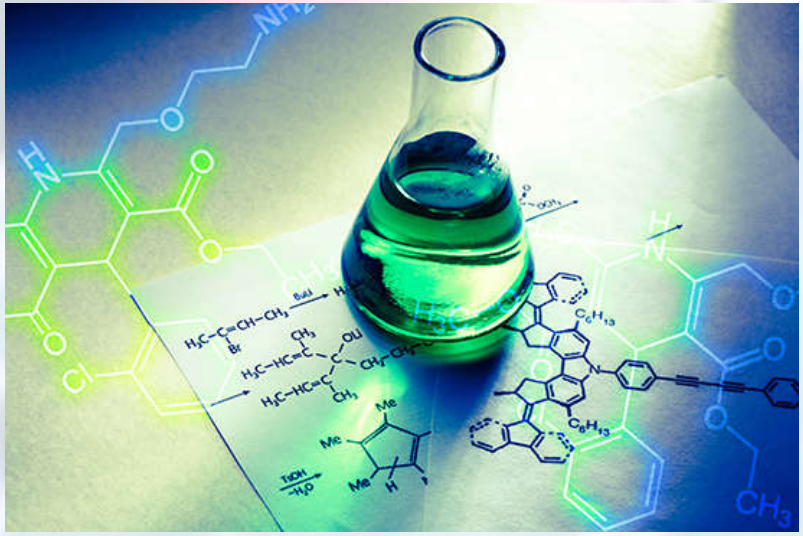
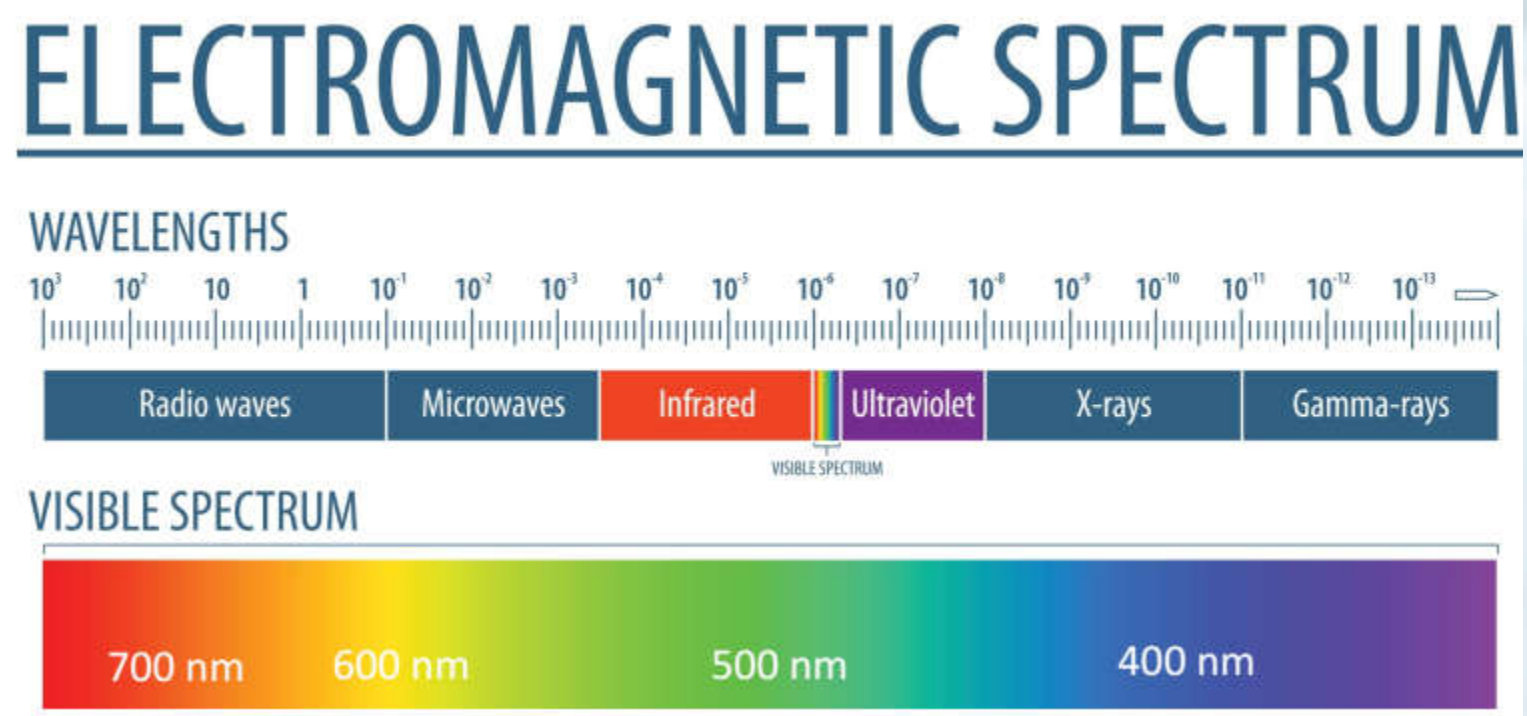
Photochemistry

