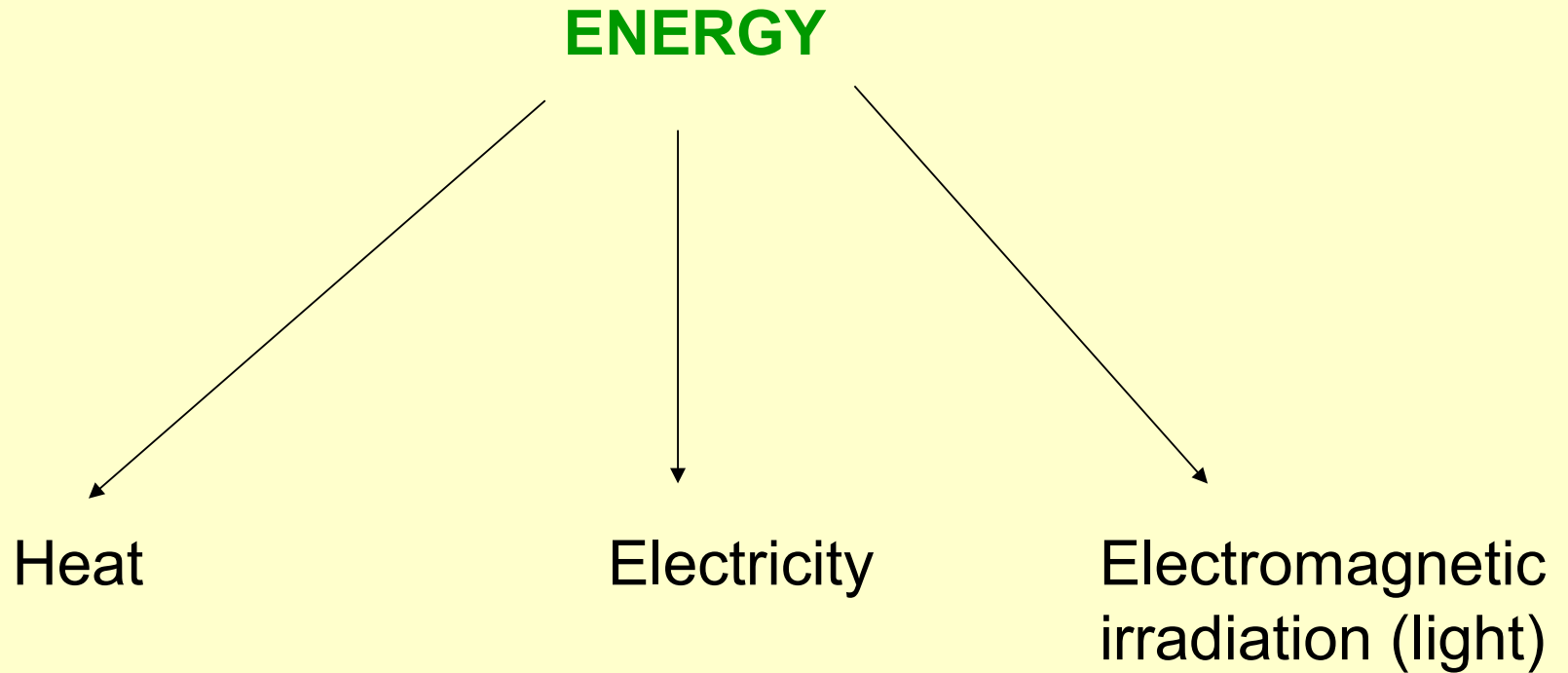


# Photochemistry

# Introduction



# Photochemistry

**Chemical reactions accompanied with light.**

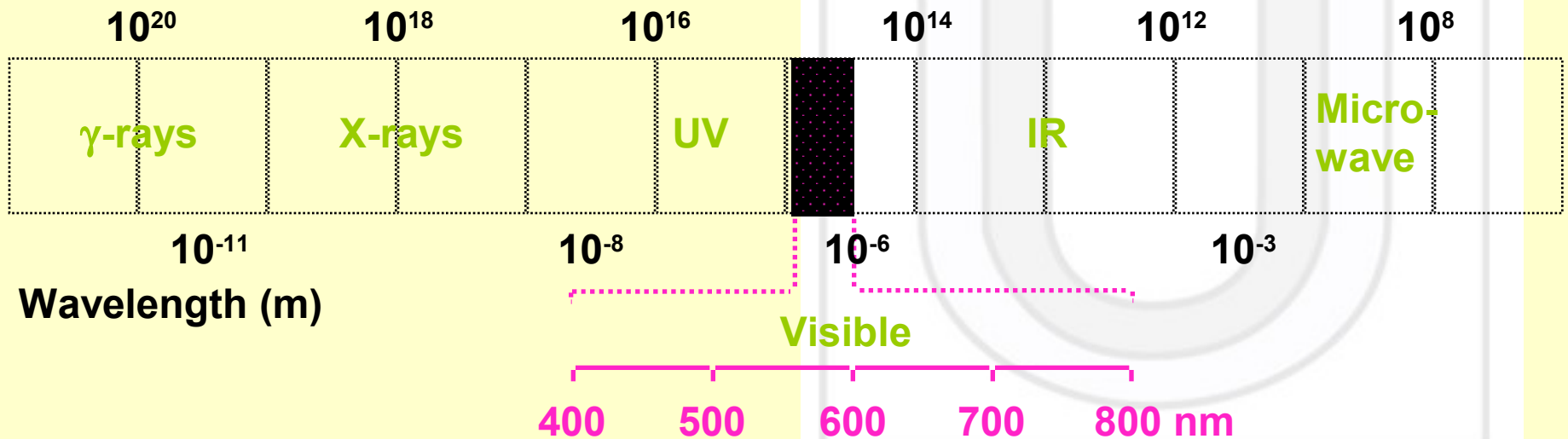
1. Action of light → chemical change  
(light induced reactions)

