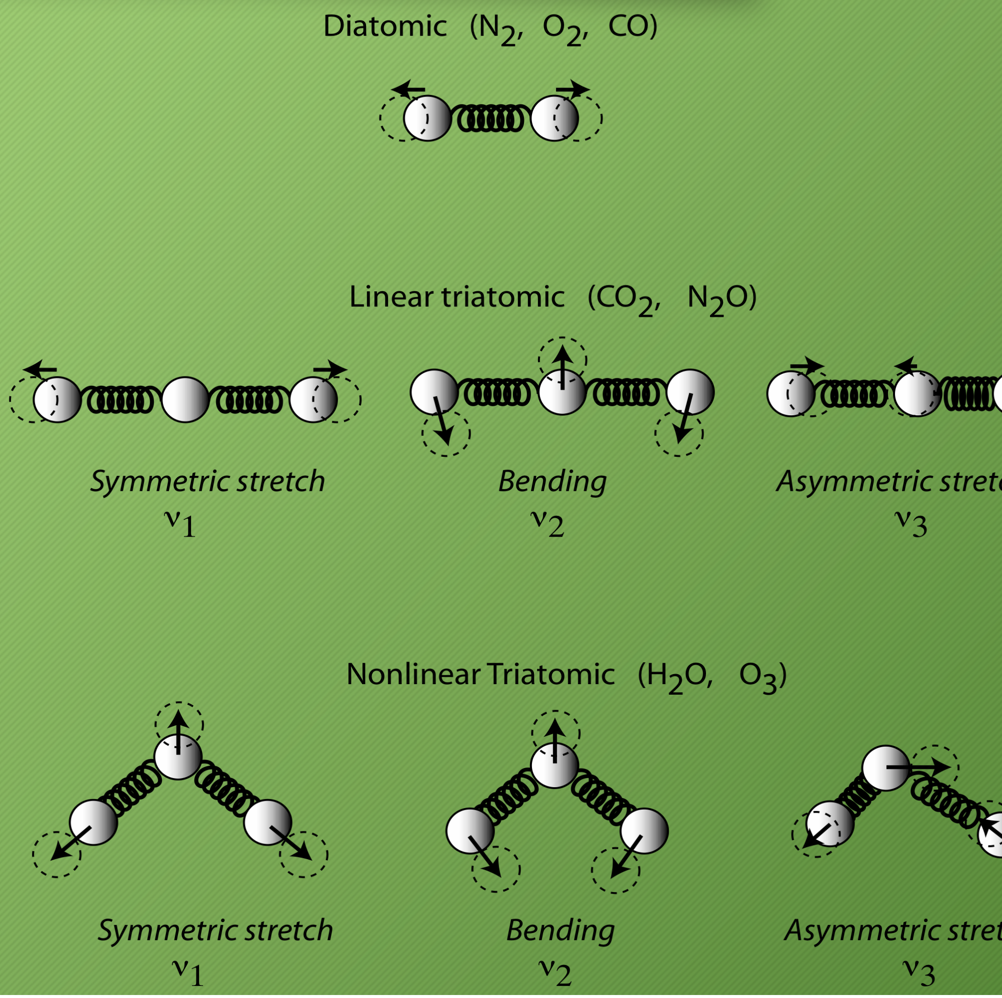
ν_2 **Bend (Scissoring)**

ν_3 **Asymmetric stretch**

normal mode is IR-active if the dipole moment anges during mode motion.

ertones, combinations and differences of ndamental vibrations are also possible (e.g., $2\nu_1$, ν_3 etc.)

non-linear molecule of N atoms has 3N-6 normal odes of vibration; a linear molecule has 3N-5.