Photochemistry is the branch of chemistry which deals with the rate and mechanism of reaction taking place due to exposure of light. The reactions which can be brought about by light radiations are called photochemical reactions.

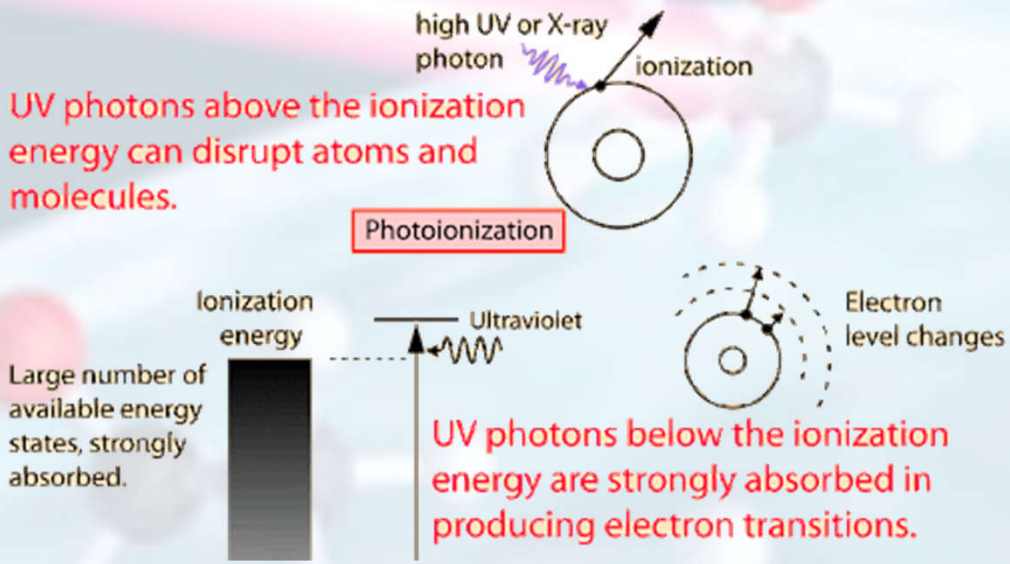


The chemistry concerned with the chemical effects of light.

Generally, a chemical reaction is caused by using UV, visible, infrared light.