2. Chemical reaction → light emission  
(chemiluminescence)

# The Electromagnetic Spectrum

- Names of the regions are historical.
- There is no abrupt or fundamental change in going from one region to the next.
- Visible light represents only a very small fraction of the electromagnetic spectrum.

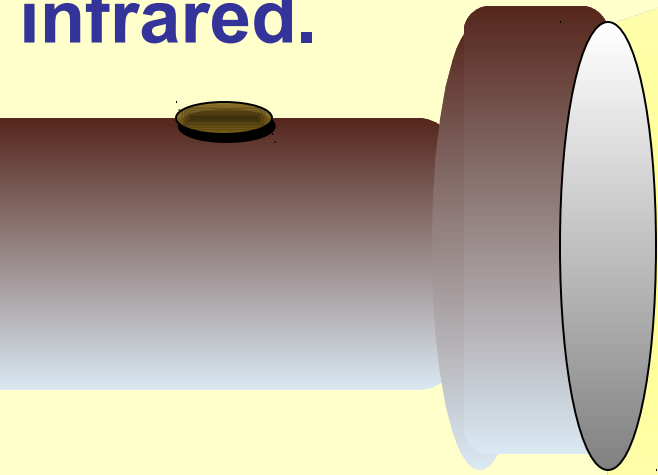
Frequency (Hz)



**Photon a particle of light.**

**Electromagnetic radiation**

**ALL light. Visible AND invisible  
visible light , x-rays, gamma rays, radio  
waves, microwaves, ultraviolet rays,  
infrared.**



