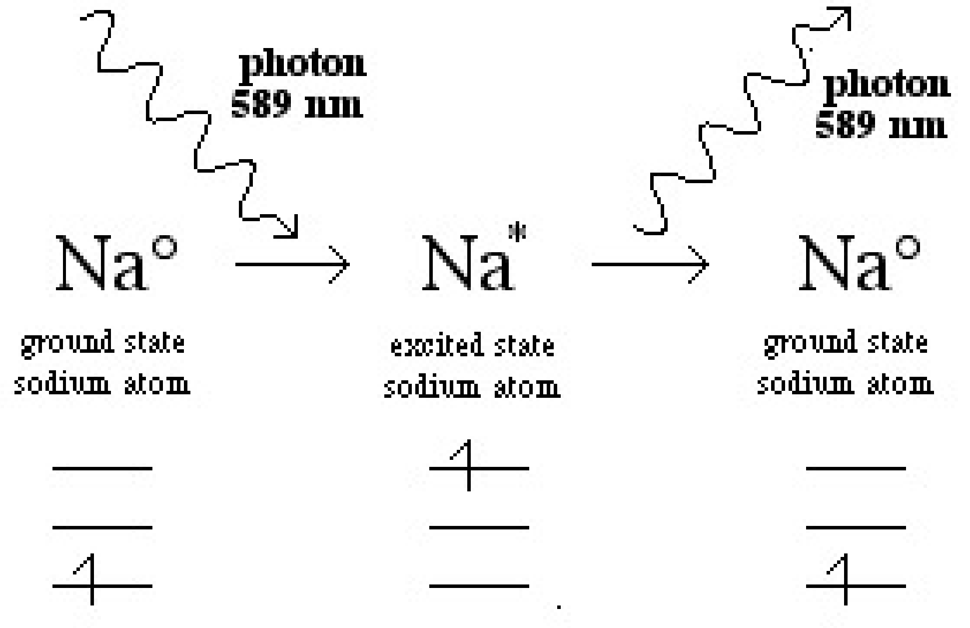
Chapter 1

Photochemical principles

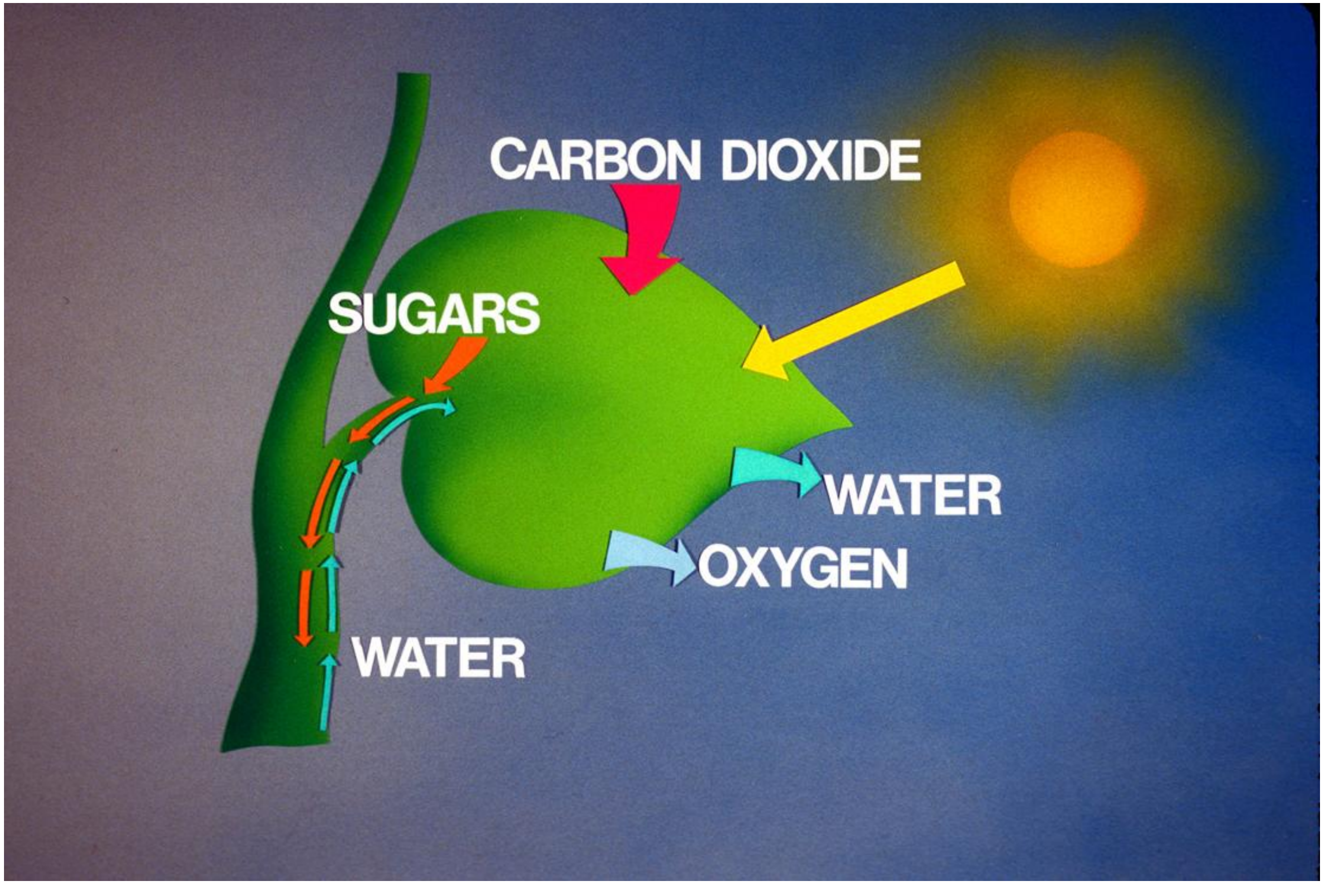
Photochemistry

- **Photochemistry** is concerned with the absorption, excitation and emission of photons by atoms, atomic ions, molecules, molecular ions, etc.
- **Photochemistry** is the study of the interactions between atoms, molecules, and light.
- The simplest photochemical process is seen with the absorption and subsequent emission of a photon by a gas phase atom such as sodium.

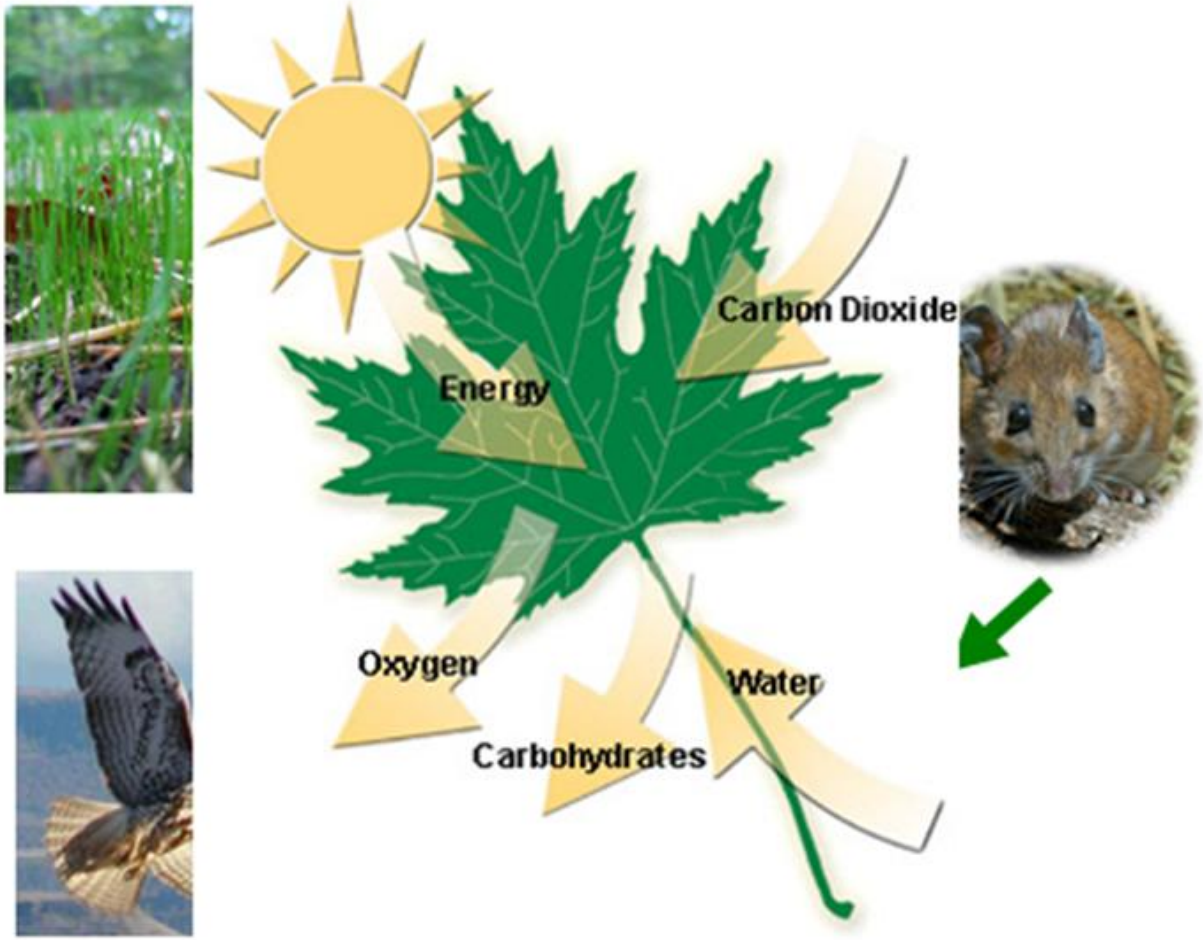
- When the sodium atom absorbs a photon it is said to be excited. After a short period of time, the excited state sodium atom emits a photon of 589 nm light and falls back to the ground state:



Photosynthesis



$$6\ CO_2 + 6\ H_2O + \text{light energy} \longrightarrow C_6H_{12}O_6 + 6\ O_2$$


Carbon Dioxide
Energy
Oxygen
Water
Carbohydrates

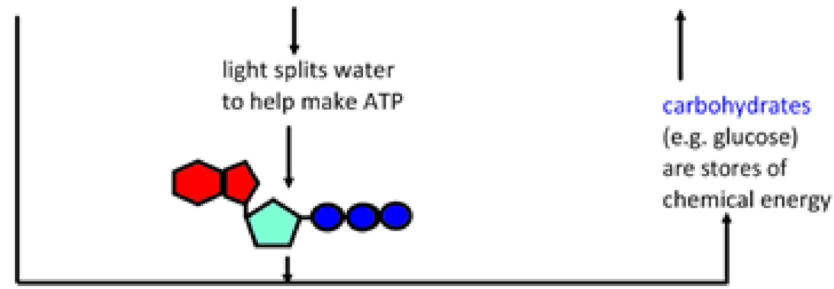
PHOTOSYNTHESIS

USING LIGHT TO PRODUCE

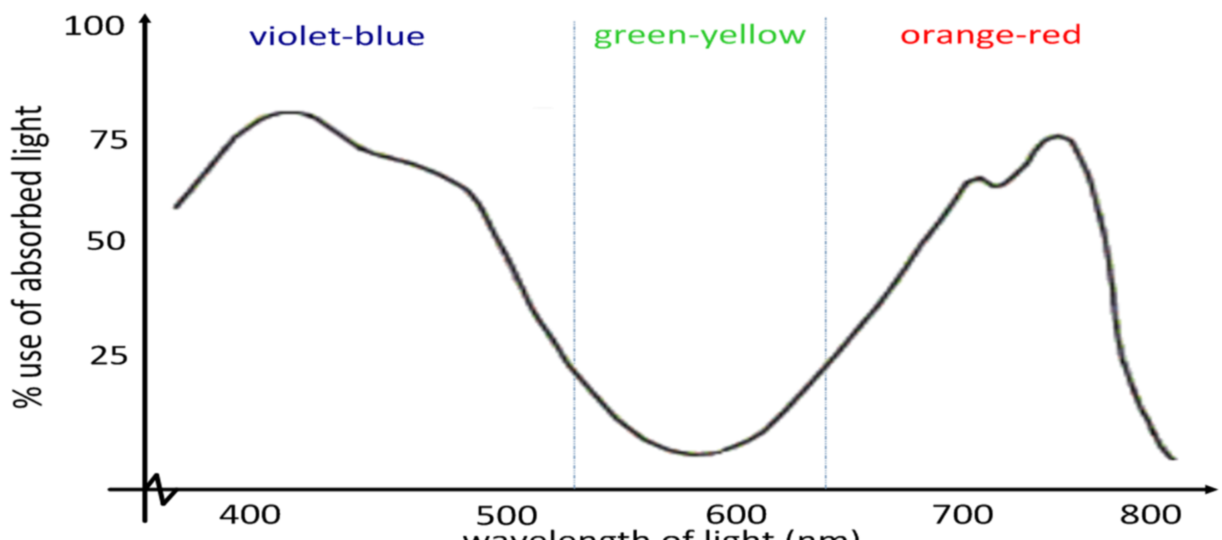
Light energy is converted to chemical energy.

carbon dioxide + water $\xrightarrow[\text{chlorophyll}]{\text{light}}$ glucose + oxygen

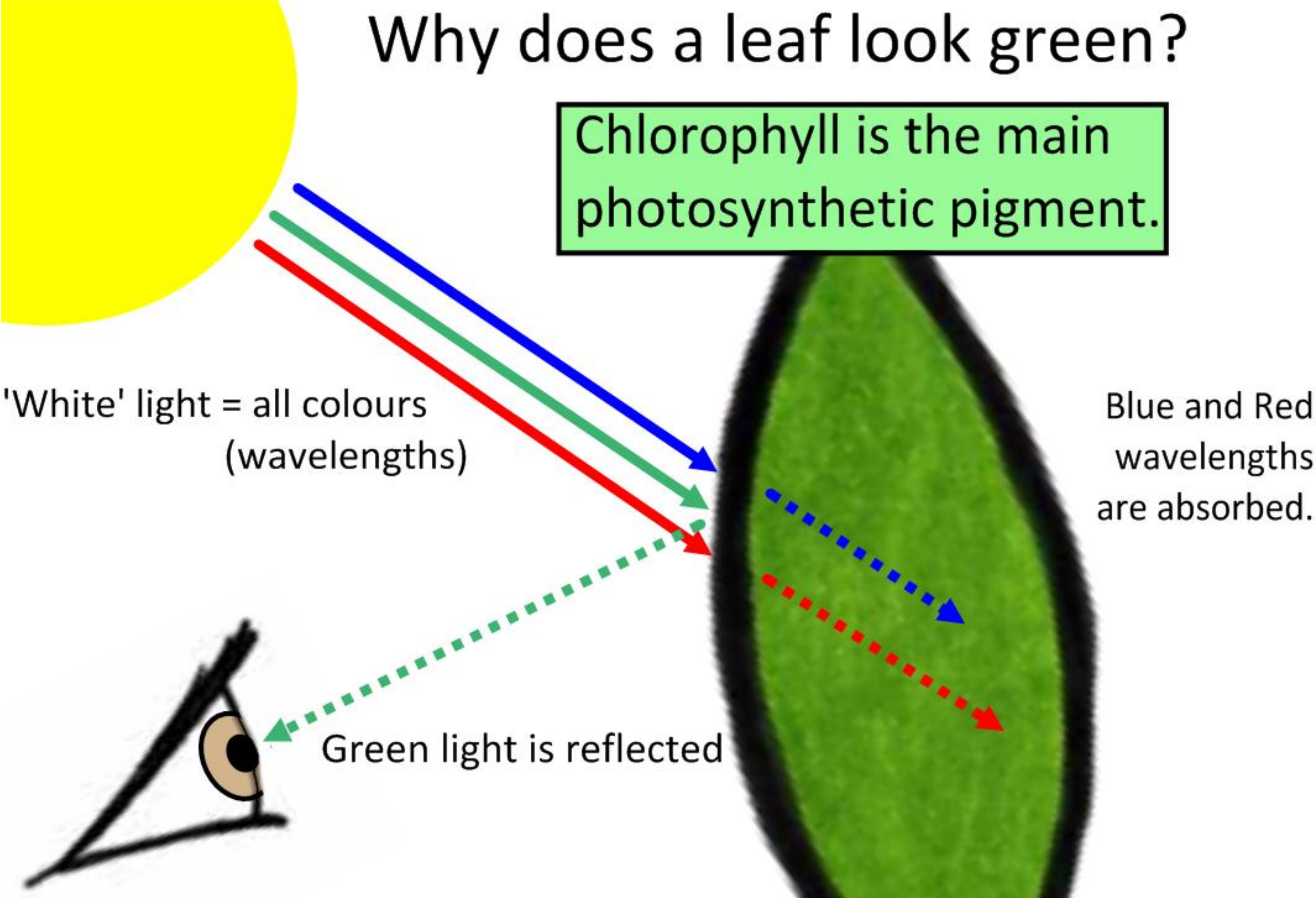
$6CO_2$ $6H_2O$ $C_6H_{12}O_6$ $6O_2$



How much of the light absorbed is used?
This is the ACTION SPECTRUM of photosynthesis:



Why does a leaf look green?