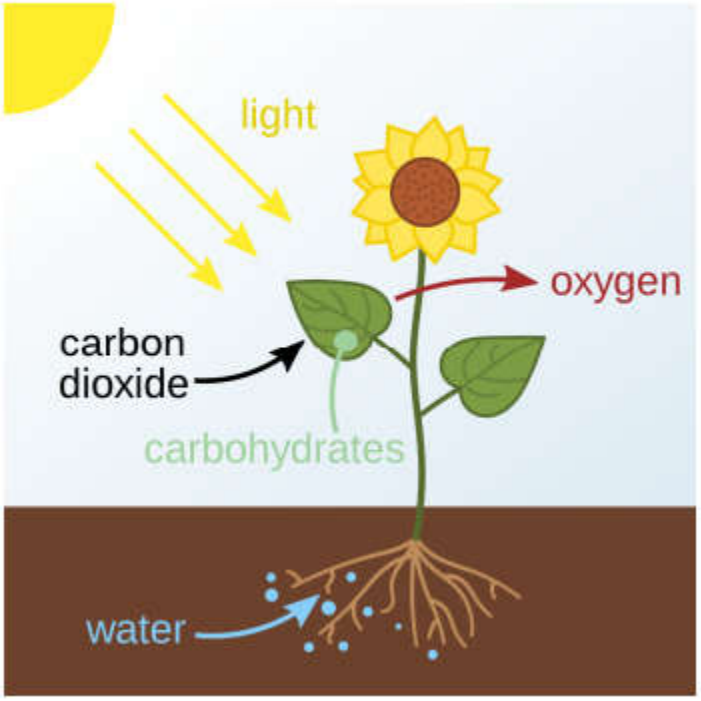


The term radiation includes radio-waves, x-rays, gamma rays and also beams of particles like α-particle, neutrons, electrons and protons. The study of photochemistry helps us to know the changes when a molecule absorbs radiations.

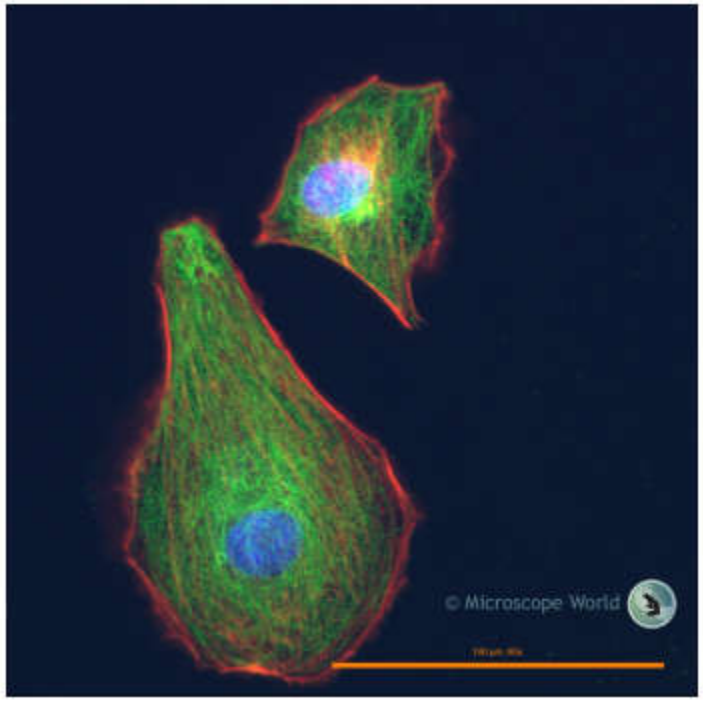


Why Important?

Photosynthesis is Driven by Light!