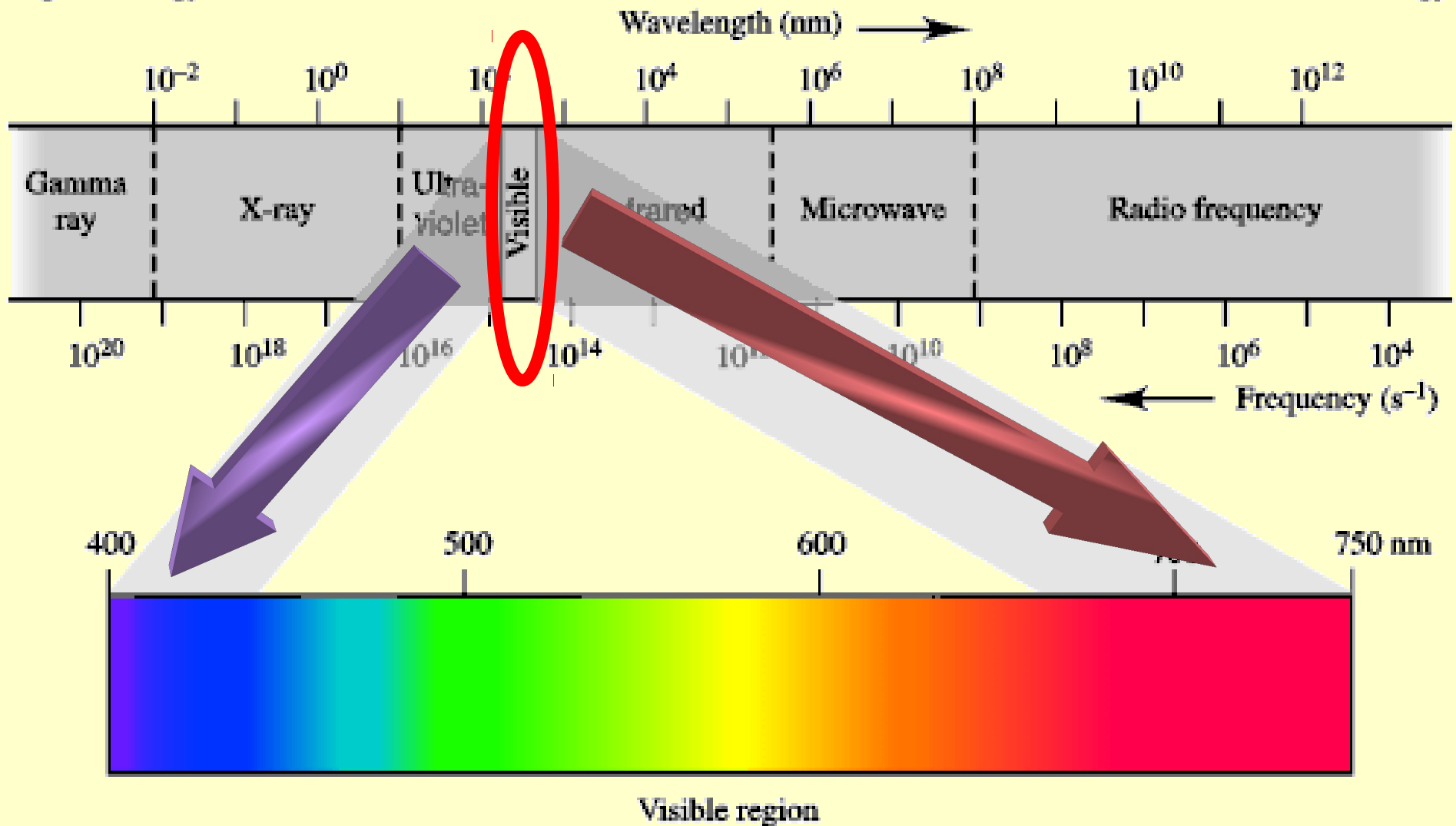
# Photon a particle of light



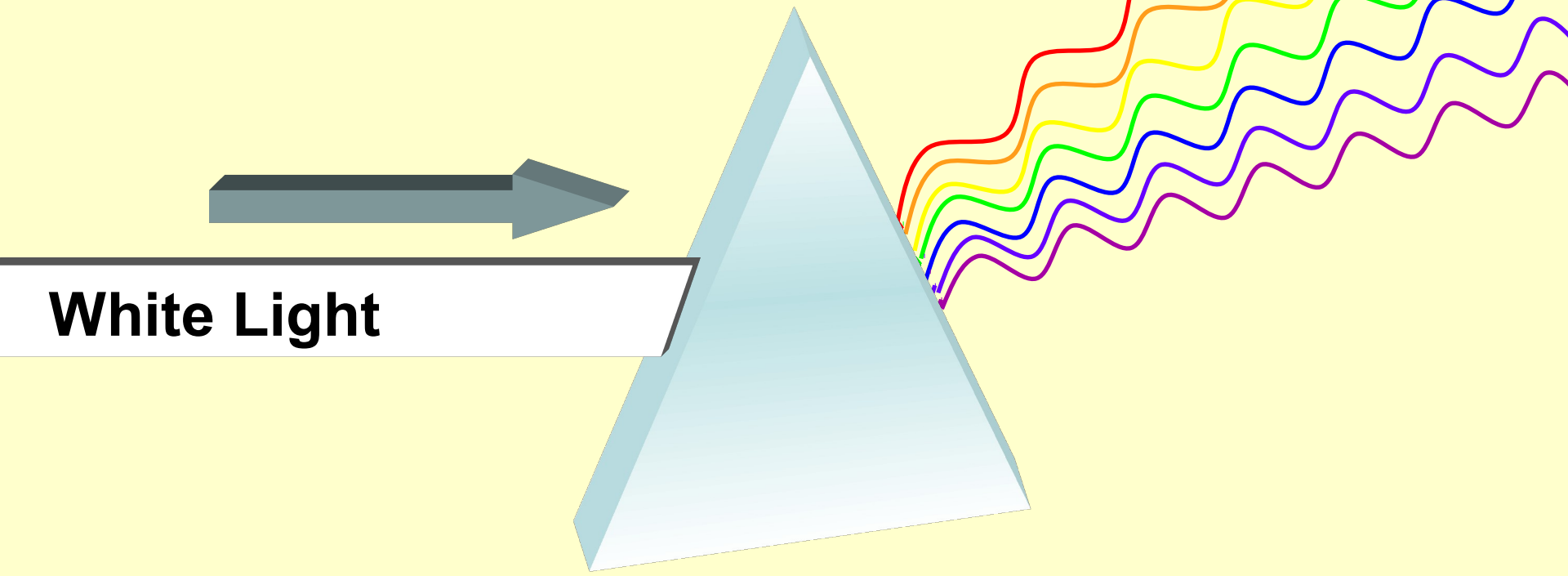
# Electromagnetic radiation

Highest energy

Lowest energy



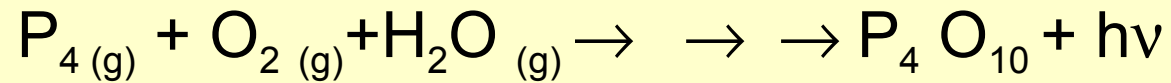
**A prism bends light.  
Different Colors are bent  
by different amounts.**