ROTATIONAL MOLECULAR LEVELS

- In quantum mechanics - the rigid rotor has energy levels

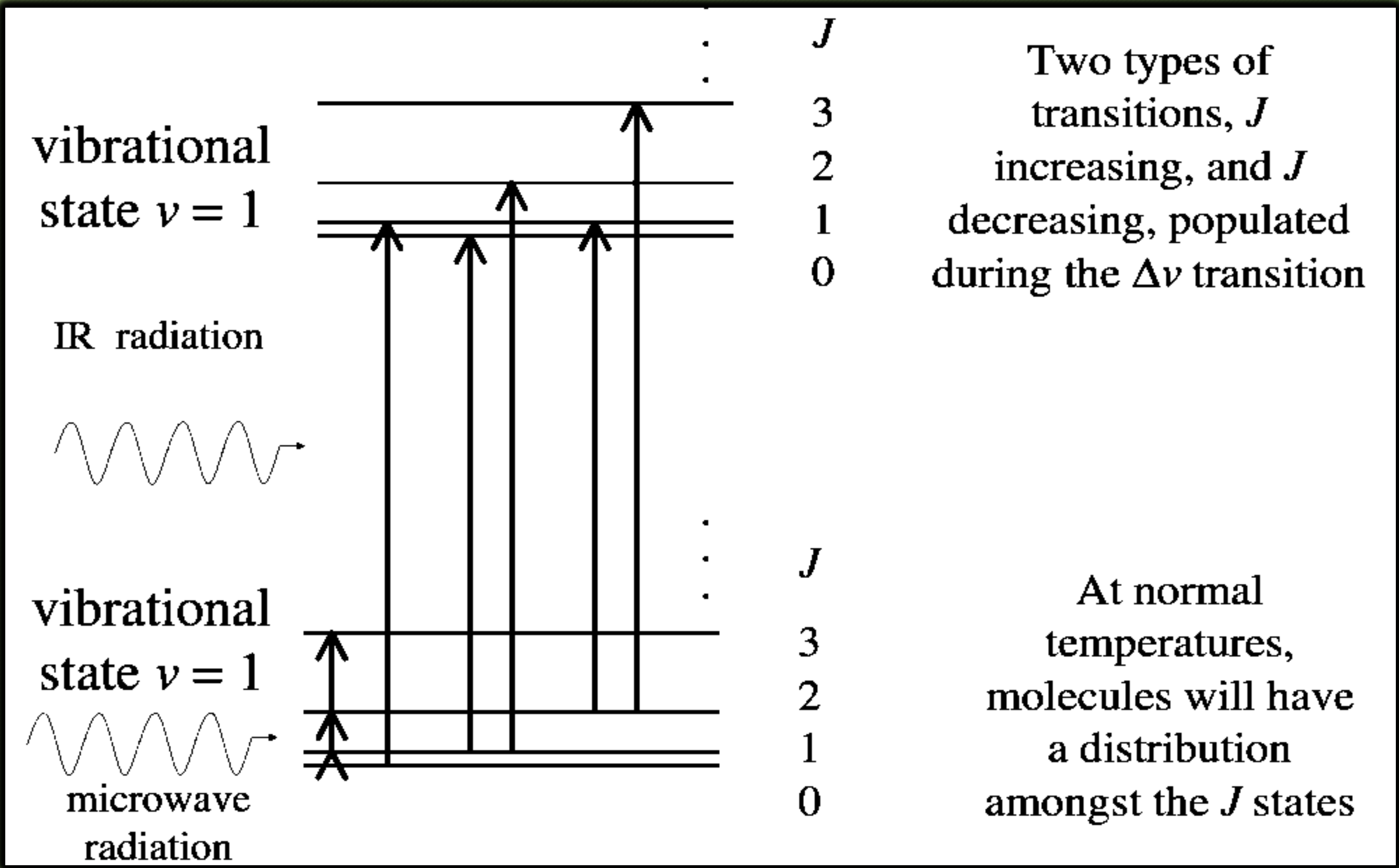
$E_J = \hbar^2 / 2\mathfrak{I}\ J(J+1)$

- $\mathfrak{I}$ is the moment of inertia
- J is the angular momentum: J = 0,1,2,3,...
- The quantity $\hbar^2 / 2\mathfrak{I}$ is called the rotational parameter
- Moment of inertia - hence rotational parameter - can be different for each rotation axis