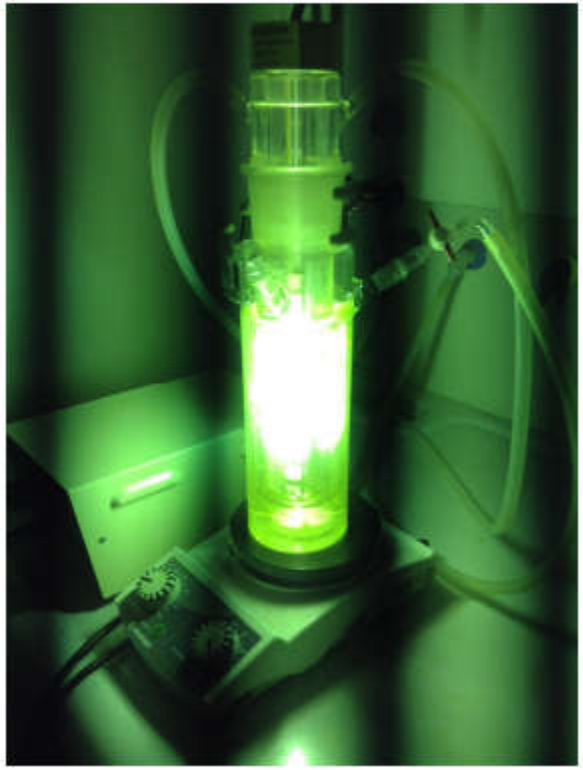


We can see "inside" by Light!

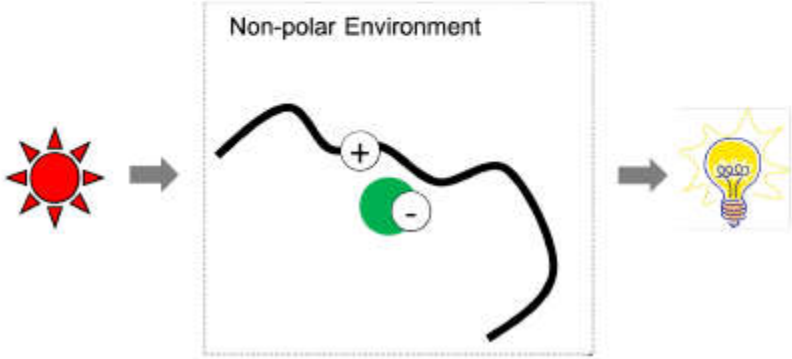


Converting Light to Something Else.

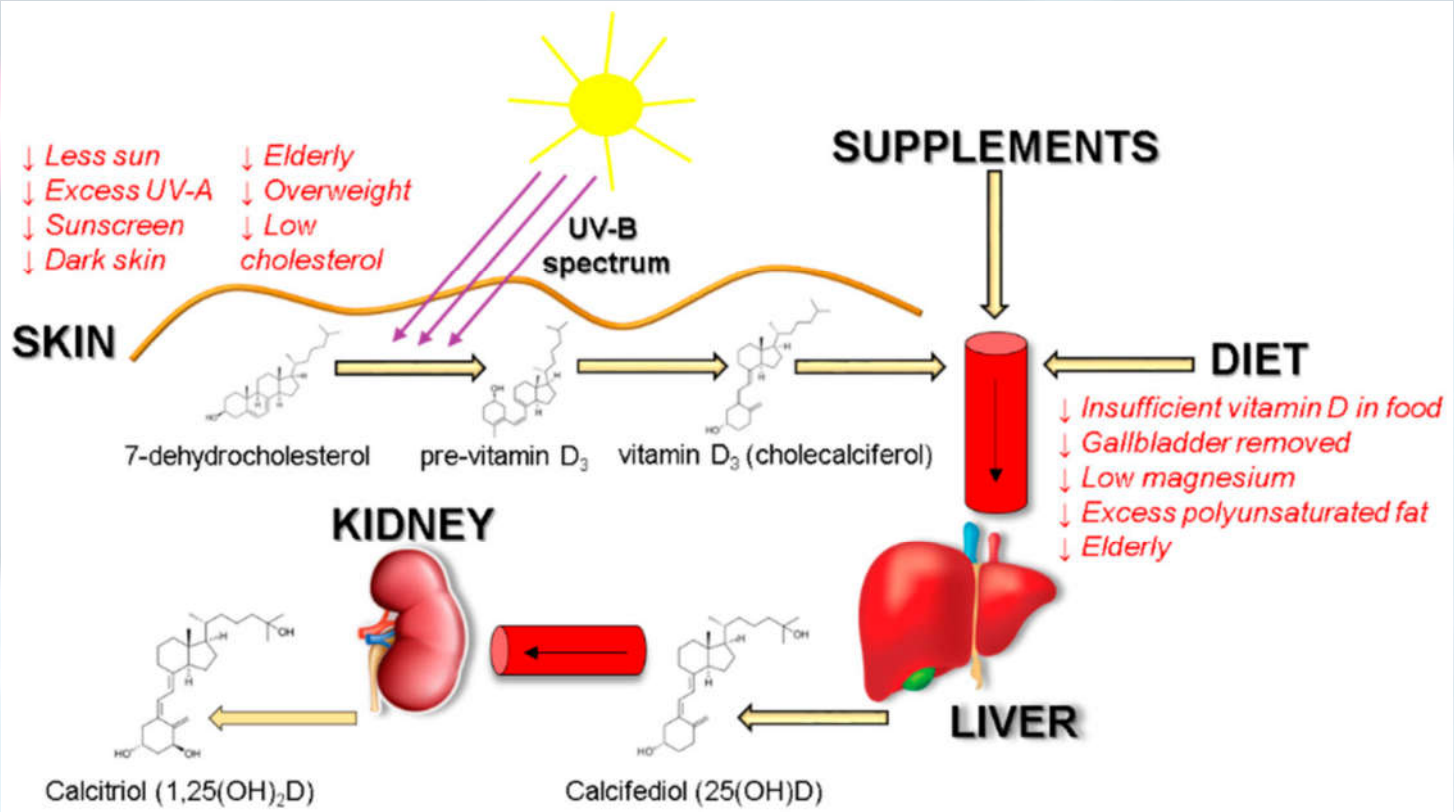
Making Molecules with Light.