THE NATURE OF LIGHT

Light is an ELECTROMAGNETIC WAVE

Light is also a PARTICLE: the PHOTON

This is principle of

Wave- Particle Duality

theory.

- Einstein:

Radiation behaves as though it consists of a stream of particles, or photons. Each of these photons has a fixed energy depends on the frequency or wavelength.

Quantum Theory

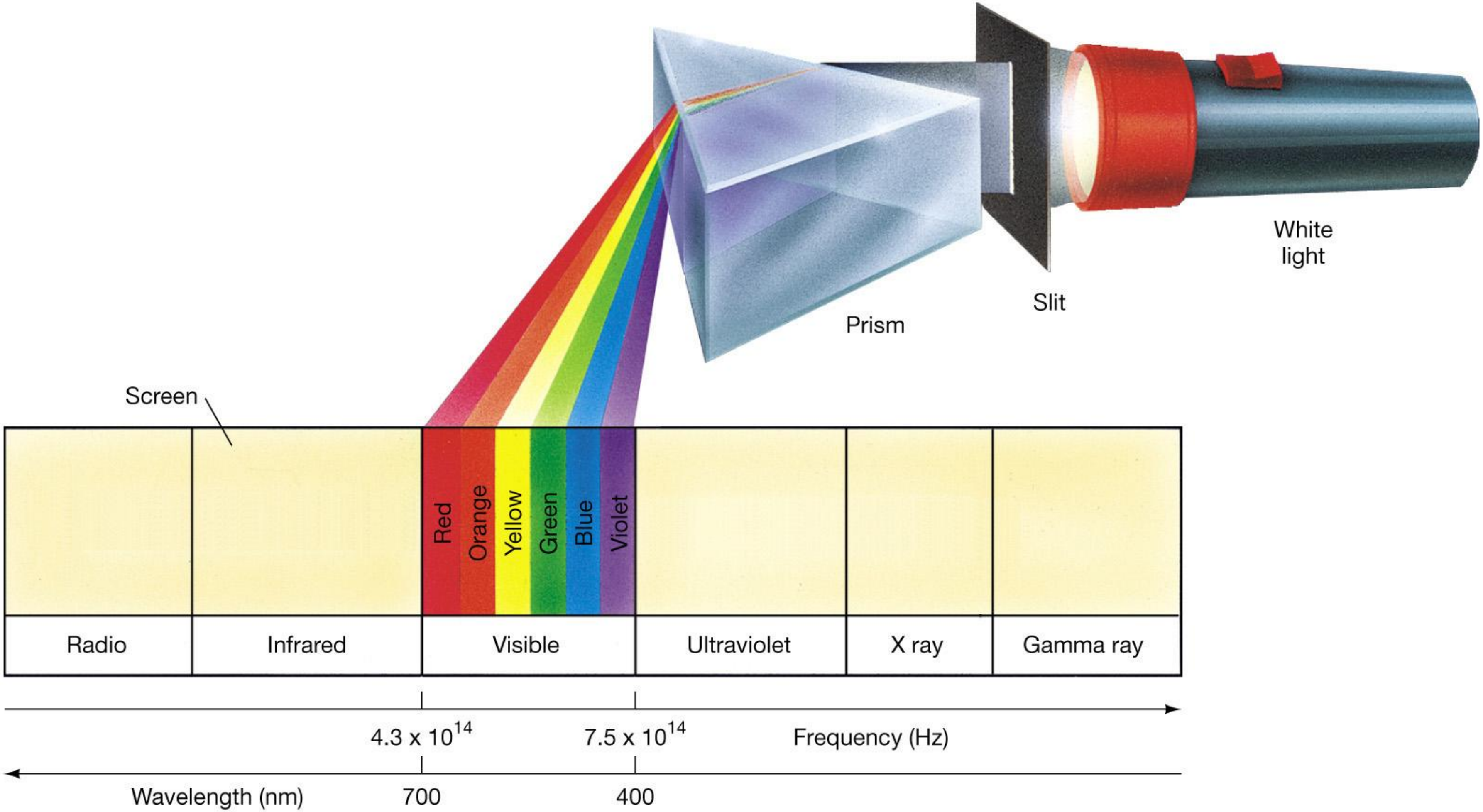
- Max Blanck:

The chemical changes wrought by electromagnetic radiation in its interaction with matter would be very difficult to interpret without assuming that the radiation can behave as particles whose energy is quantized.

$$E=h\upsilon$$

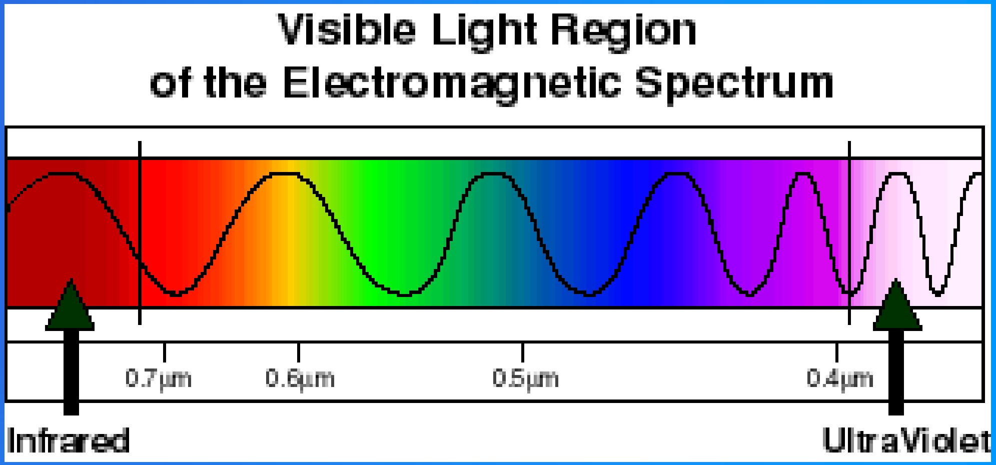
1- Light as a Waves

The Seven Bands of the EM Spectrum



⇑ Microwave or millimeter between Radio and IR

Visible light is that portion of the electromagnetic spectrum which stimulates the retina of the human eye.



Visible spectrum wavelengths range from about 400 nm (violet) to 760 nm (red).

Light travels at about 3×10^8 m/s through empty space and slightly slower through air.

Remember that for all waves, $v = f\lambda$.

The Wave Nature of light

- There are two types of waves:

1- Transverse waves: light waves.
(electromagnetic waves, water waves)

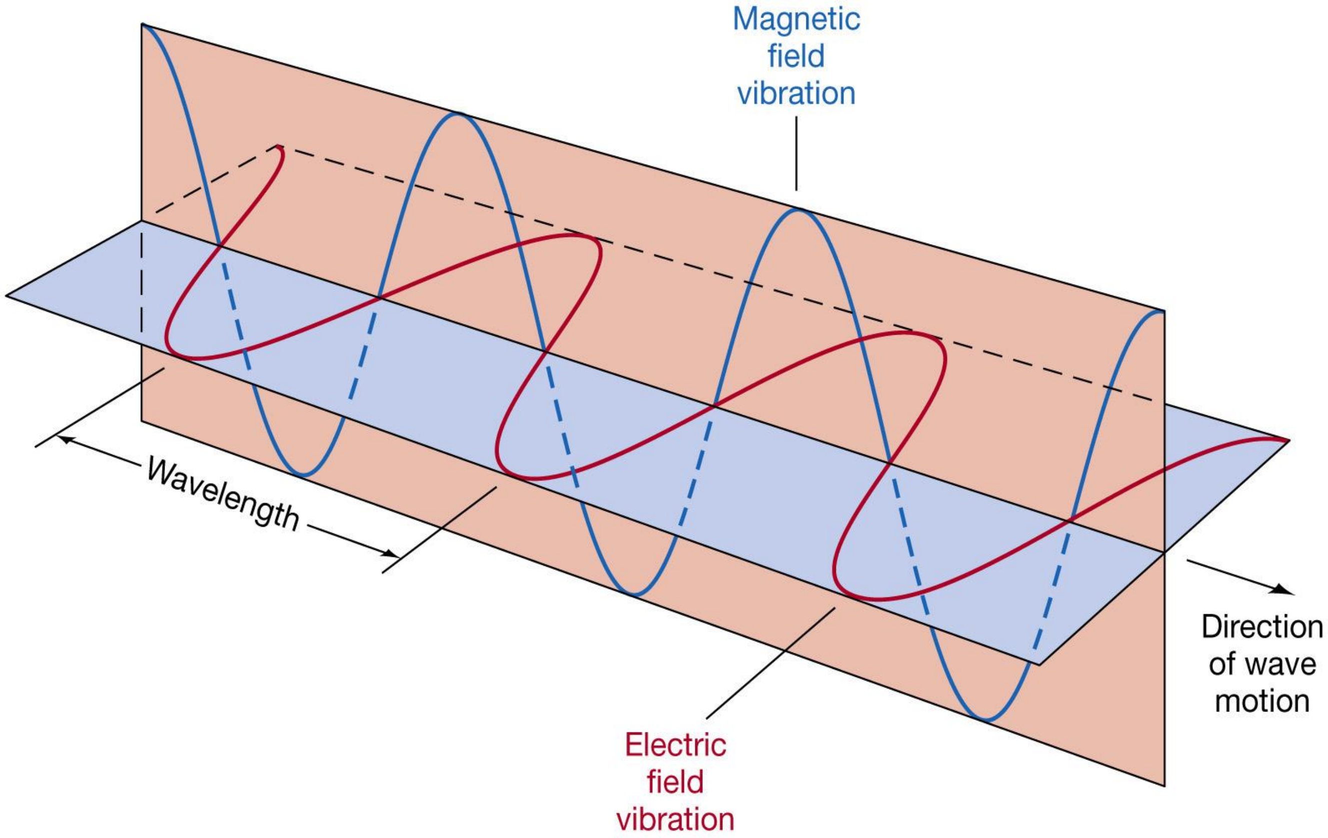
2- Longitudinal waves: sound waves.

Electromagnetic field= (electric +magnetic) field

- Electric (E) fields oscillate perpendicular to Magnetic (B) fields.

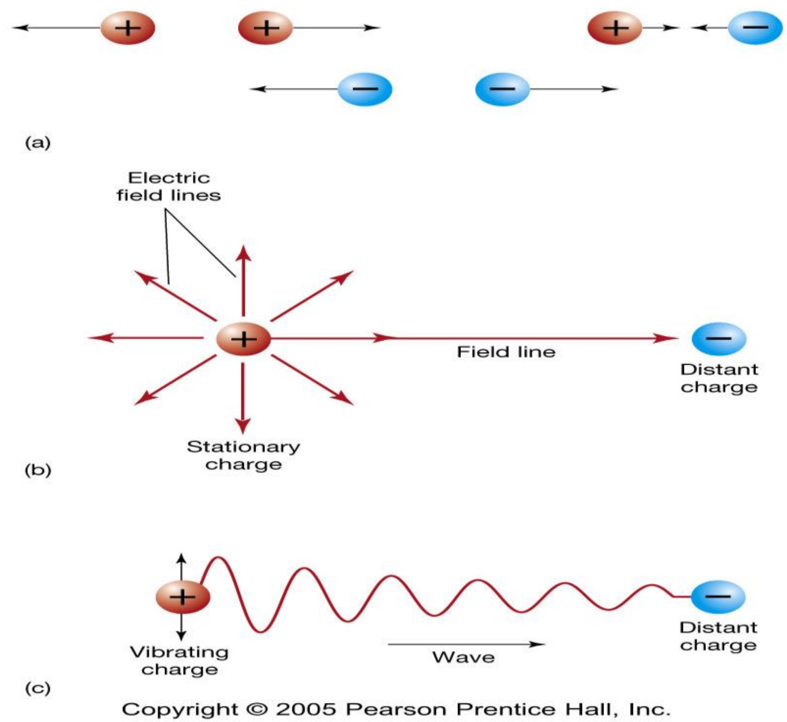
James Clerk Maxwell

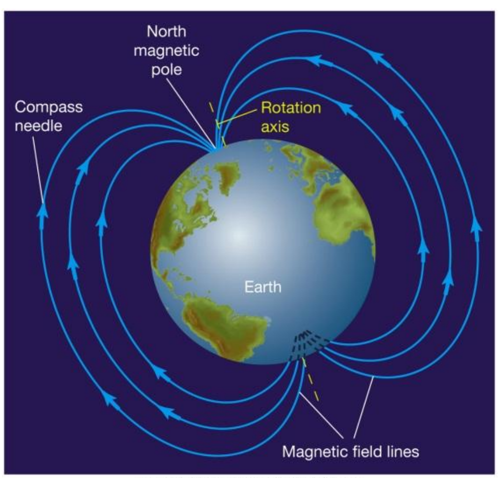
Transverse of Electric and magnetic fields (EM) in planes perpendicular to each other



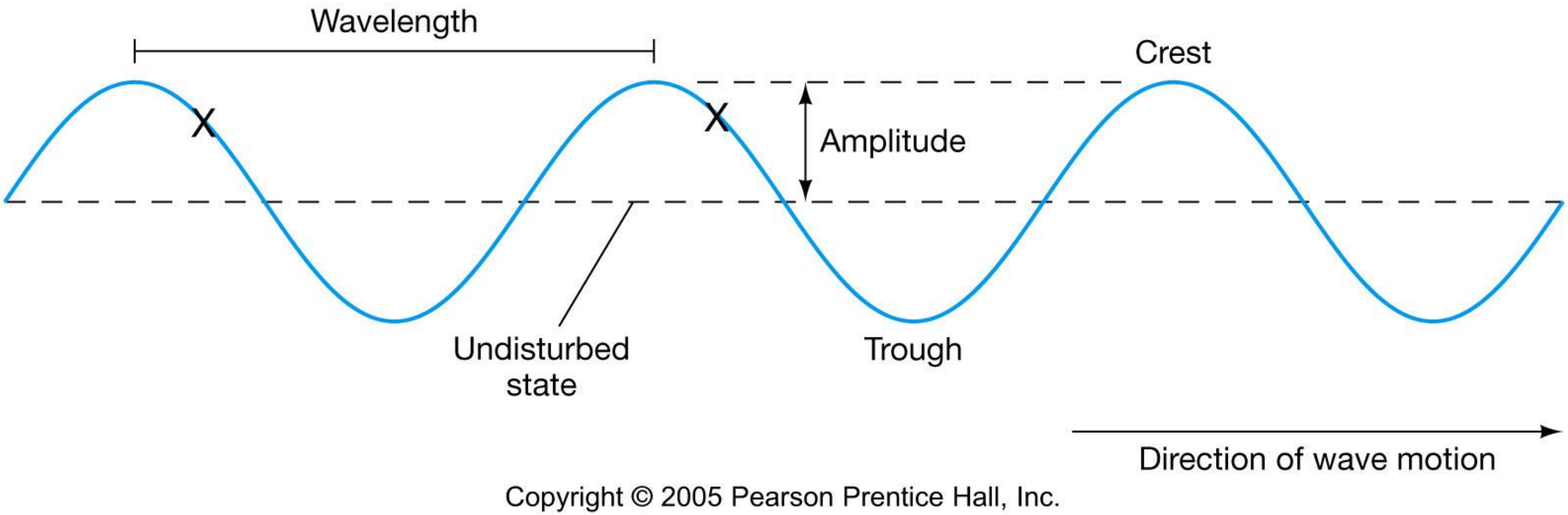
Electric and Magnetic Fields

- Charged particles (protons or ions +, electrons -) attract or repel each other.
- Electric fields accelerate charged particles along the lines.
- Charged particles orbit around magnetic field lines.