# Luminescence:

## - Chemiluminescence:

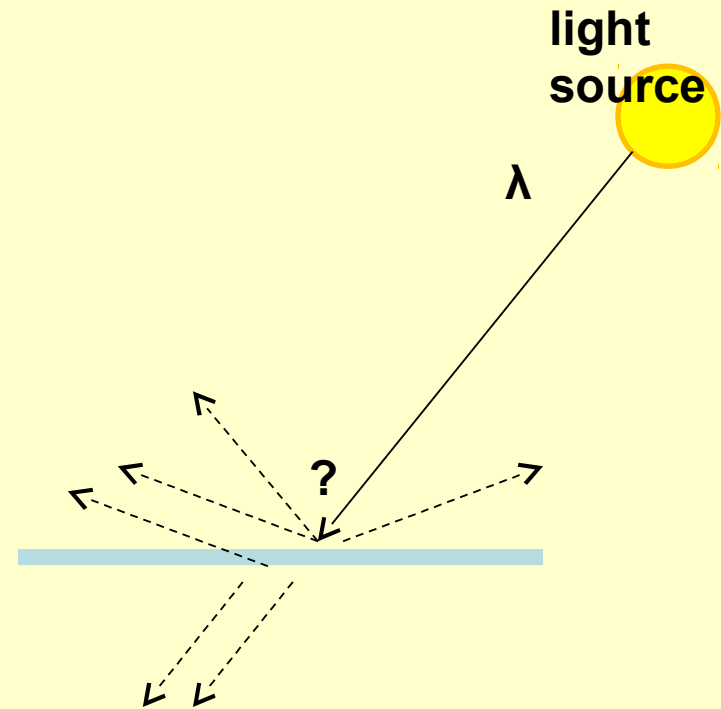


green

- Bioluminescence:
  - mushrooms
  - insects
  - fishes

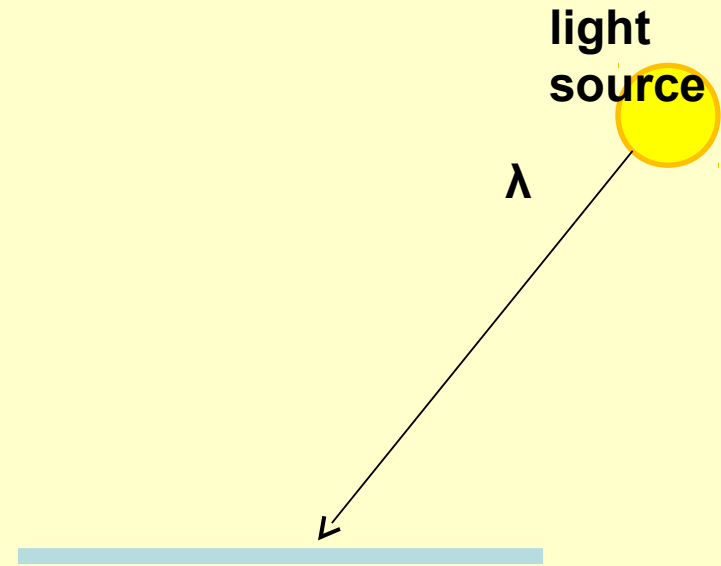
# A photon's life choices

- Absorption
- Diffusion
- Reflection
- Transparency
- Refraction
- Fluorescence
- Subsurface scattering
- Phosphorescence
- Interreflection



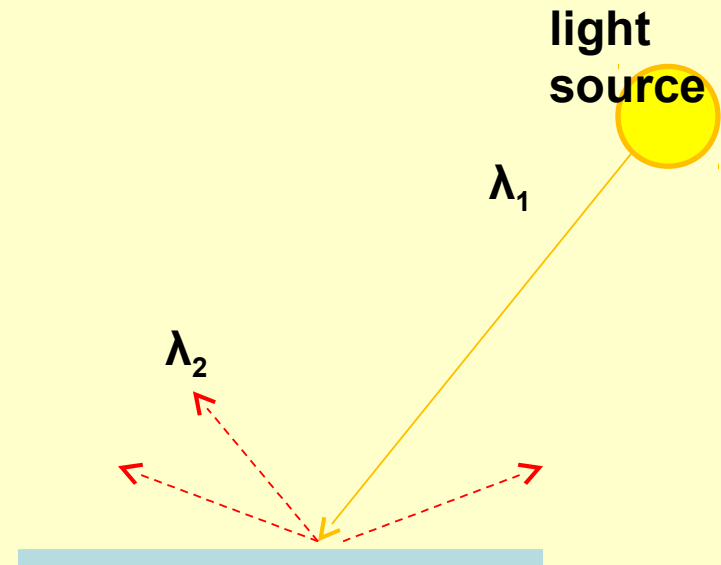
# A photon's life choices

- **Absorption**
- Diffusion
- Reflection
- Transparency
- Refraction
- Fluorescence
- Subsurface scattering
- Phosphorescence
- Interreflection



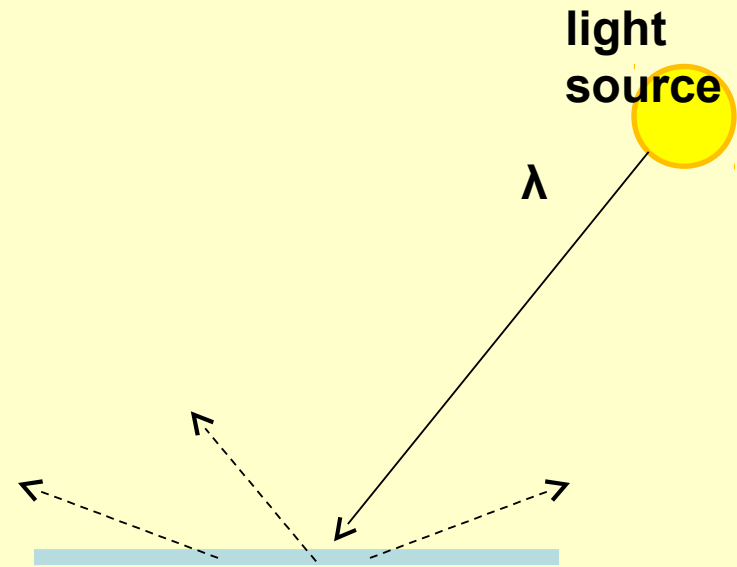
# A photon's life choices

- Absorption
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- Transparency
- Refraction
- **Fluorescence**
- Subsurface scattering
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- Interreflection