Making Electricity from Light.

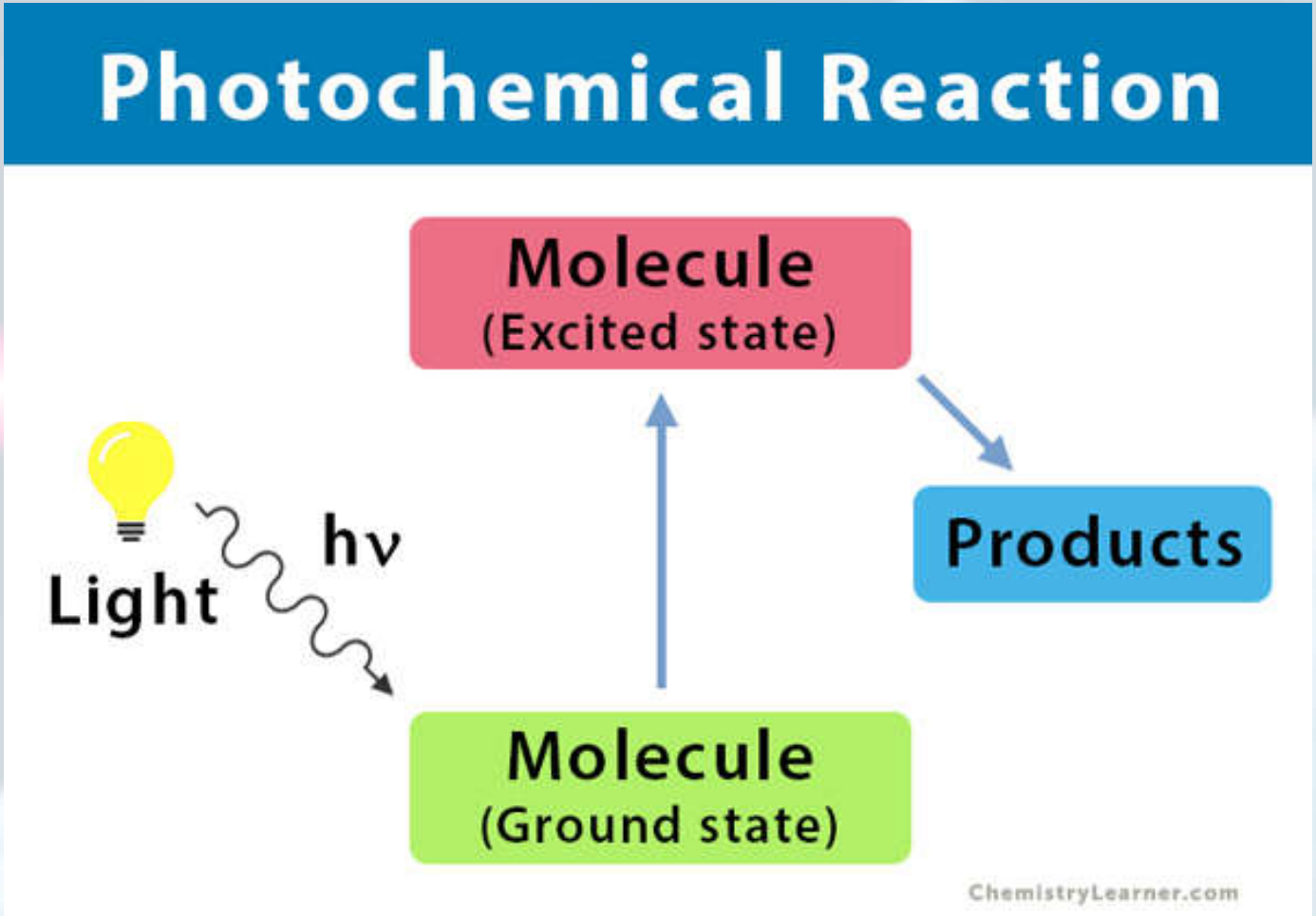


Photochemistry is crucial in nature since it is the core of photosynthesis, vision, and the creation of vitamin D from sunshine.