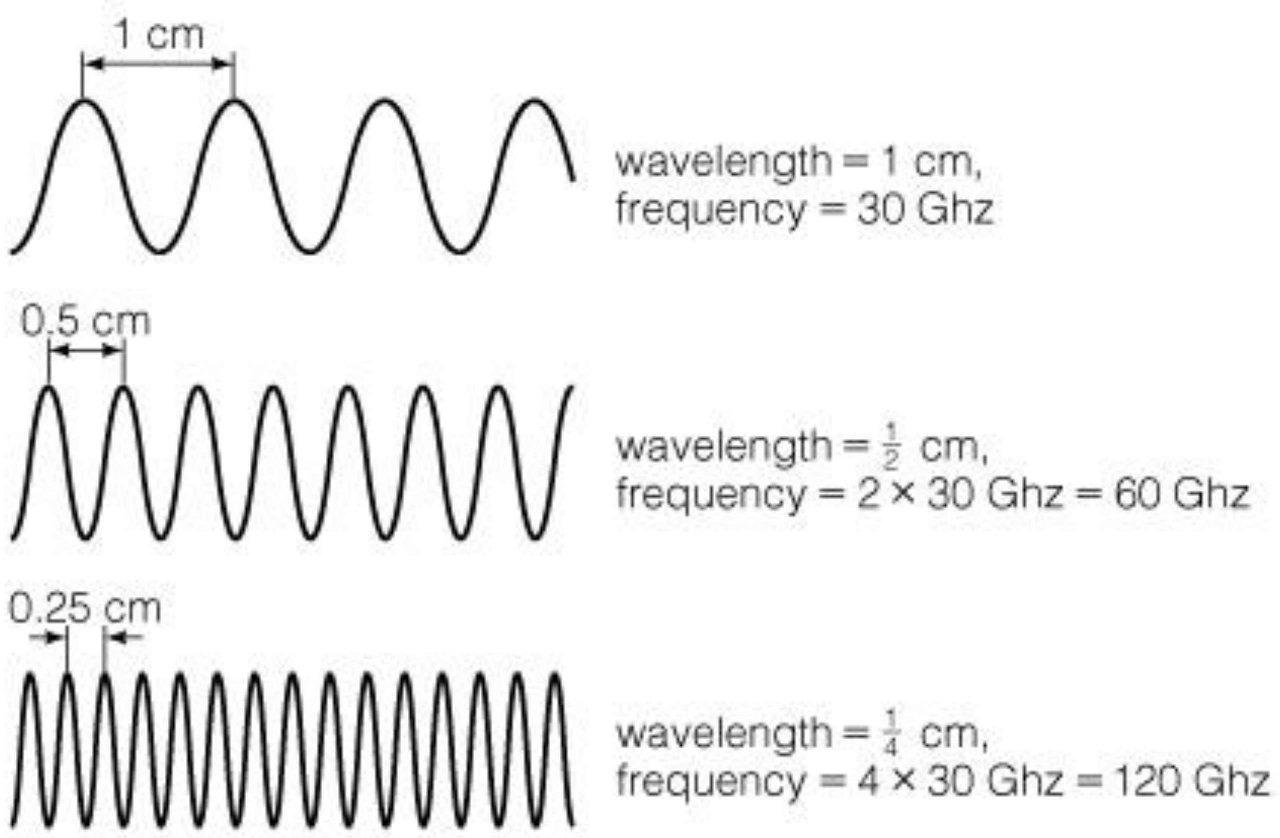


Characteristics of All Waves



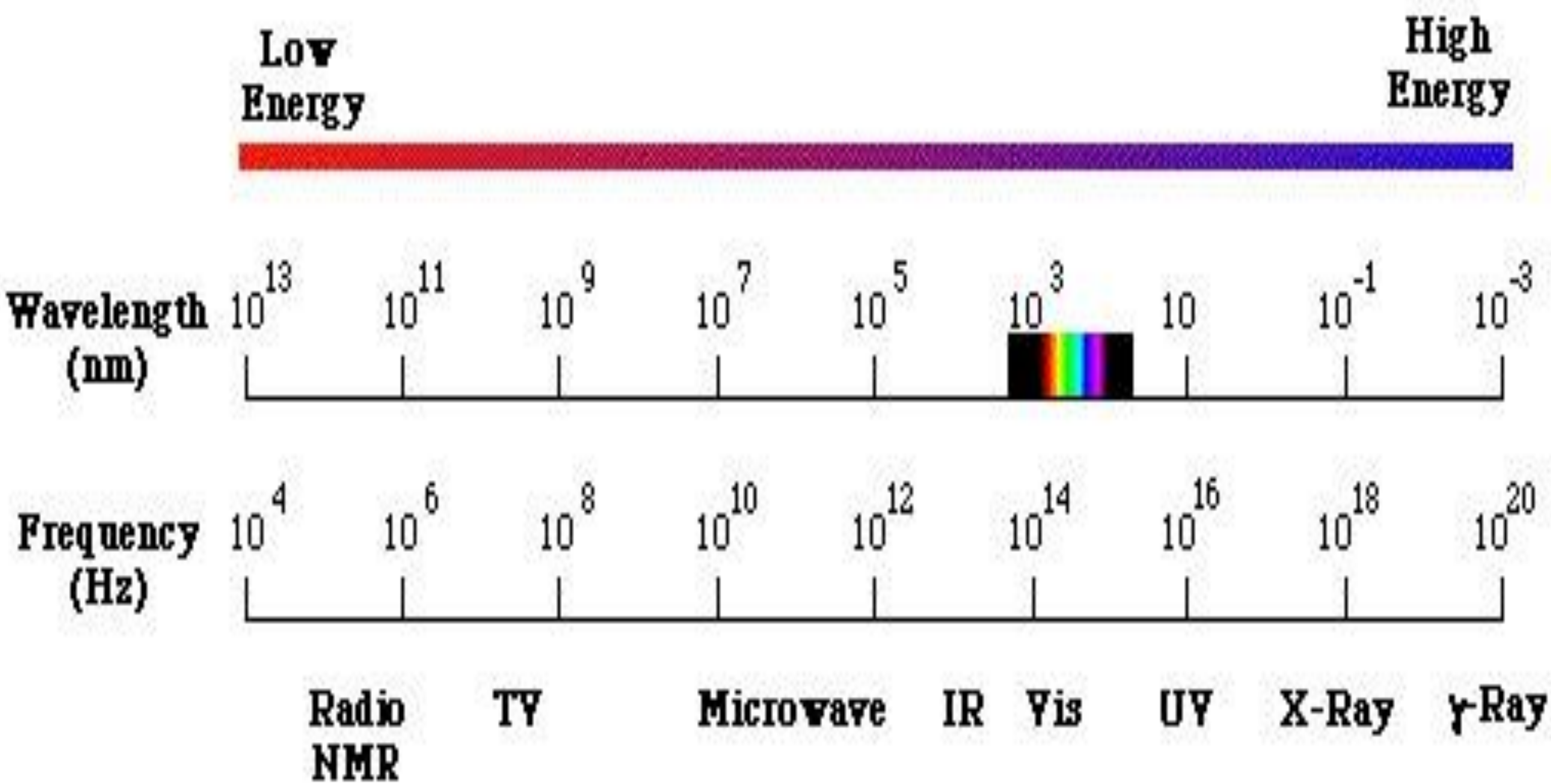
- Frequency (f or ν [nu]): oscillations per sec (Hz)
- Speed (v): depends on medium (m/s)
- Wavelength (λ [lambda]): distance between crests (nm)
- Amplitude (A): strength of oscillation

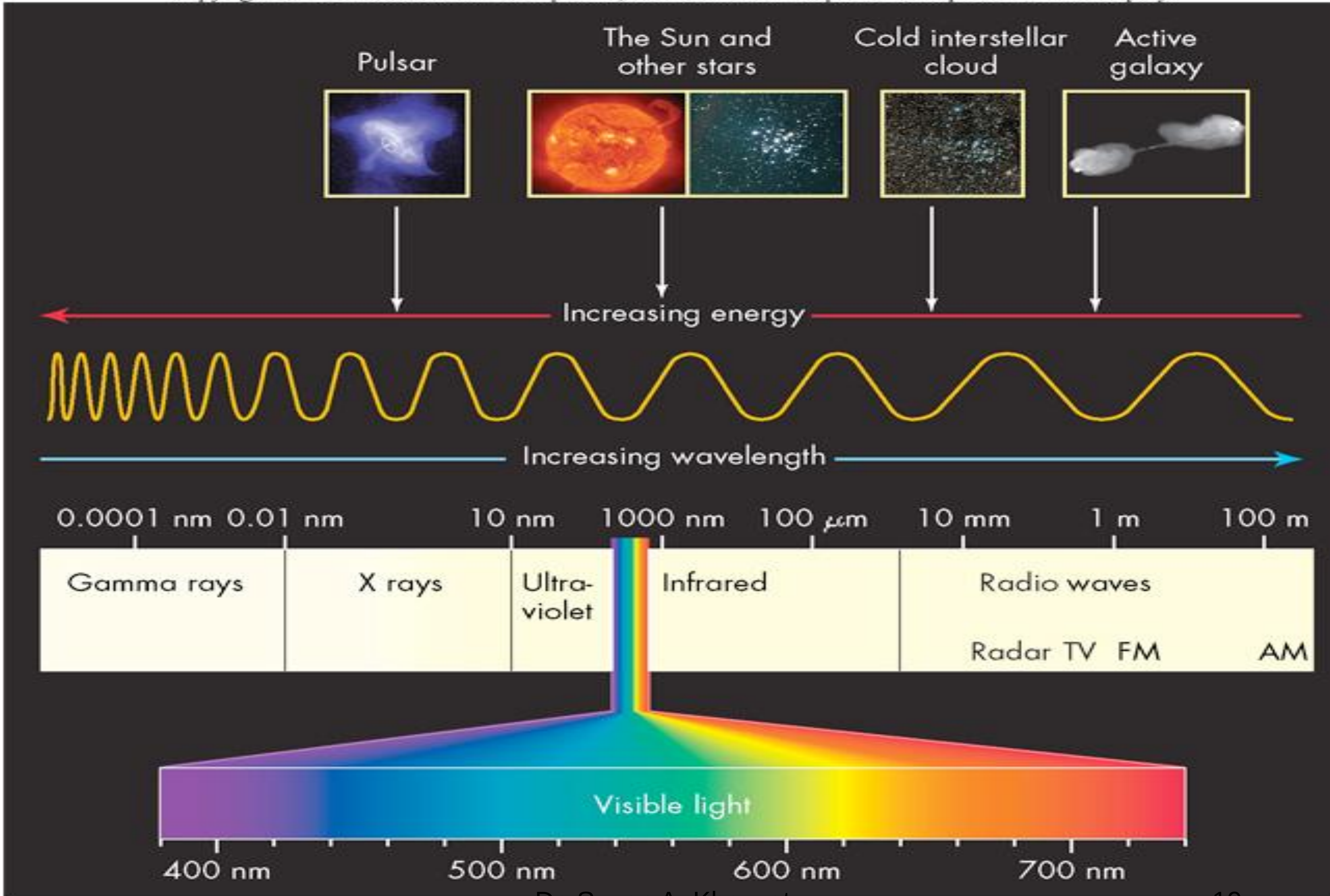
Wavelength and Frequency for Light



wavelength x frequency = speed of light = constant

$v = f\lambda.$


Low Energy
High Energy
Wavelength (nm)
10 13
10 11
10 9
10 7
10 5
10 3
10
10 -1
10 -3
Frequency (Hz)
10 4
10 6
10 8
10 10
10 12
10 14
10 16
10 18
10 20
Radio NMR
TV
Microwave
IR
Vis
UV
X-Ray
γ-Ray



Pulsar
The Sun and other stars
Cold interstellar cloud
Active galaxy
Increasing energy
Increasing wavelength
0.0001 nm
0.01 nm
10 nm
1000 nm
100 μm
10 mm
1 m
100 m
Gamma rays
X rays
Ultra-violet
Infrared
Radio waves
Radar
TV
FM
AM
Visible light
400 nm
500 nm
600 nm
700 nm

Regions of the electromagnetic spectrum

- Visible Light: 400–700 nanometer (nm) wavelength range
- Ultraviolet: 100–400 nm wavelength range
- Near Infrared: 700–1000 nm wavelength range
- Far infrared: 15–1000 micrometer (µm) wavelength range

How are Electromagnetic Waves Made?

- Most come from
  ATOMIC,
  MOLECULAR or
  NUCLEAR TRANSITIONS.
  I.e., electrons or protons changing quantum states.
- BUT FUNDAMENTALLY, EM RADIATION IS PRODUCED BY AN ACCELERATED CHARGED PARTICLE.
- Since ELECTRONS have the LOWEST MASSES
  they are MOST EASILY ACCELERATED,
  therefore, electrons produce most EM waves.

Shortest Wavelengths

- ULTRAVIOLET (UV): 380 nm > λ > 300Å = 30nm
  Mostly absorbed in atmosphere: ozone (O_3)
  Good thing, since UV radiation causes skin cancer.
- X-RAY: 300 Å > λ > 0.1 Å = 0.01nm,
  Absorbed in atmosphere: by any atom (N, O)
  A good thing too: X-rays can penetrate the body and cause cancer in many organs.
- **GAMMA-RAY (γ-ray)**: λ < 0.1 Å =0.01 nm,
  The most energetic form of EM radiation.
  Absorbed high in atmosphere: by any atomic nucleus.
  A VERY good thing: gamma-rays quickly cause severe burns and cancer.

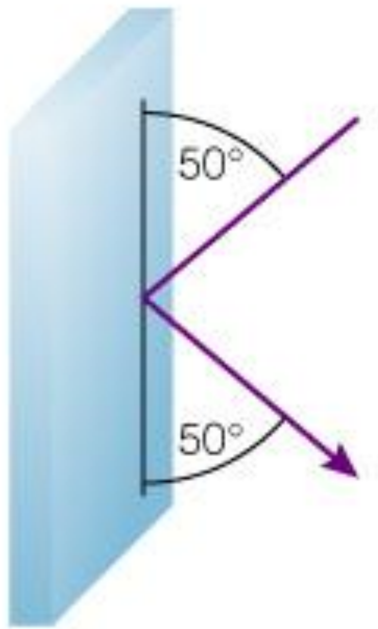
Colors of Light

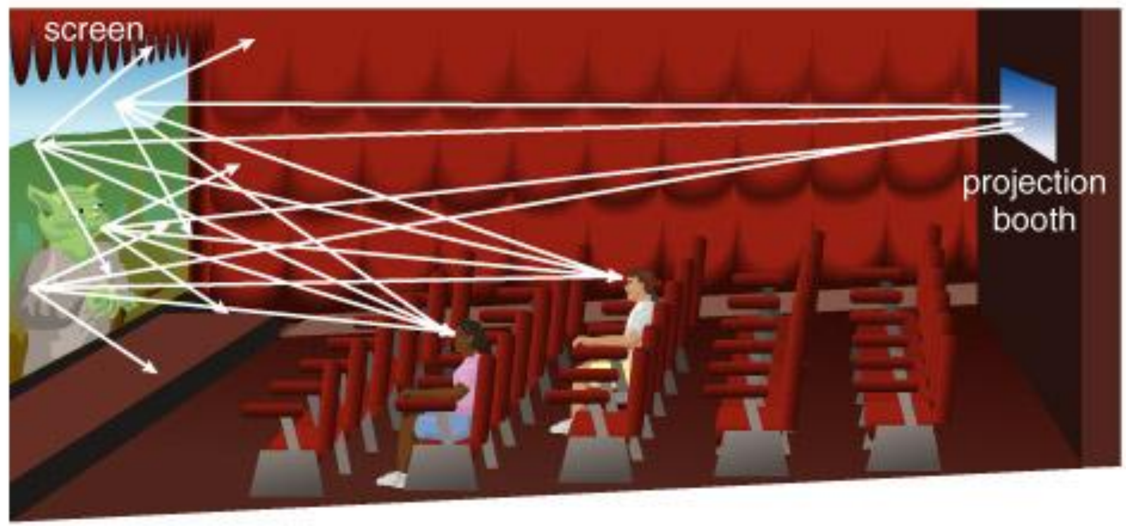
- **White light is made up of many different colors**

How do Waves Interact with Matter?

- EMIT (light is sent out when a bulb is turned on)
- REFLECT (angle of incidence = angle of reflection) or Scatter (spread out reflection)
- TRANSMIT (low opacity)
- ABSORB (high opacity)
- REFRACT (bend towards normal when entering a medium with a slower propagation speed)
- INTERFERE (only a WAVE can do this) Either:
  CONSTRUCTIVE (waves add when in phase)
  DESTRUCTIVE (waves cancel when out of phase)
- DIFFRACT (only a WAVE can do this)
  Waves spread out when passing through a hole or slit.
  This is important only if the size of the hole or slit is comparable to the wavelength.