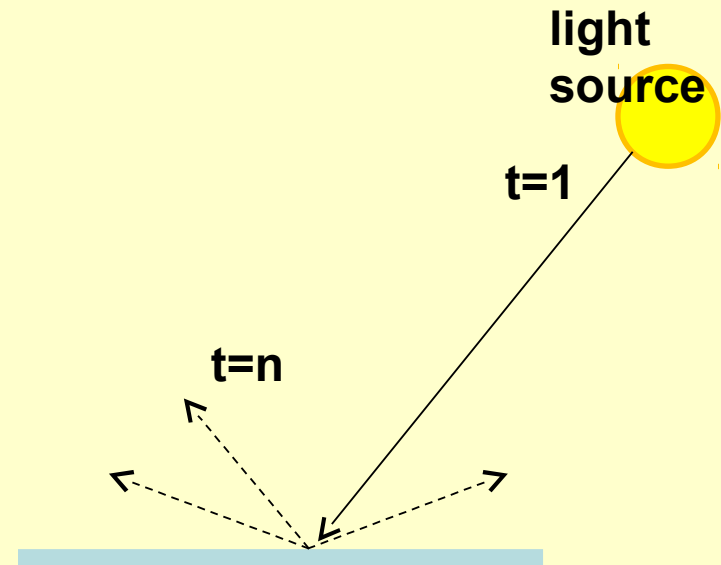
# A photon's life choices

- Absorption
- Diffusion
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- Fluorescence
- **Subsurface scattering**
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- Interreflection



# A photon's life choices

- Absorption
- Diffusion
- Reflection
- Transparency
- Refraction
- Fluorescence
- Subsurface scattering
- **Phosphorescence**
- Interreflection



# Definitions and terms

**Light:** electromagnetic field vibration  
spreading in quanta  
(photons)

**Photon:** the smallest amount of light  
carrying energy

# Energy of photons (A. Einstein)

$$E = h\nu = h \frac{c}{\lambda}$$

$h$  = Planck's constant ( $6.6 \cdot 10^{-34}$  Js)

$c$  = speed of light ( $3 \cdot 10^8$  ms<sup>-1</sup>)

$\lambda$  = wavelength

$\nu$  = frequency



# Einstein's Equivalency Principle

*One particle* of a chemical substance can absorb only *one photon* from a light beam:  $\Delta E = h\nu$

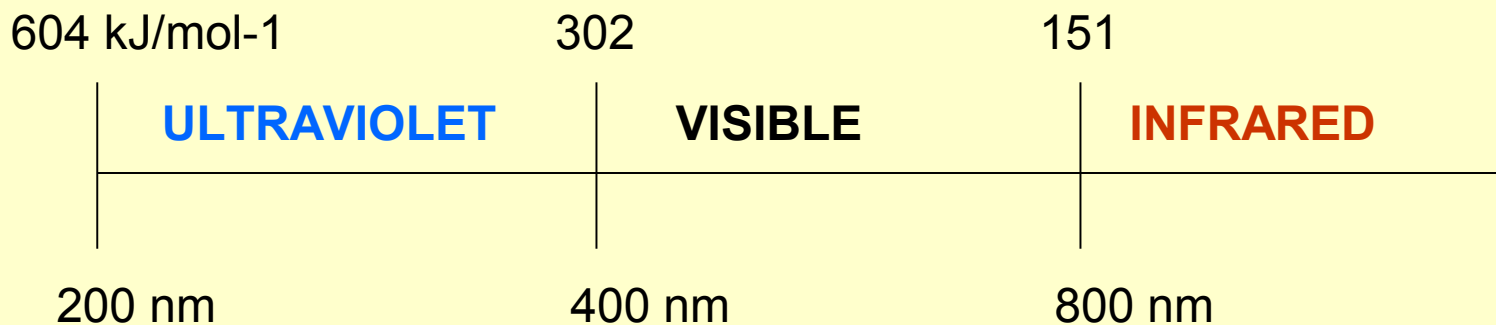
For one mole:  $\Delta E = N h \nu$

$N = \text{Avogadro's number } (6.02 \cdot 10^{23})$

## Chemical bond energies:

from 100 – 1000 kJ/mol

## Light energies:



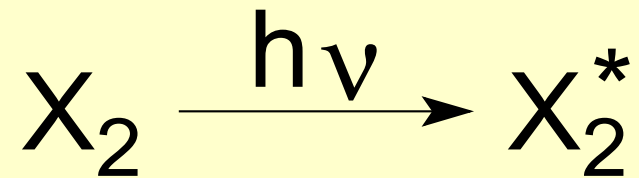
So UV – and VIS region is expected to induce chemical reactions.