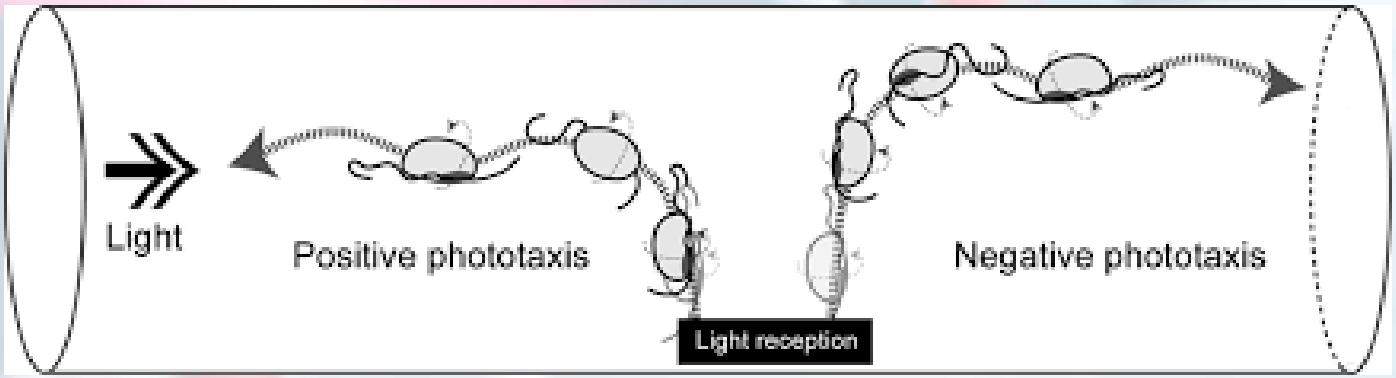


Difference between Photochemical and thermal Reaction:-

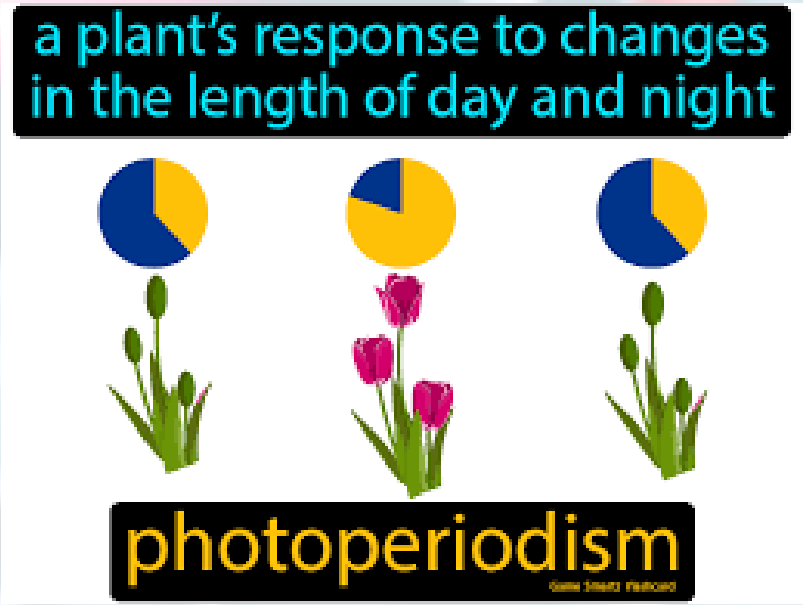
Photochemical Reaction	Thermal Reaction
These reactions involve absorption of light radiations.	These reactions involve absorption or evolution of heat energy.
Presence of light is the primary requirement.	These reactions can take place in light as well as in dark.
Temperature has very small effect.	Temperature has significant effect.
ΔG may be +ve or –ve.	ΔG is always –ve.
Photochemical activation is highly selective process.	Thermal activation is not selective in nature.


Photochemical Reaction
Molecule
(Excited state)
Light
hν
Products
Molecule
(Ground state)
ChemistryLearner.com

Phototaxis is a kind of taxis, or locomotory movement, that occurs when a whole organism moves towards or away from a stimulus of light. This is advantageous for phototrophic organisms as they can orient themselves most efficiently to receive light for photosynthesis.