Reflection and Scattering

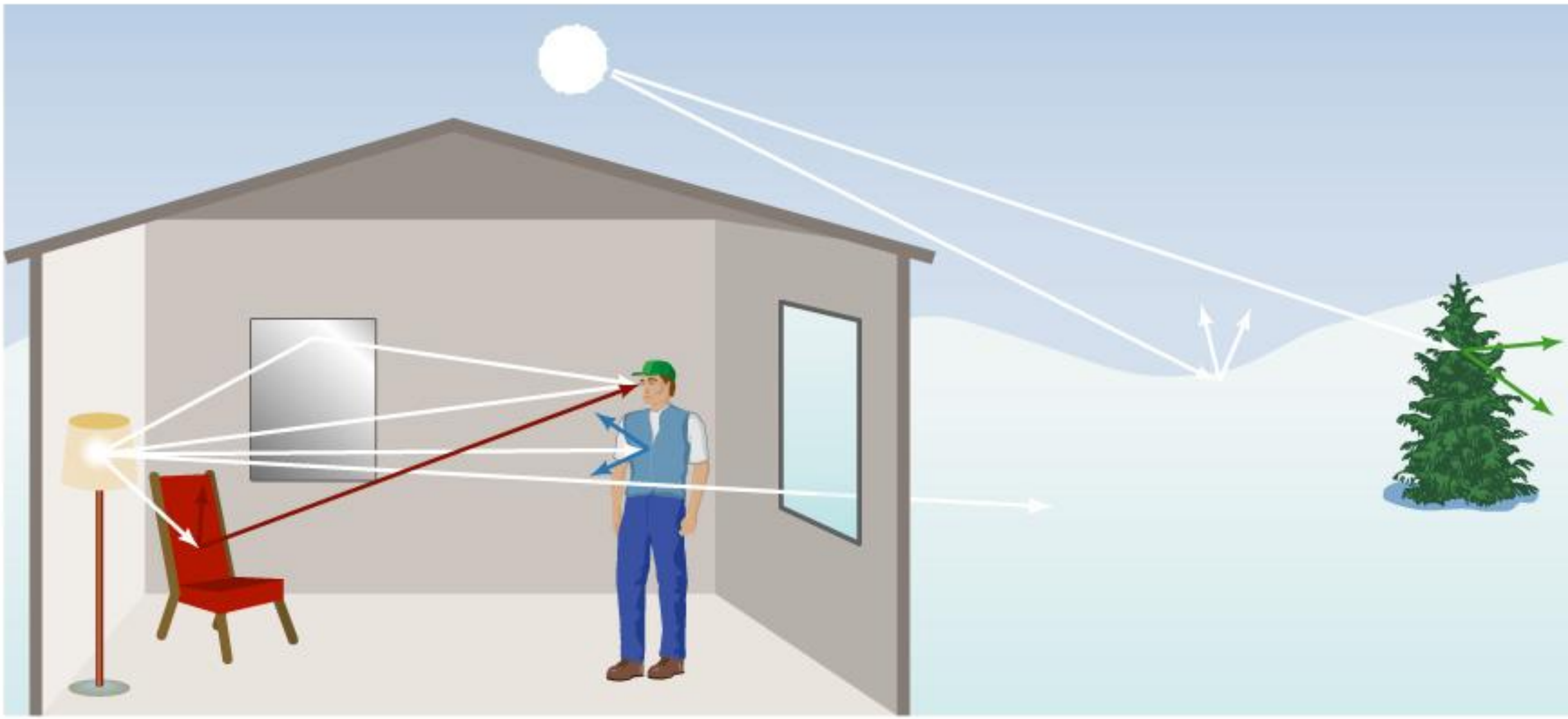




Mirror reflects light in a particular direction

Movie screen scatters light in all directions

Interactions of Light with Matter



Interactions between light and matter determine the appearance of everything around us: objects reflect some wavelengths, absorb others and emit others.

Blue light is (compared to red light),

1. Shorter wavelength
2. Longer wavelength
3. Higher energy photons
4. **1 and 3**
5. None of the above

We can’t see infrared, but we can perceive it as:

1. Heat
2. Radar
3. Sound
4. AM
5. FM

When light approaches matter, it can

1. Be *absorbed* by the atoms in the matter
2. Go through the matter, and be *transmitted*
3. Bounce off the matter, and be *reflected*
4. Any of the above
5. Only 2 or 3

When light approaches matter, it can

1. Be *absorbed* by the atoms in the matter
2. Go through the matter, and be *transmitted*
3. Bounce off the matter, and be *reflected*
4. **Any of the above**
5. Only 2 or 3

Thought Question
Why is a rose red?

a) The rose absorbs red light.
b) The rose transmits red light.
c) The rose emits red light.
d) The rose reflects red light.

Thought Question
Why is a rose red?

a) The rose absorbs red light.
b) The rose transmits red light.
c) The rose emits red light.
d) The rose reflects red light.

2- Light as Particles

- ELECTROMAGNETIC ENERGY IS CARRIED BY **PHOTONS:**
- A PHOTON is a SINGLE QUANTUM OF LIGHT.
- The energy of one photon of a particular frequency is:

$$E = h\upsilon = h\,c\,/\,\lambda$$

$h = 6.63 \times 10^{-34}$ Joule sec = is PLANCK's CONSTANT.

c is the speed of light.

Thought Question
The higher the photon energy…

a) the longer its wavelength.
b) the shorter its wavelength.
c) energy is independent of wavelength.

Thought Question
The higher the photon energy…

a) the longer its wavelength.

b) the shorter its wavelength.

c) energy is independent of wavelength.

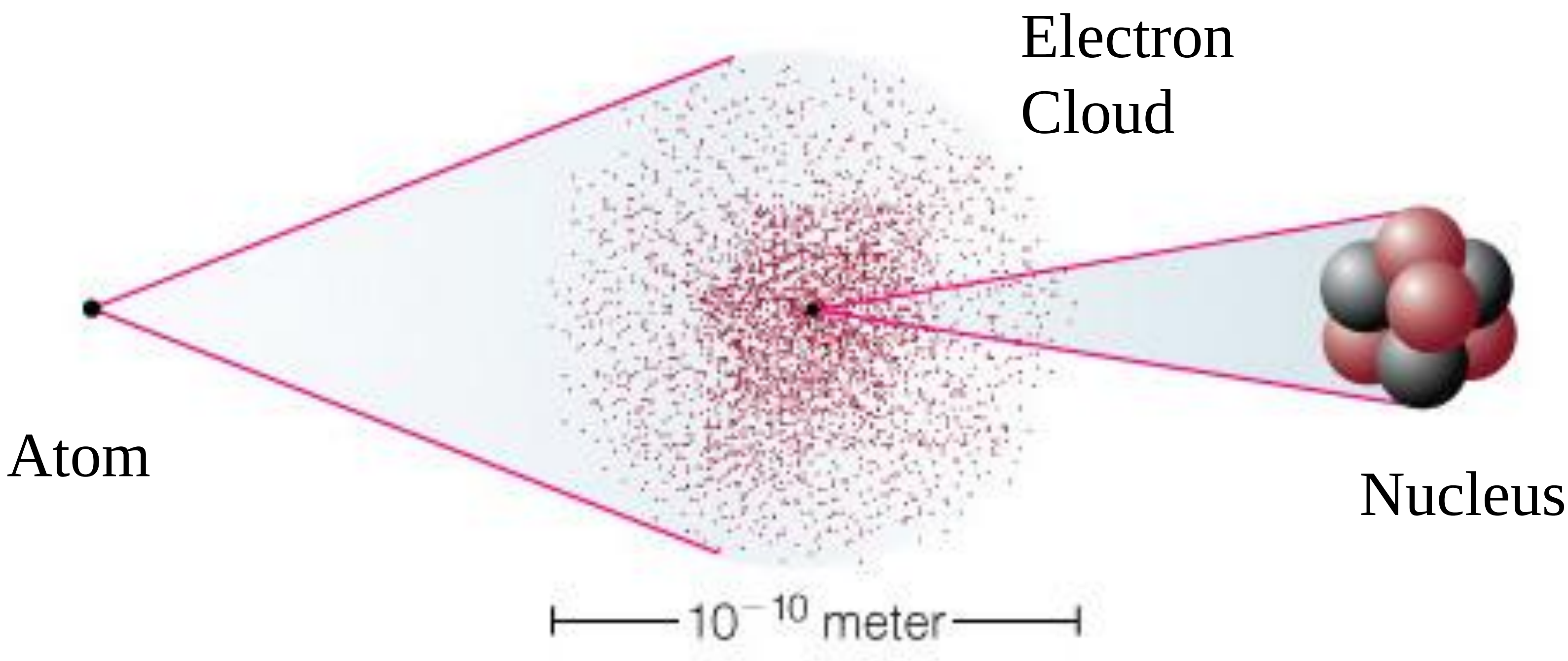
How can light behave as both a wave and a particle?

1. It doesn't really
2. It really is simultaneously *both a* wave and a particle
3. Light and small objects such as atoms behave in ways we never see in everyday objects, so we can't describe them in everyday terms
4. This is what *quantum mechanics* describes
5. 3 and 4

Thought Question
Why don’t we glow in the dark?

a) People do not emit any kind of light.
b) People essentially only emit light that is invisible to our eyes.
c) People are too small to emit enough light for us to see.
d) People do not contain enough radioactive material.

WHAT IS THE STRUCTURE OF MATTER?

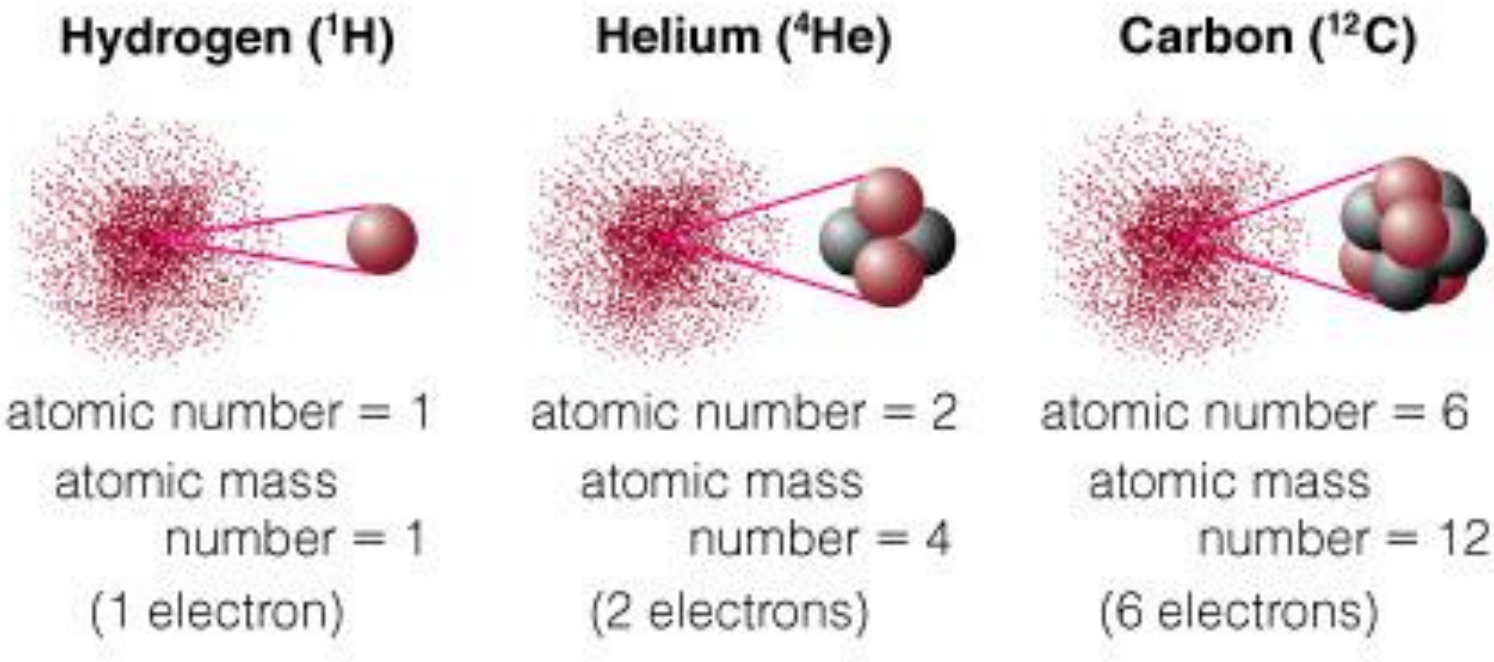


Nucleus size only around 10^{-15}m while electron clouds are roughly 10^{-10}m = 0.1 nm = 1Å

As nearly all of the mass is in the nucleus, matter is mostly empty space!

Atomic Terminology

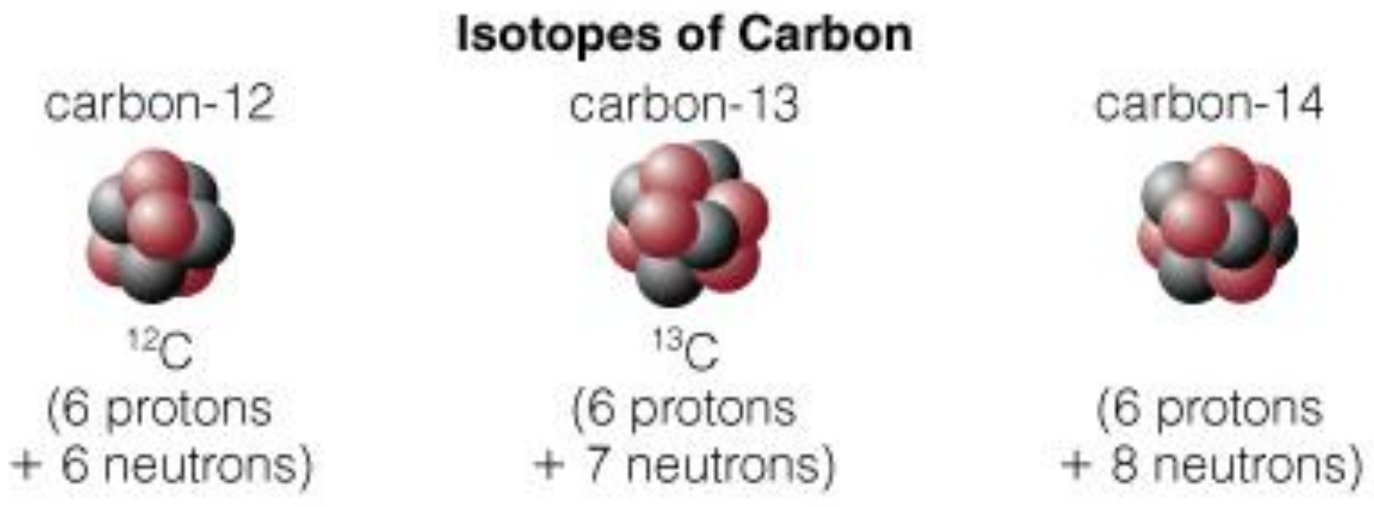
- Atomic Number = # of protons in nucleus
- Atomic Mass Number = # of protons + neutrons



- Molecules: consist of two or more atoms (H_2O, CO_2)

Atomic Terminology

- Isotope: same # of protons but different # of neutrons. (^{4}He, ^{3}He)



What is found in the nucleus of atoms?

1. Protons with a + charge
2. Neutrons with no charge
3. Electrons with a – charge
4. All of the above
5. 1 and 2

What is found in the nucleus of atoms?

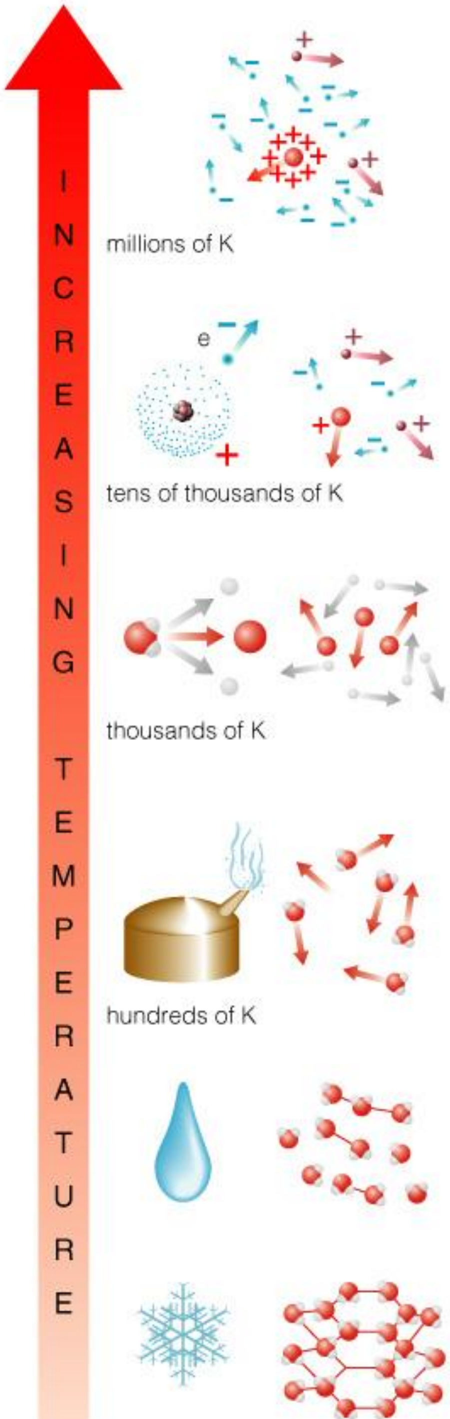
1. Protons with a + charge
2. Neutrons with no charge
3. Electrons with a – charge
4. All of the above
5. **1 and 2**

How is the isotope ^{14}C different from ^{12}C?