# Laws of Photochemistry

1. Only light that is absorbed can produce photochemical change (**Grotthus, Draper**)
2. A molecule absorbs a single quantum of light is becoming **excited** (**Stark, Einstein**)

# Mechanisms of Light Absorption

Excitation:



A bonding electron is lifted to a higher energy level  
(higher orbital)

## INTERACTION OF LIGHT AND MATERIALS:

a)  $X_2^* \rightarrow X_2 + M^*$  (excess energy transferred to the surrounding)

b)  $X_2^* \rightarrow X_2 + h\nu$  (fluorescence or phosphorescence)

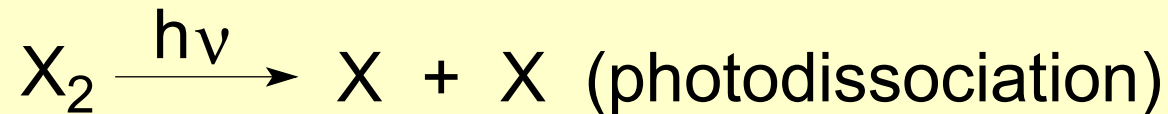
c)  $X_2^* + Y \rightarrow$  **chemical reaction** (excess energy supplies the activation energy of the reaction)

## Types of photochemical reactions:

a) **Photodissociation**

b) **Photosynthesis**: when a larger molecule is formed from simple ones

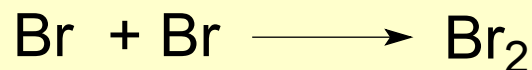
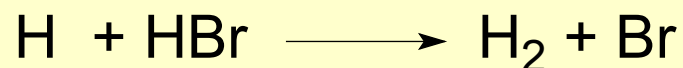
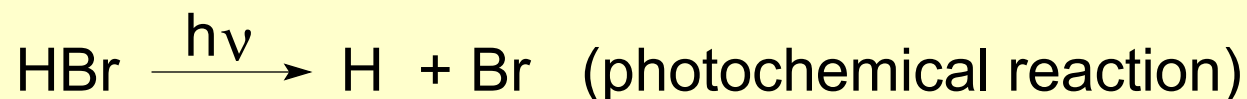
2. c) **Photosensitized reactions**: when an excited molecule supplies activation energy for the reactants



(energy of the photon supplies the „dissociation heat”)

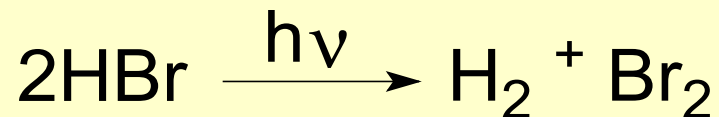
## Photodissociation

### Photolysis of hydrogen bromide



(dark reactions)

Overall:



Note:

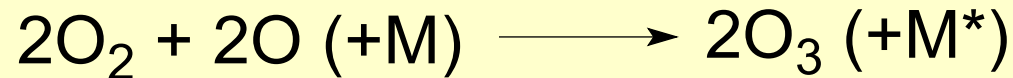
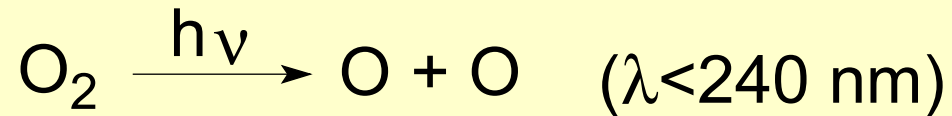
1 photon absorbed, 2 molecules of HBr dissociated:

$$\text{QUANTUM YIELD} = \frac{2}{1} = 2$$

$$\Phi = \frac{\text{number of molecules undergoing the process}}{\text{number of quanta absorbed}}$$



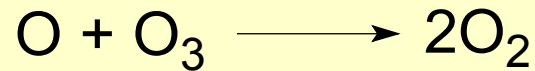
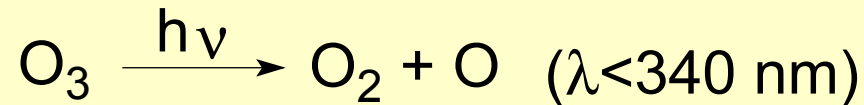
Ozone formation in the atmosphere  
(at about 25 km altitude)



**Notes:** M absorbs energy released in the reaction

$$\text{QUANTUM YIELD} = \frac{2}{1} = 2$$

Ozone formed in the reaction above absorbs UV light as well:



### Notes:

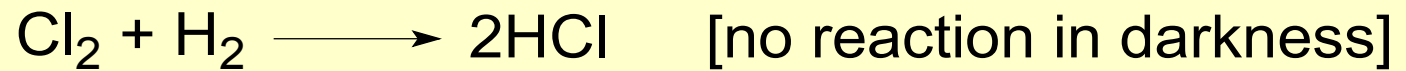
**1. Ozone shield** protects the Earth surface from high energy UV radiation (of the Sun)

**2. Air pollution** (freons: fully halogenated hydrocarbons; nitrogen oxides emitted by aeroplanes etc.) may accelerate the decomposition of ozone  $\Rightarrow$  ozone hole