❑ ROTATIONAL MOLECULAR LEVELS _ CONT'D

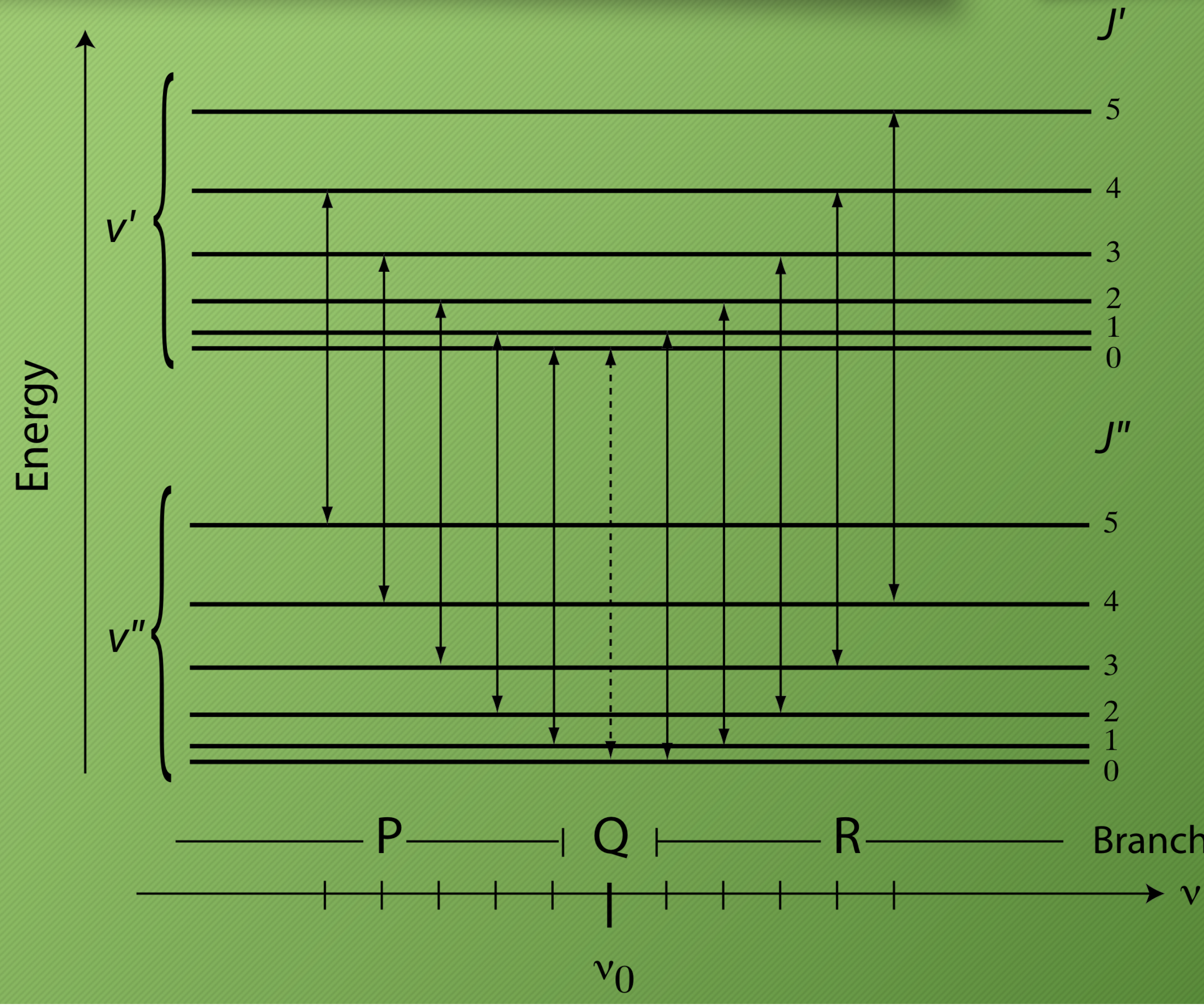
- ❑ Excitation energies correspond to the microwave region
- ❑ Energy scale for rotations << vibrations
- ❑ Each vibrational level has rotational bands built on it
- ❑ Selection rule $\Delta J = \pm 1$

ROTATIONAL LEVELS



❑ VIBRATIONAL-ROTATIONAL TRANSITION

- ❑ Relative positions of transitions in the absorption spectrum of a molecule
  - ❑ P branch (ΔJ = -1)
  - ❑ Q branch (ΔJ = 0) (pure vibration)
  - ❑ R branch (ΔJ = +1)



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 the binding force will change, i.e. the net potential energy of the molecule will change.
- This means that the inter-atomic distance will change
- Different electronic levels will have different rotational and vibrational constants