1. It has more protons
2. It has more neutrons
3. It has more electrons
4. All of the above
5. None of the above

How is the isotope ^{14}C different from ^{12}C?

1. It has more protons
2. **It has more neutrons**
3. It has more electrons
4. All of the above
5. None of the above



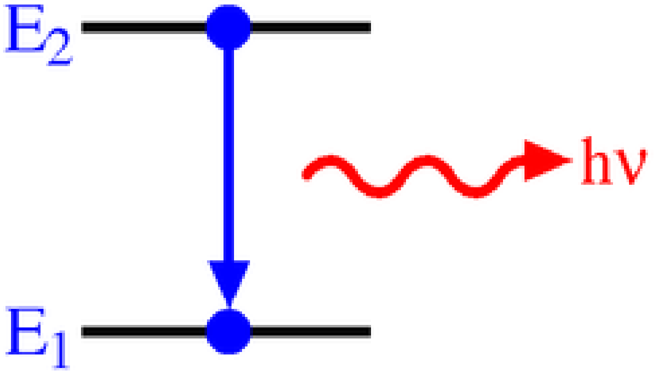
Phase Changes

- **Ionization:** Stripping of electrons, changing atoms into plasma
- **Dissociation:** Breaking of molecules into atoms
- **Evaporation:** Breaking of flexible chemical bonds, changing liquid into gas
- **Melting:** Breaking of rigid chemical bonds, changing solid into liquid
- **Sublimation:** from solid to gas

Review of the Nature of Matter

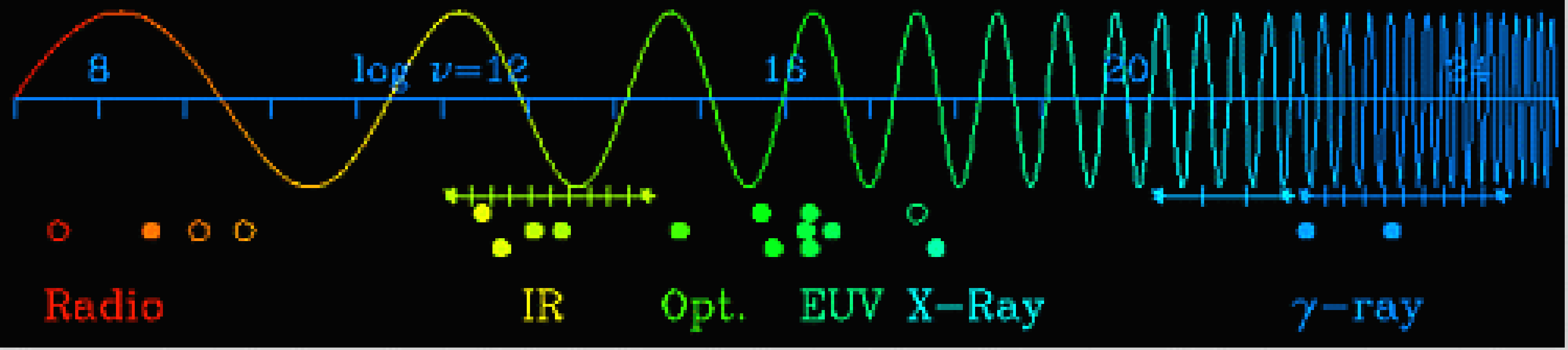
- What is the structure of matter?
  - Matter is made of atoms, which consist of a nucleus of protons and neutrons surrounded by a cloud of electrons
- What are the phases of matter?
  - Adding heat to a substance changes its phase by breaking chemical bonds.
  - As temperature rises, a substance transforms from a solid to a liquid to a gas, then the molecules can dissociate into atoms
  - Stripping of electrons from atoms (ionization) turns the substance into a plasma

Absorption and emission of radiation



- Energy levels in matter are quantized. In addition to its translational energy, a species may possess other sorts of internal energy. Each of which is quantized: rotational energy, vibrational energy which arises from the periodic oscillation of atoms in a molecule, and electronic energy which depends on the distance of the electron from the nucleus and the type of orbital that it occupies.

- When a species absorbs a quantum of radiation, it becomes excited. How the spices assimilates that energy __ in rational, vibrational, or electronic modes __ depends on the wavelength of the indicate radiation. The longer the wavelength of electromagnetic radiation, the lower the energy.



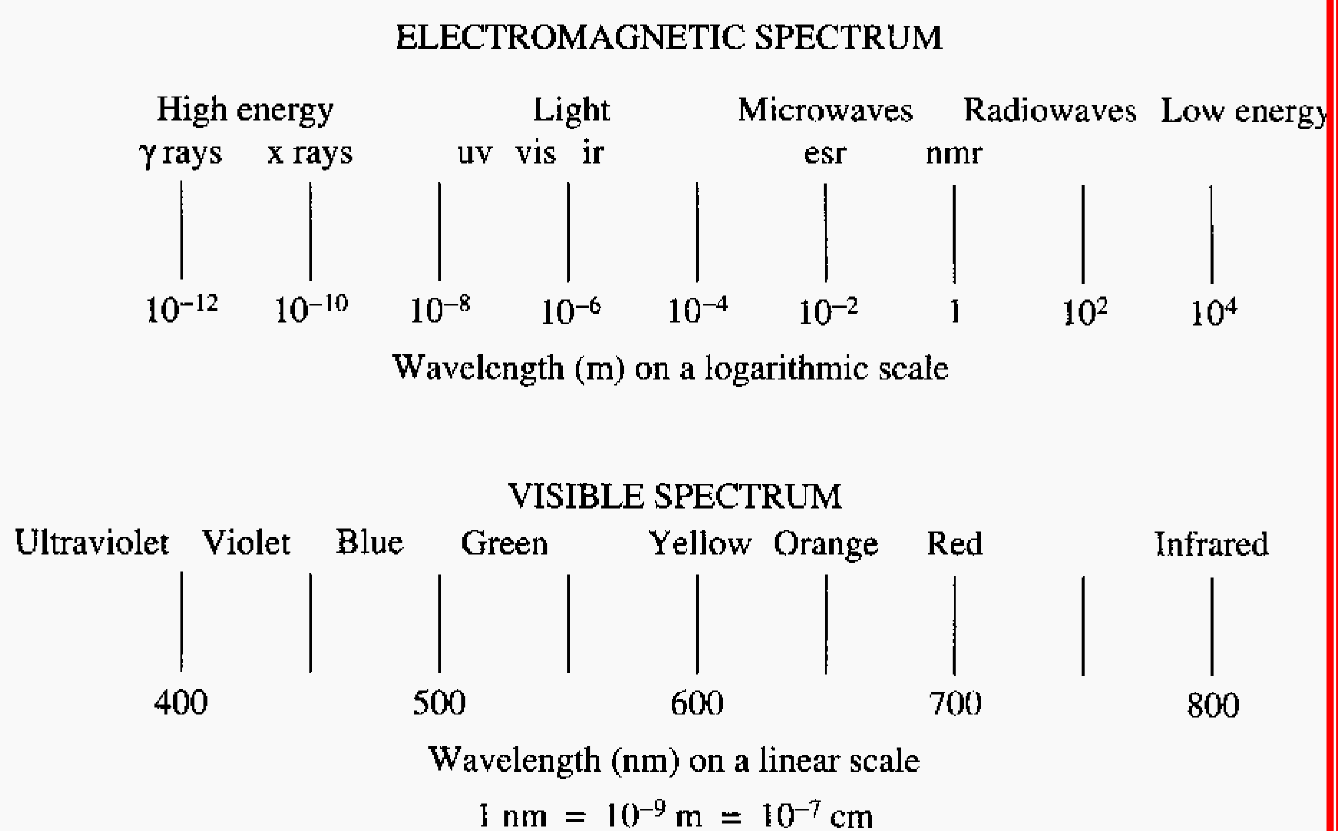
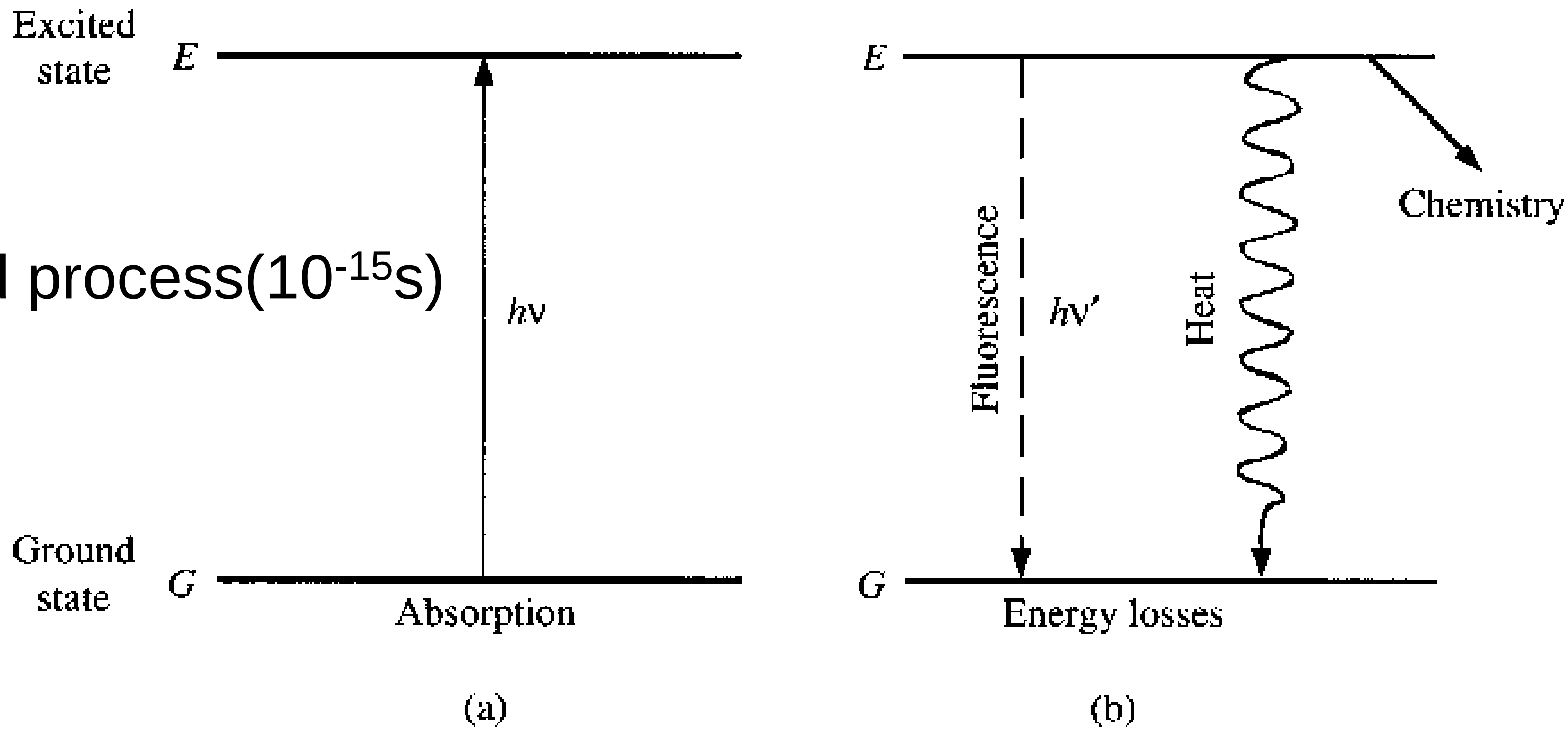


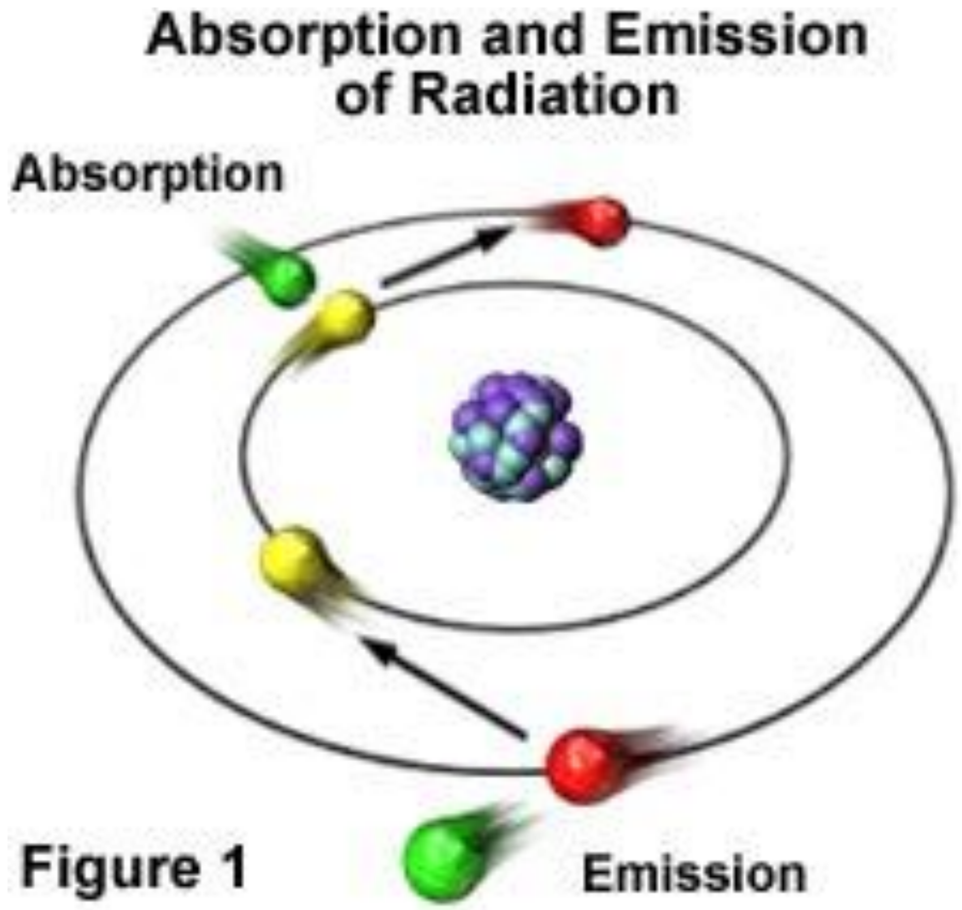
Fig. 10.1 Wavelength regions of the electromagnetic spectrum.

Absorption & Emission

Rapid process(10^{-15}s)



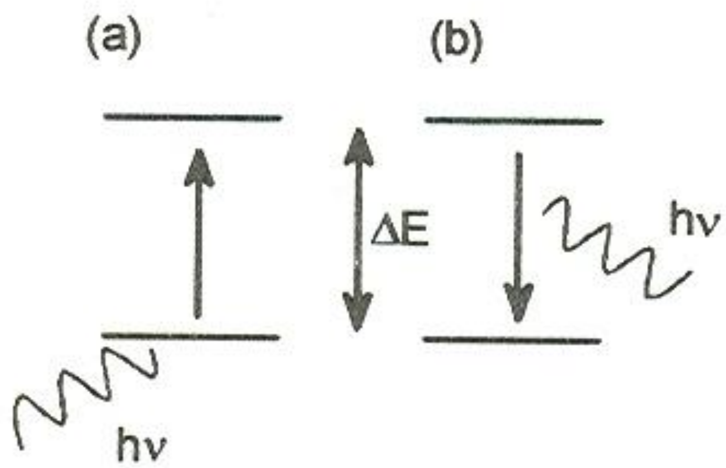
Absorption and Emission of Photons



http://micro.magnet.fsu.edu/optics/lightandcolor/frequency.html

Absorption and Emission

Absorption



Emission

<u>Absorption</u>: A transition from a lower level to a higher level with transfer of energy from the radiation field to an absorber, atom, molecule, or solid.