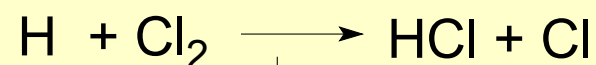
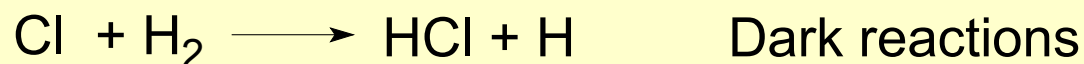
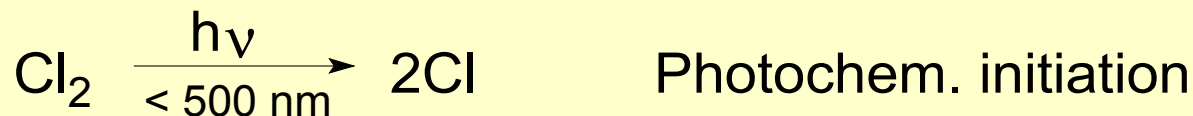
# Photosynthesis

The photosynthesis of hydrogen chloride

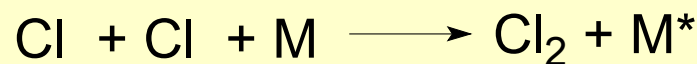
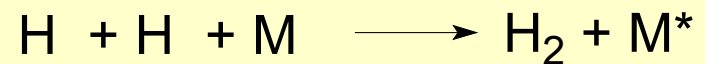
Overall reaction:



## Mechanism:



↓  
Chain reaction



} Recombination  
reactions (chain  
is terminated)

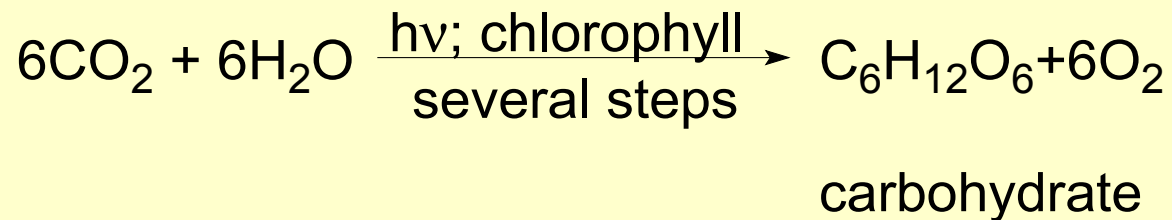
## Note: \_

Quantum yield is about  $10^6$  (explosion)

# Photosensitized reactions

## Photosynthesis in plants

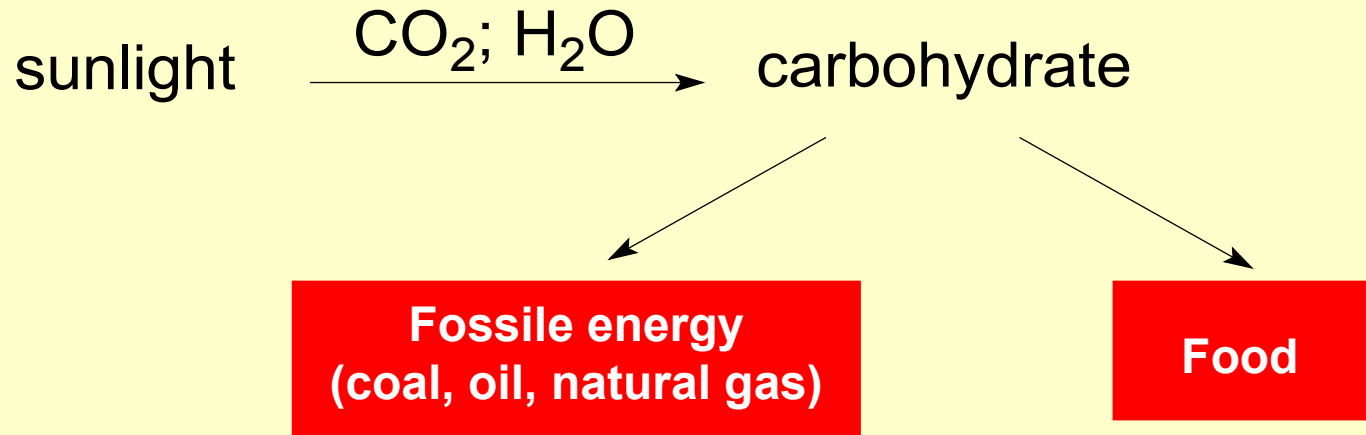
Overall reaction:



## Notes:

1. Chlorophyll acts as a catalyst absorbing and transferring the photon energy for reduction of carbon dioxide to carbohydrate

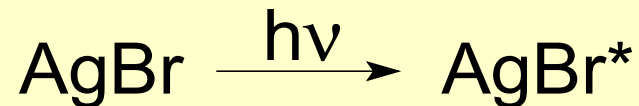
2. This reaction maintains the life on the Earth:



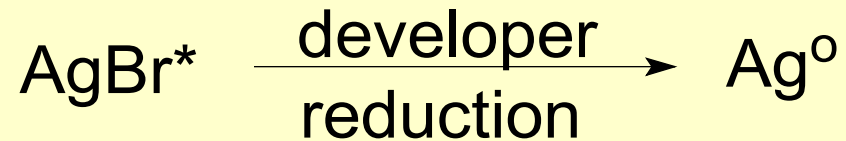
# Photography

a) **Photographic film:** colloidal suspension of finely powdered silver halogenide in gelatine

b) When exposed to light AgBr granuli become activated according to the intensity of light:

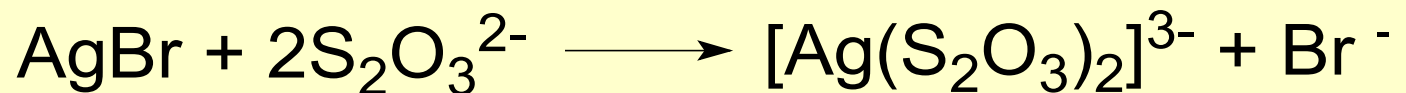


c) **Development:** Treating the exposed film with a mild reducing agent the activated granuli will accelerate the reduction to metallic silver (black)



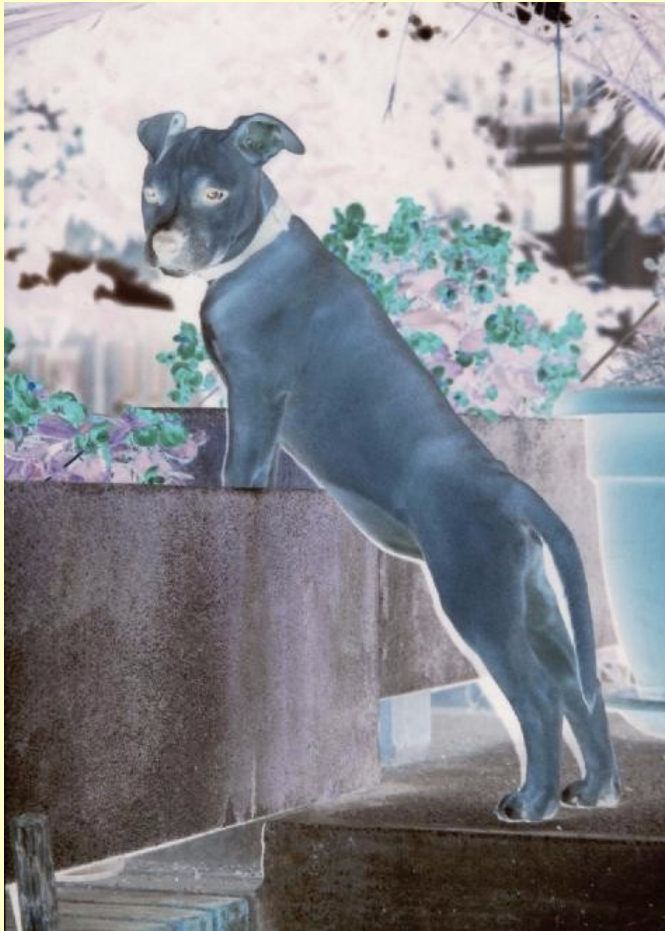
Unactivated granuli will be unaffected (but photosensitive!)

d) **Fixation:** Unaffected (photosensitive) AgBr should be removed:

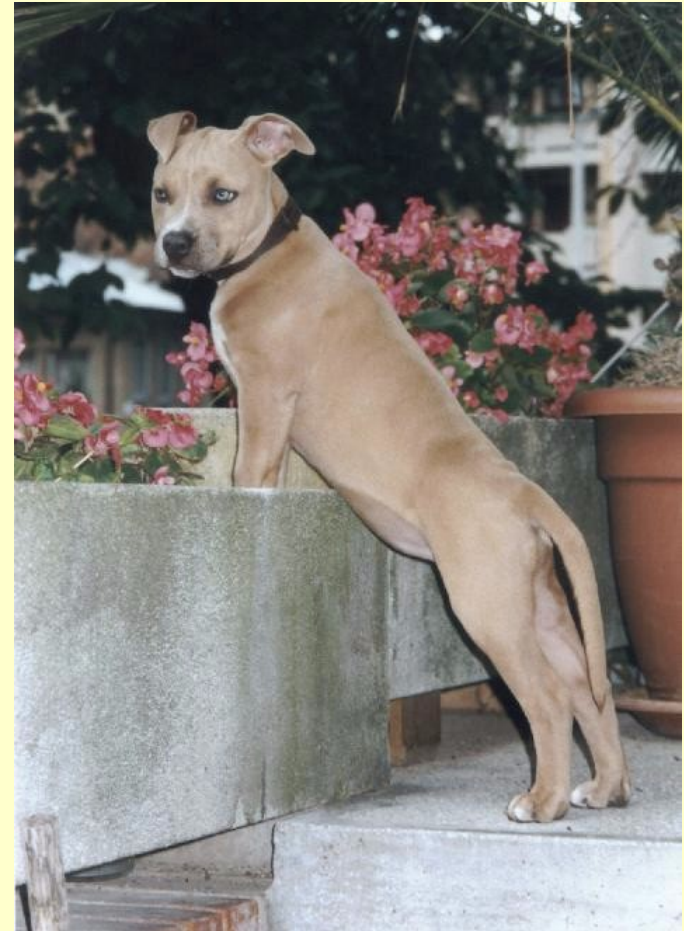




e) The resulted photograph is **negative** (light spots of the object are black and vice versa):



**Negative film**



**Object**





f) The negative film should be inverted placing it onto a new non-exposed sheet, illuminating, and repeating the development + fixation procedure



Misike

**THANKS**