ENERGY LEVELS

- Taking rotations, vibrations, and electronic excitation into account

$$E_{n,v,J} = E_n + E_v + E_J$$

- Complex molecules may have many vibrational modes, rotational modes, etc
- The combination of these different modes leads to a "smearing" of the discrete spectrum - so that broad bumps appear rather than discrete lines

Simple versus Complex molecules

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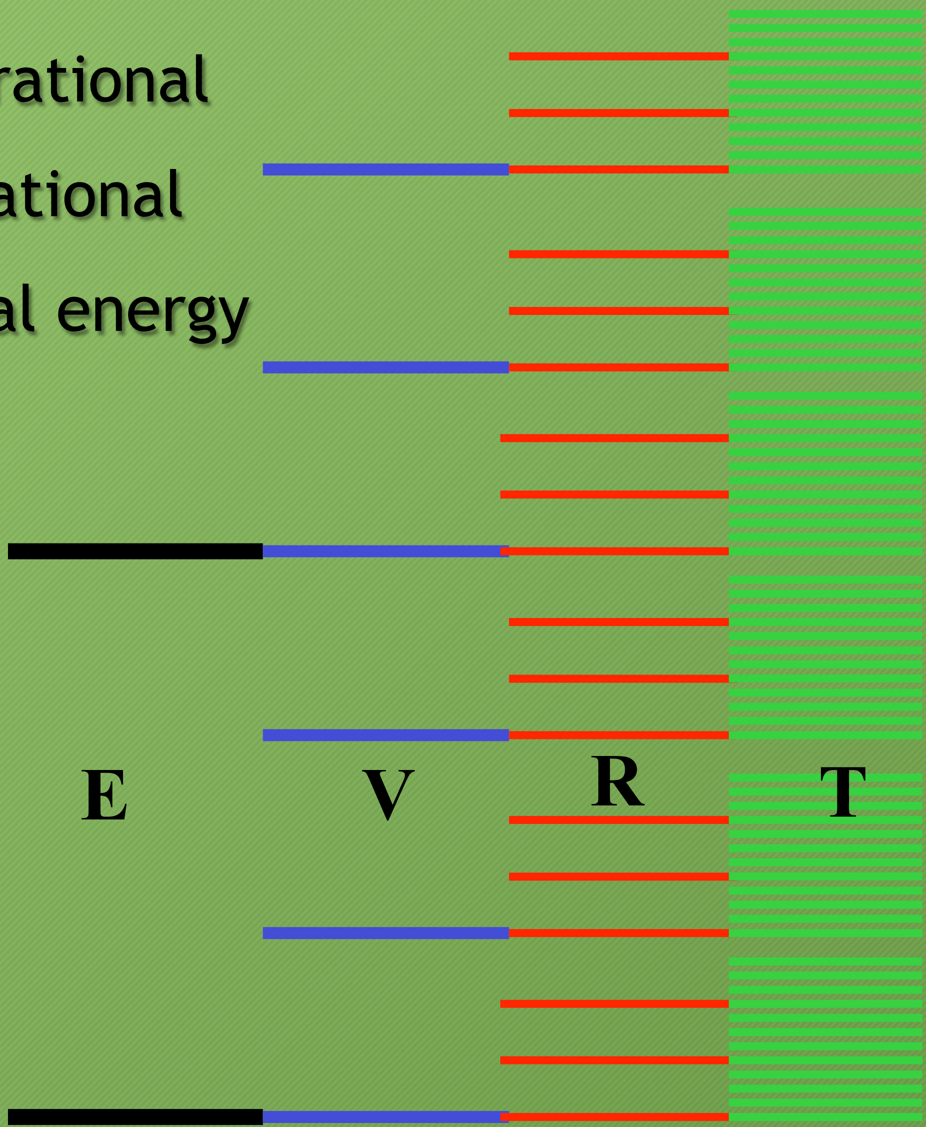
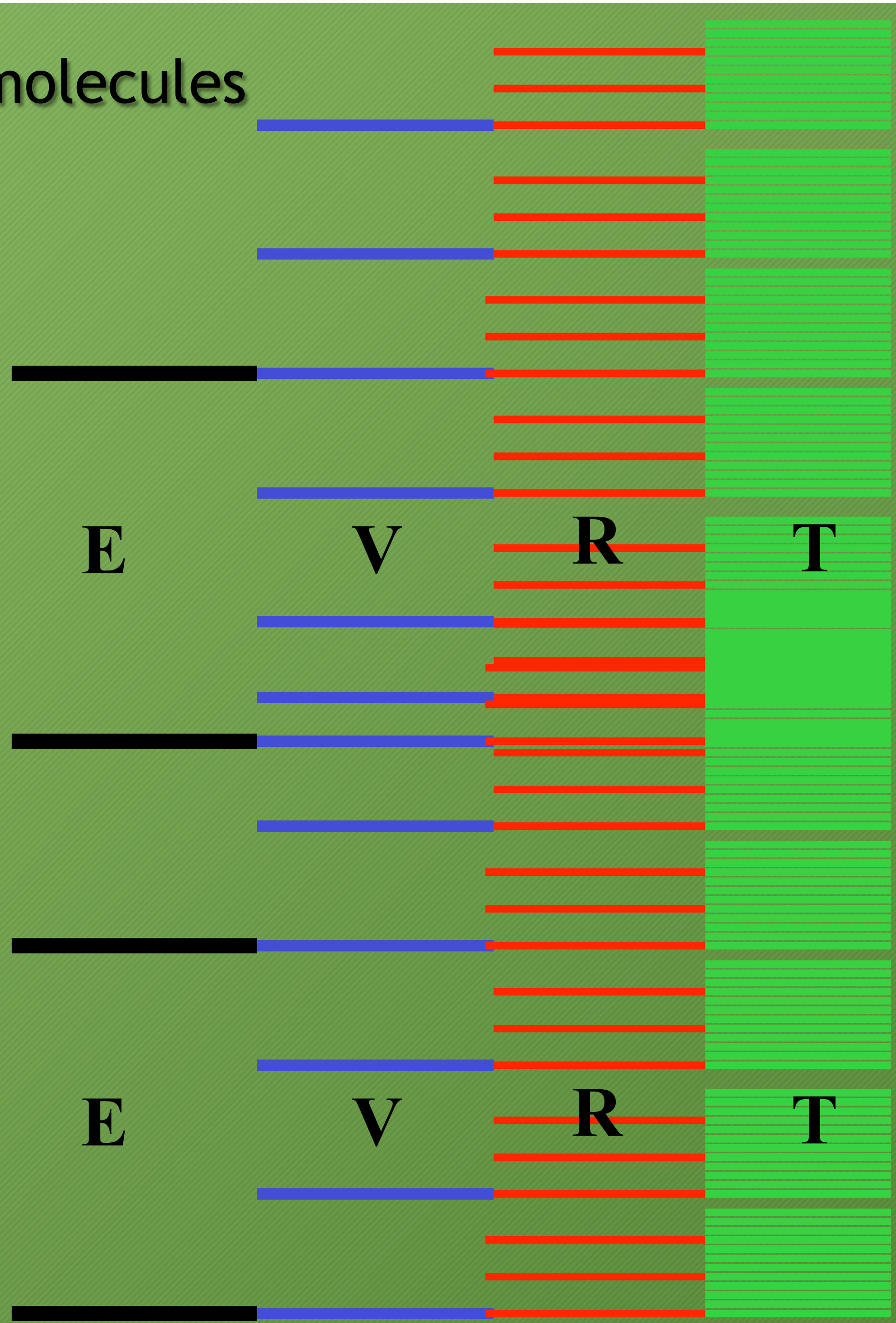
ibrational

otational

otal energy





ENERGY LEVELS _CONT'D

- Ignoring electronic excitation _ the total internal energy of a molecule i the sum of its vibrational and rotational energy.

$$E_{v,J} = \hbar\omega\,(v + ½) + \hbar^2 / 2\mathfrak{I}\; J(J + 1)$$

- The wave-number of a spectral line is given by the difference of the ter values of the two states
- A change in vibrational quantum number v is accompanied by a change i rotational quantum number J - according to the selection rule $\Delta J = 0, \pm 1$

ENERGY LEVELS _CONT'D

- The complete set of rotational transitions between two vibrational levels is known as a 'band'
- A band normally consists of three separate sequences; If
  - $\Delta J=0$ we have the Q branch
  - $\Delta J=1$ the R branch
  - $\Delta J=-1$ the P branch

THANK YOU