<u>Emission</u>: A transition from a higher level to a lower level with transfer of energy from the emitter to the radiation field. If no radiation is emitted.

http://www.chemistry.vt.edu/chem-ed/spec/spectros.html

- Types of emission:

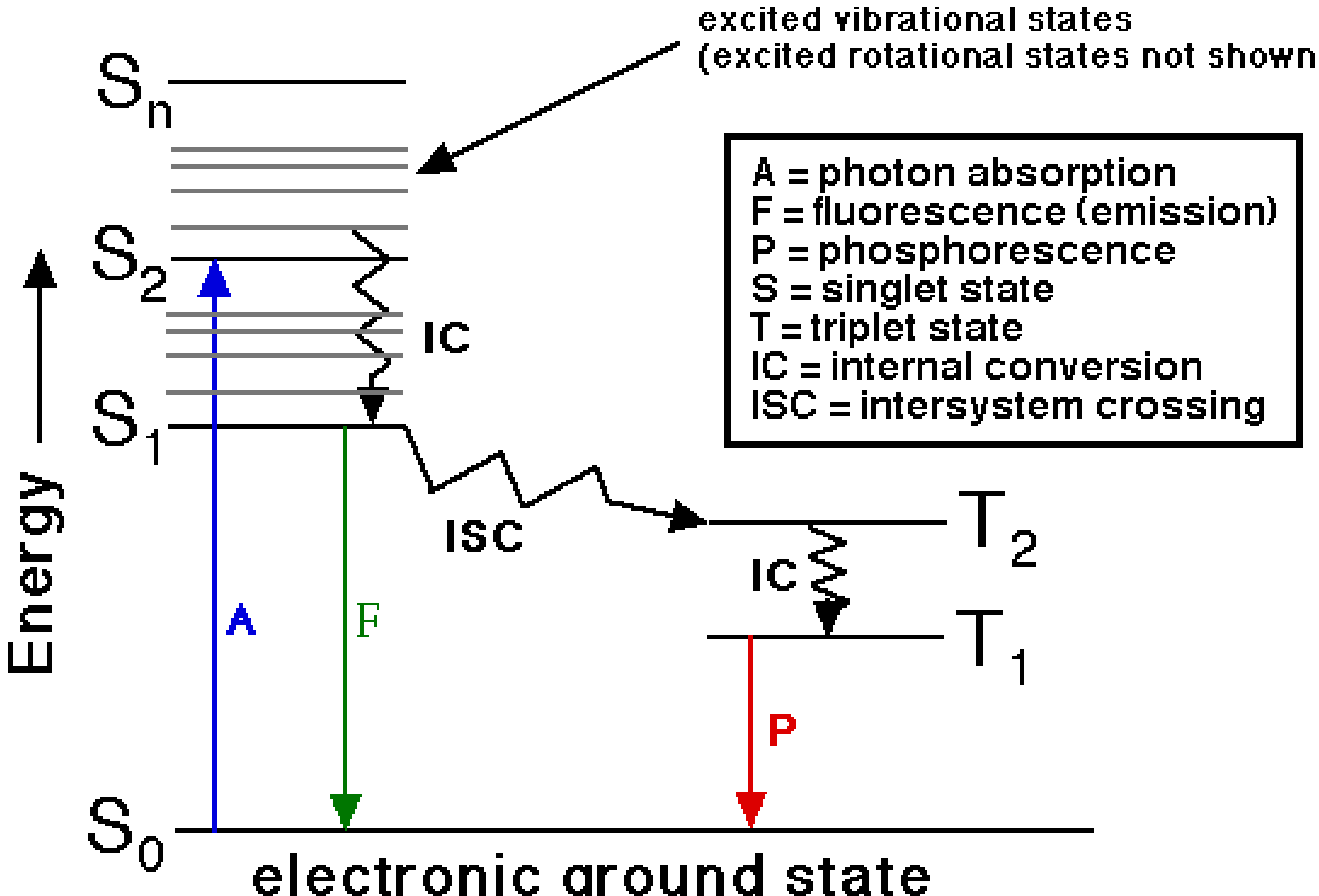
1- Stimulated emission

eg. laser

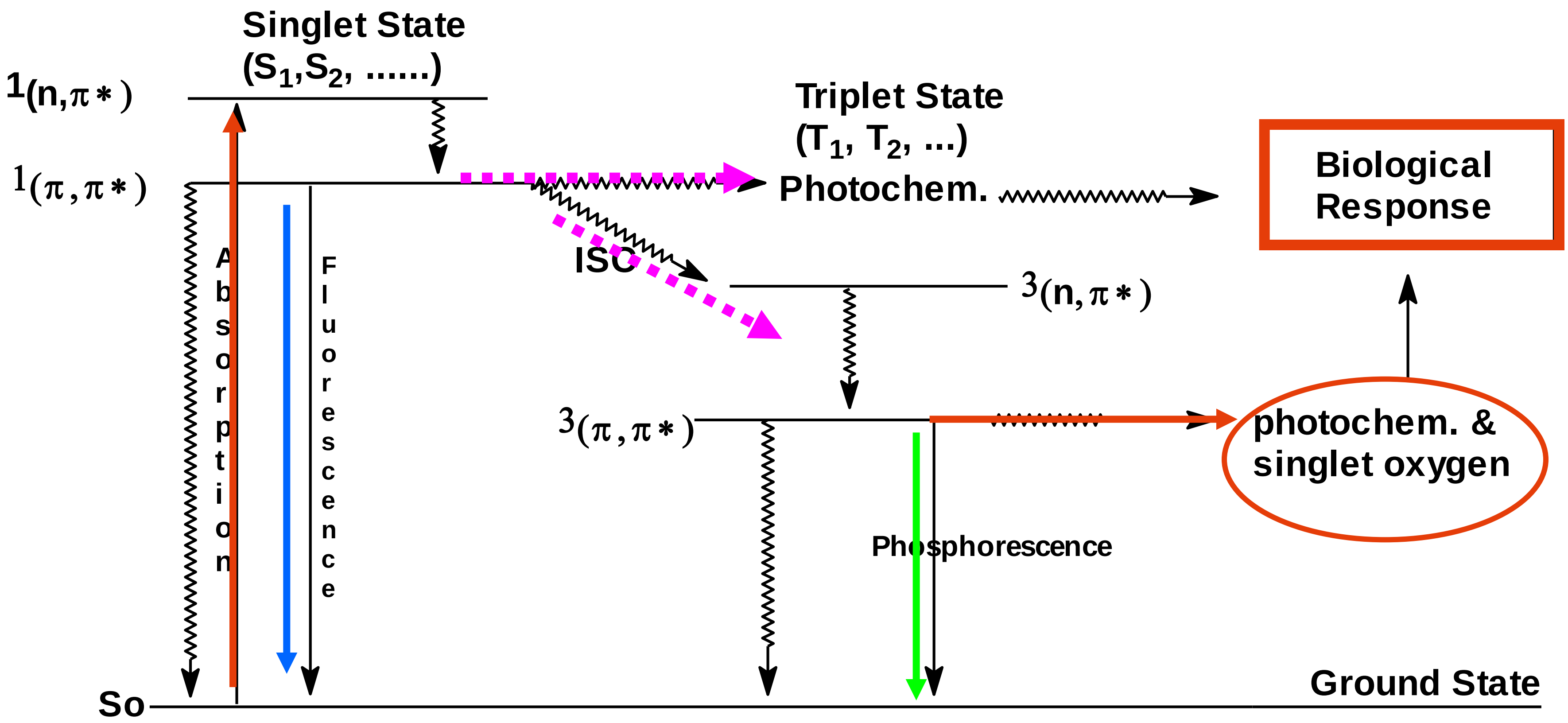
2- Spontaneous emission.

eg. Fluoresecence, phosphorescence and chemiluminescence.

Absorption and emission pathways



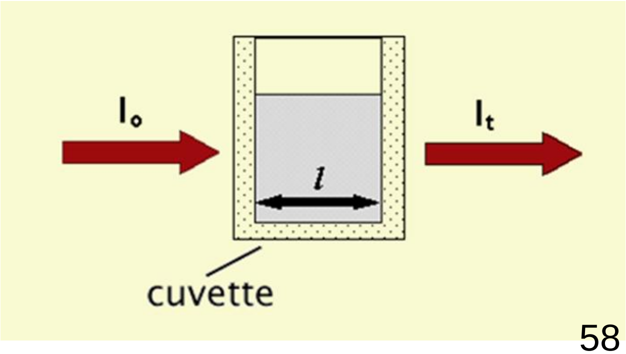
McGarvey and Gaillard, Basic Photochemistry at http://classes.kumc.edu/grants/dpc/instruct/index2.htm



Jablonski energy diagram

Beer-Lambert Law

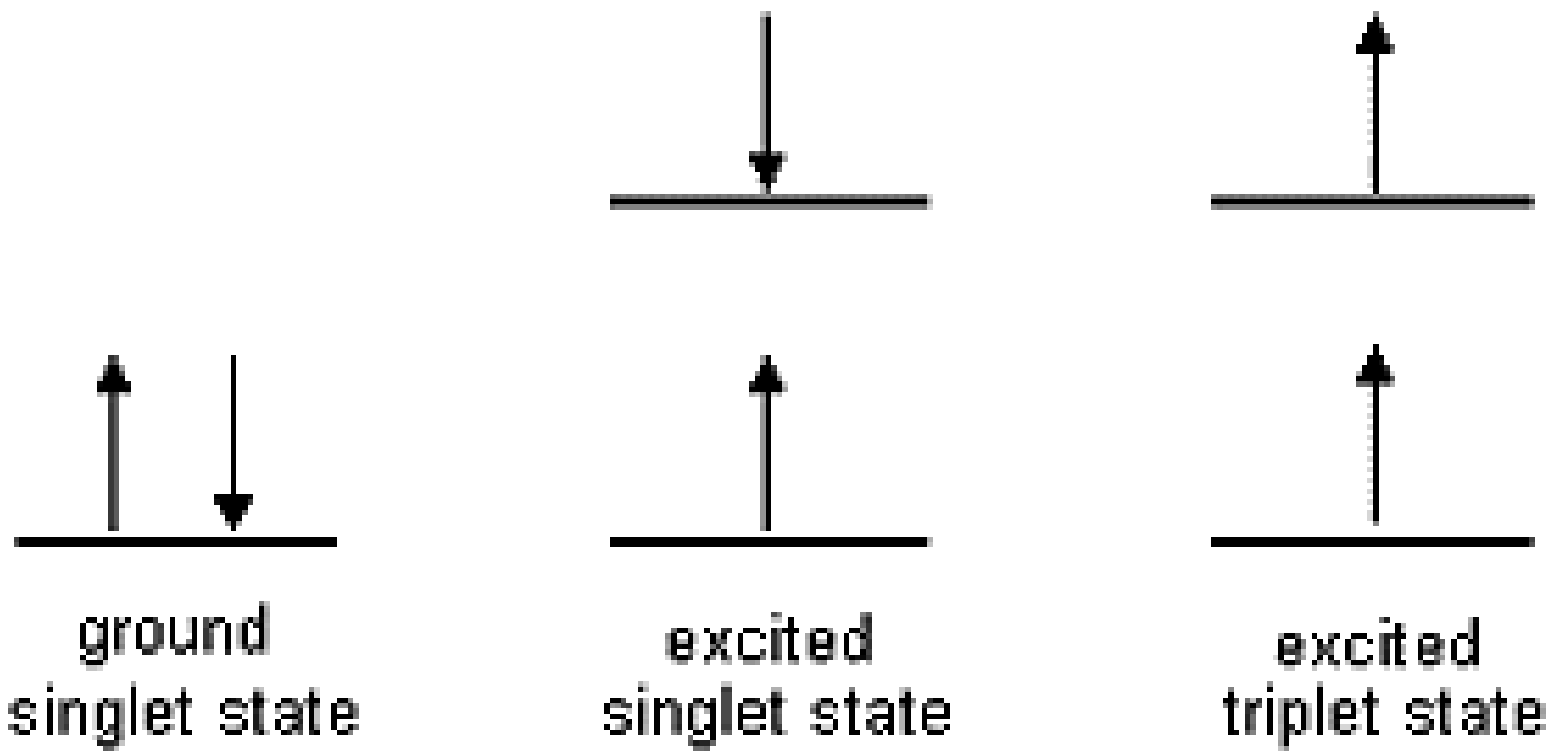
- The Beer-Lambert law is of particular importance in determining the intensity of absorbed radiation in photochemical experimentation, and in calculating concentrations from absorption measurements.



Electronic excitation

- First, the energies are of the same order of magnitude as bond energies, so that electronic excitation can have a considerable on the bond in species. Secondly, the energies correspond roughly with typical activation energies for reactions, and the excitation energy can help a species to either partially or completely overcome an activation barrier.

Wave mechanics and Quantum numbers



Singlet and Triplet Excited States

http://www.shu.ac.uk/schools/sci/chem/tutorials/molspec/lumin1.htm

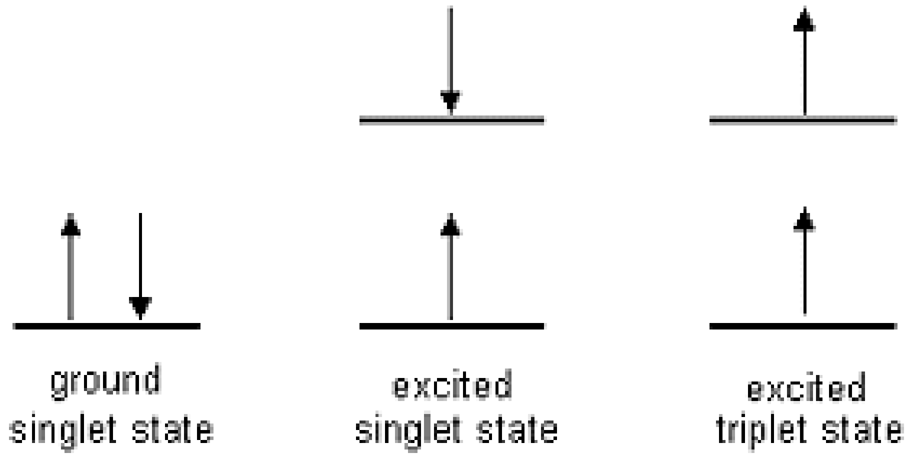
Selection Rules

In electronic spectroscopy there are three selection rules which determine whether or not transitions are formally allowed:

1. Spin selection rule: $\Delta S = 0$

allowed transitions: singlet $\rightarrow$ singlet or triplet $\rightarrow$ triplet
forbidden transitions: singlet $\rightarrow$ triplet or triplet $\rightarrow$ singlet

Changes in spin multiplicity are forbidden



http://www.shu.ac.uk/schools/sci/chem/tutorials/molspec/lumin1.htm

Selection rules

2. Laporte selection rule: there must be a change in the parity (symmetry) of the complex

   Laporte-allowed transitions: $g \rightarrow u$

   Laporte-forbidden transitions: $g \rightarrow g$ *or* $u \rightarrow u$

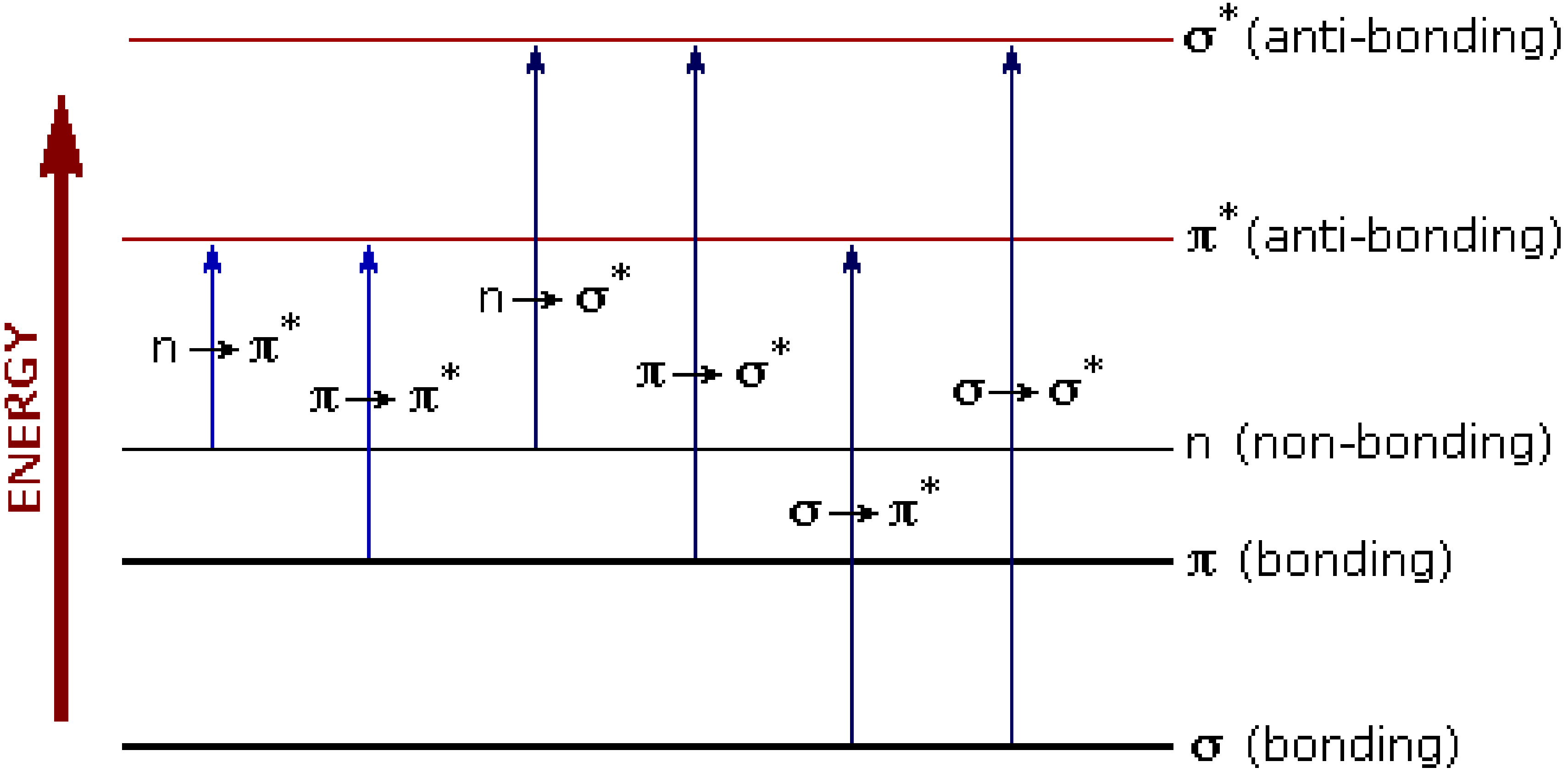
   g stands for *gerade* – compound with a center of symmetry

   u stands for *ungerade* – compound without a center of symmetry

3. Selection rule of $\Delta\ell = \pm 1$ (ℓ is the azimuthal or orbital quantum number, where $\ell = 0$ (s orbital), 1 (p orbital), 2 (d orbital), etc.)

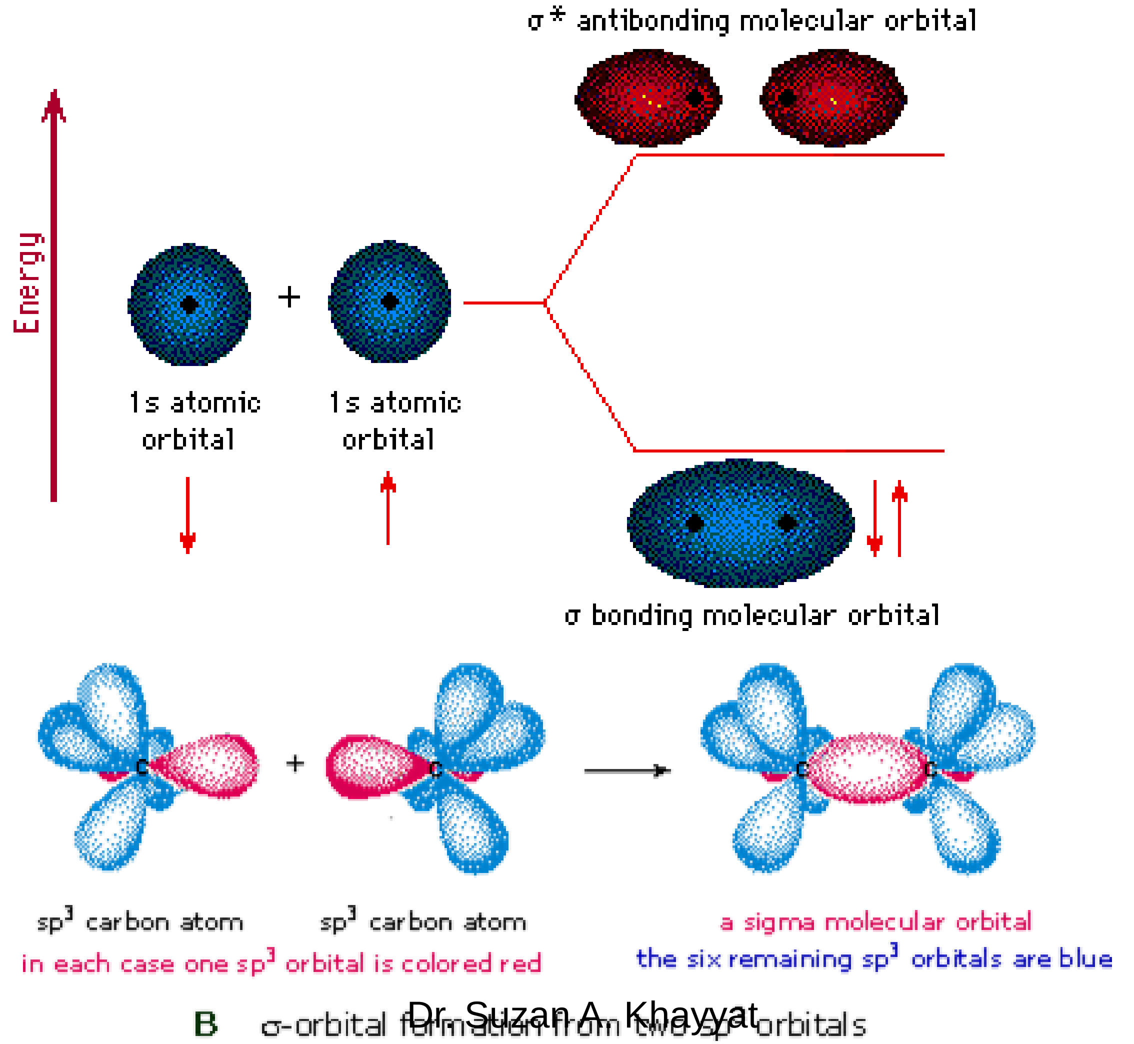
   allowed transitions: s $\rightarrow$ p, p $\rightarrow$ d, d $\rightarrow$ f, etc.

   forbidden transitions: s $\rightarrow$ s, d $\rightarrow$ d, p $\rightarrow$ f, etc.



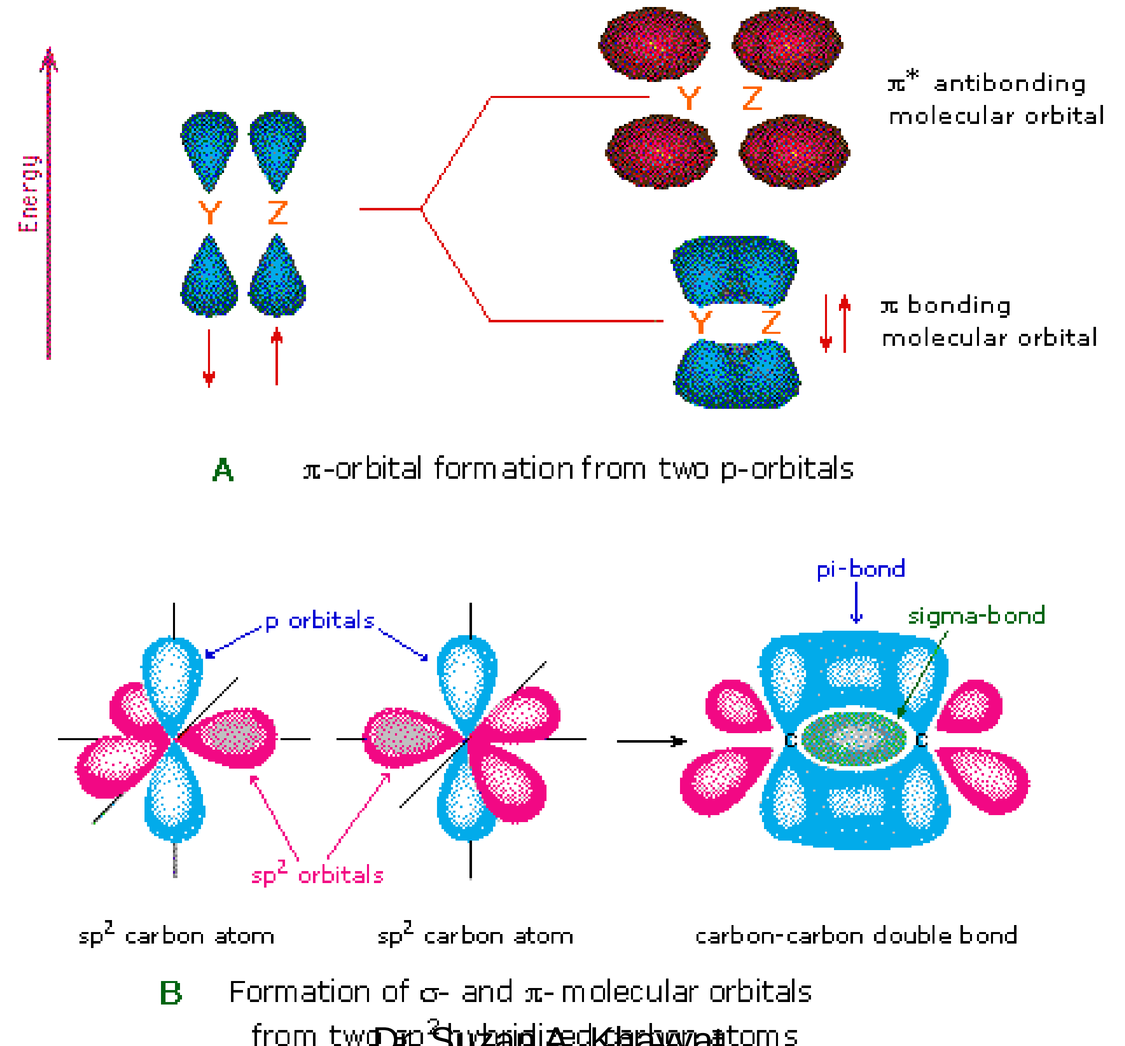
ENERGY
σ* (anti-bonding)
π* (anti-bonding)
n (non-bonding)
π (bonding)
σ (bonding)
n → π*
π → π*
n → σ*
π → σ*
σ → π*
σ → σ*

σ and σ* orbitals



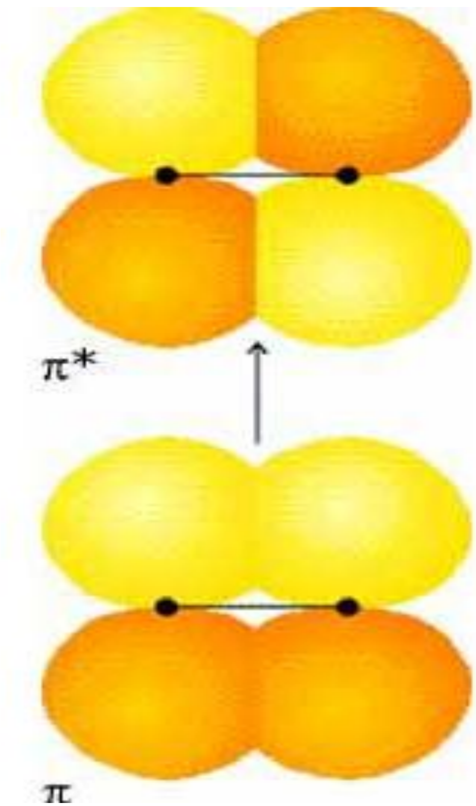
http://www.cem.msu.edu/~reusch/VirtualText/intro3.htm#strc8a

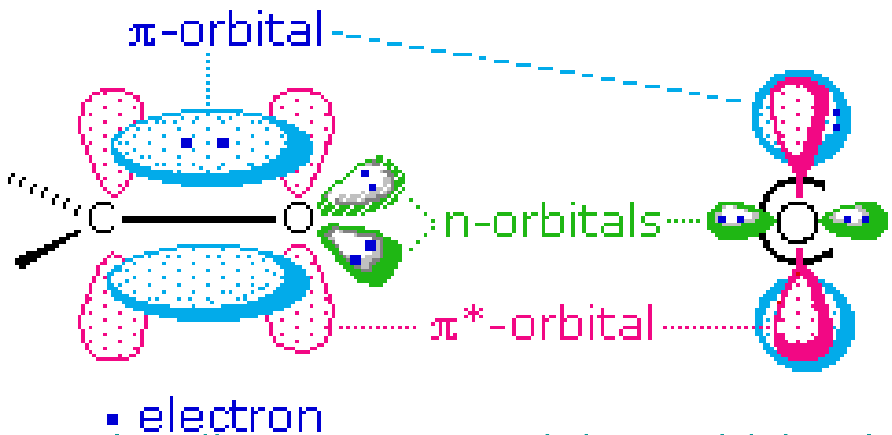
π and π* orbitals



http://www.cem.msu.edu/~reusch/VirtualText/intro3.htm#strc8a

Electronic Transitions: $\pi \rightarrow \pi^*$



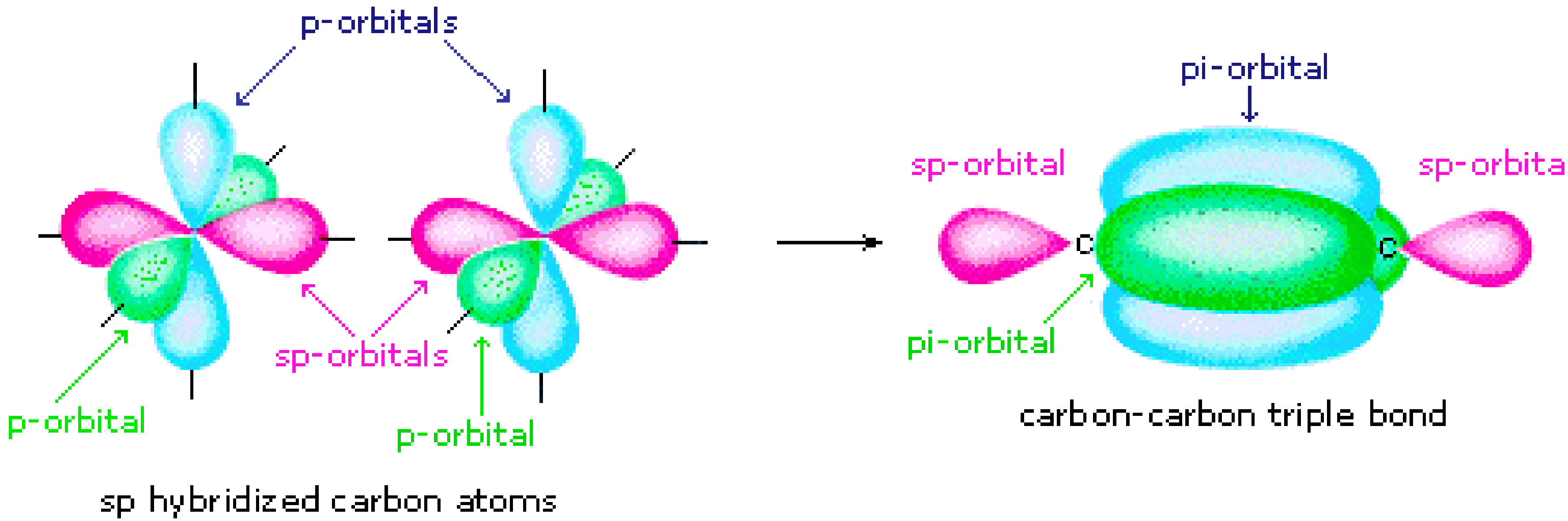


http://www.cem.msu.edu/~reusch/VirtualText/Spectrpy/UV-Vis/uvspec.htm#uv2

The $\pi \rightarrow \pi^*$ transition involves orbitals that have significant overlap, and the probability is near 1.0 as they are “symmetry allowed”.

McGarvey and Gaillard, Basic Photochemistry at http://classes.kumc.edu/grants/dpc/instruct/index2.htm

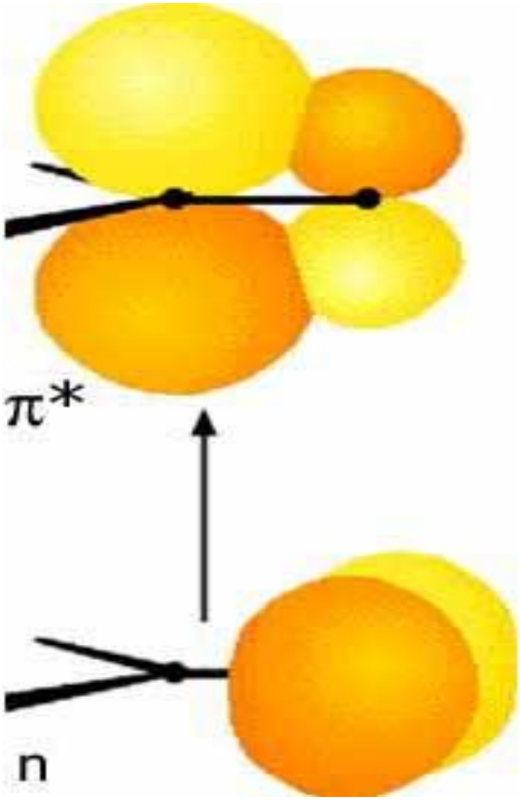
$\pi \rightarrow \pi^*$ transitions - Triple bonds



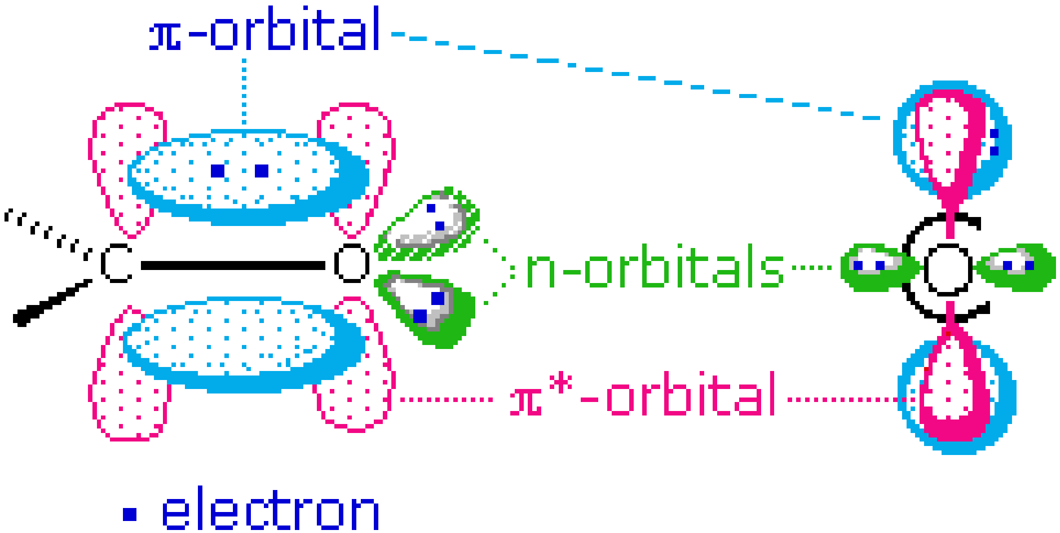
Organic compounds with -C≡C- or -C≡N groups, or transition metals complexed by $C≡N^-$ or C≡O ligands, usually have "low-lying" π^* orbitals

http://www.cem.msu.edu/~reusch/VirtualText/intro3.htm#strc8a

Electronic Transitions: n $\rightarrow$ π^*

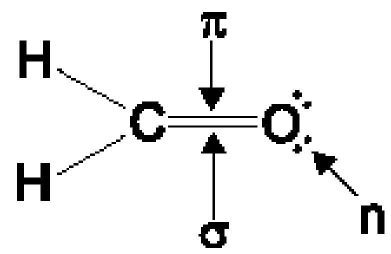


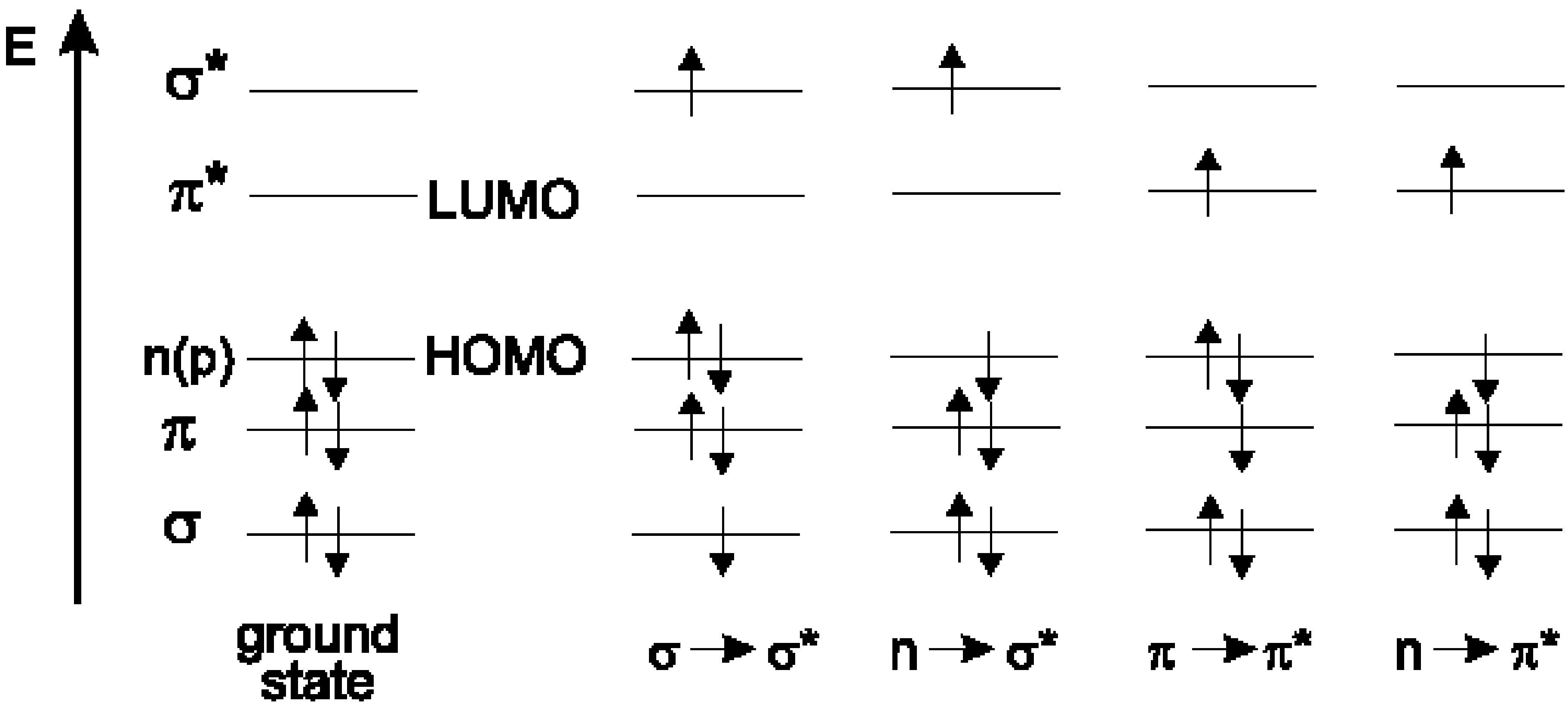
McGarvey and Gaillard, Basic Photochemistry at http://classes.kumc.edu/grants/dpc/instruct/index2.htm



http://www.cem.msu.edu/~reusch/VirtualText/Spectrpy/UV-Vis/uvspec.htm#uv2

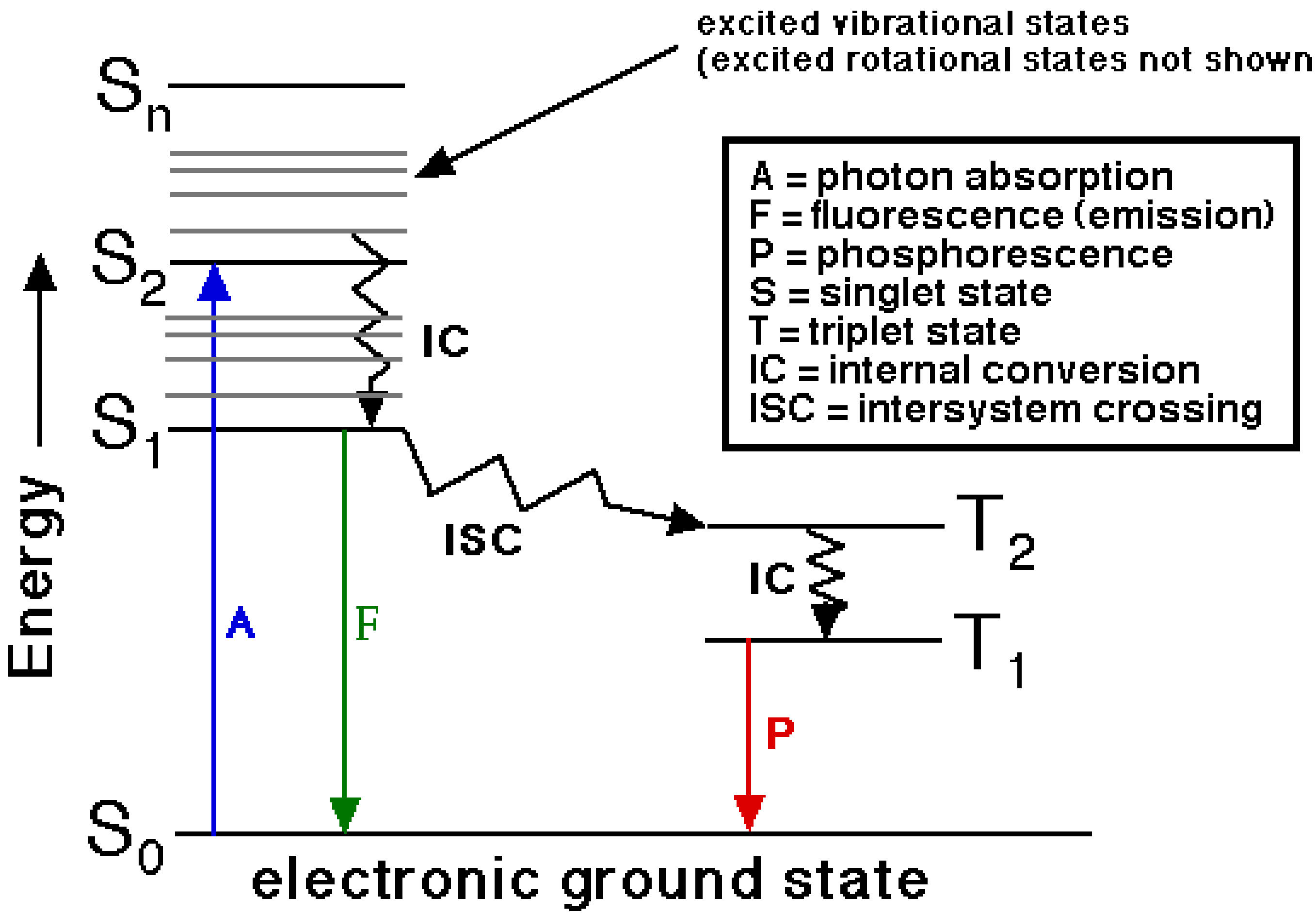
The n-orbitals do not overlap at all well with the π^* orbital, so the probability of this excitation is small. The ε of the n$\rightarrow\pi^*$ transition is about 10^3 times smaller than ε for the $\pi\rightarrow\pi^*$ transition as it is “symmetry forbidden”.


H
H
C
O
π
σ
n


E
σ*
π*
LUMO
n(p)
HOMO
π
σ
ground state
σ → σ*
n → σ*
π → π*
n → π*

Process	Transition	Timescale (sec)
Light Absorption (Excitation)	$S_0 \rightarrow S_n$	ca. 10^{-15} (instantaneous)
Internal Conversion	$S_n \rightarrow S_1$	10^{-14} to 10^{-11}
Vibrational Relaxation	$S_n^* \rightarrow S_n$	10^{-12} to 10^{-10}
Intersystem Crossing	$S_1 \rightarrow T_1$	10^{-11} to 10^{-6}
Fluorescence	$S_1 \rightarrow S_0$	10^{-9} to 10^{-6}
Phosphorescence	$T_1 \rightarrow S_0$	10^{-3} to 100
Non-Radiative Decay	$S_1 \rightarrow S_0$ $T_1 \rightarrow S_0$	10^{-7} to 10^{-5} 10^{-3} to 100

Absorption and emission pathways



McGarvey and Gaillard, Basic Photochemistry at http://classes.kumc.edu/grants/dpc/instruct/index2.htm

Fates of excited state

Photophysical processes Lead to emission of radiation Energy converted to heat

- Photochemical processes Dissociation, ionization, reaction, isomerization

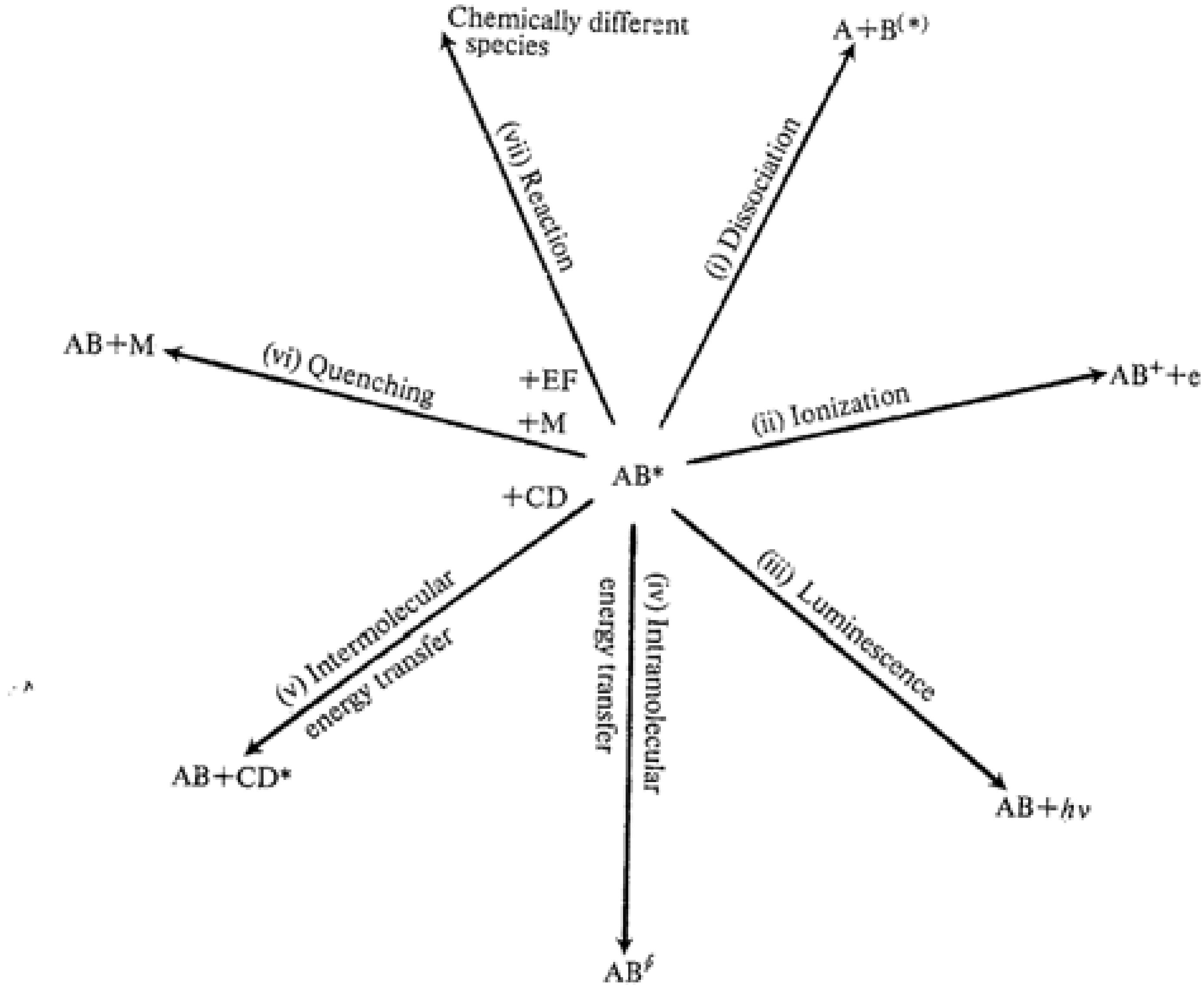


Fig. 3.1. Pathways for loss of electronic excitation that are of importance in atmospheric chemistry. The use of the symbols * and § illustrates the presence of electronic excitation: the products of any of the processes may be excited. With the exception of pathways (i) and (iv), excited atoms can participate as well as excited molecules.

Laws of photochemistry

- **The first law of photochemistry:**

Theodor Grotthuss and John W. Draper), states that light must be absorbed by a chemical substance in order for a photochemical reaction to take place.

- **The second law of photochemistry**:

the Stark-Einstein law, states that for each photon of light absorbed by a chemical system, only one molecule is activated for a photochemical reaction