Photoperiodism is the response to changes in daylength that enables plants to adapt to seasonal changes in their environment. The best studied example of photoperiodism in plants is flowering, but other responses to daylength include bud dormancy and bulb or tuber initiation.

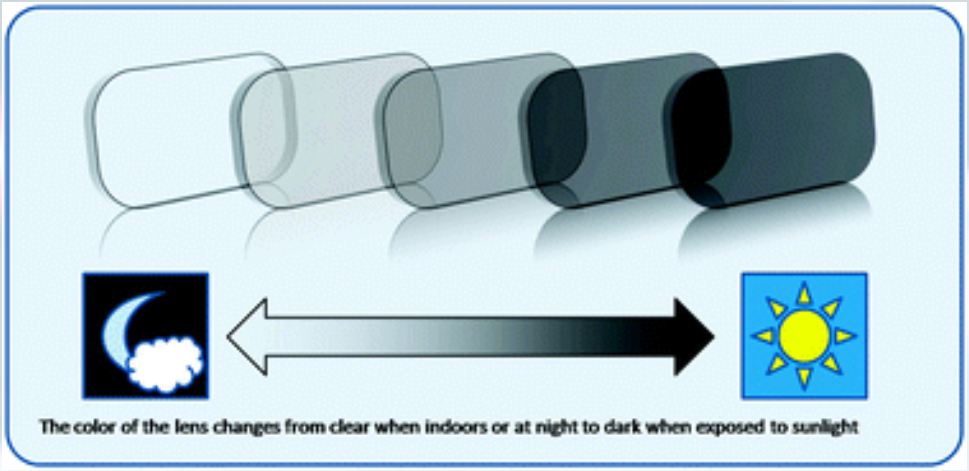


Importance of photochemistry:

- ✓Prebiotic formation of organic compounds such as proteins and nucleic acid by radiation with methane, ammonia, water and carbon dioxide as raw materials
- ✓Photochromic materials
- ✓Optical whiteners
- ✓Synthesis of antioxidants by photosulphonation, vitamin D_2, antiviral agents such as cubanes, caprolactam, cleaning agents, insecticides and halogenated aromatics
- ✓Flourescence and phosphorescence

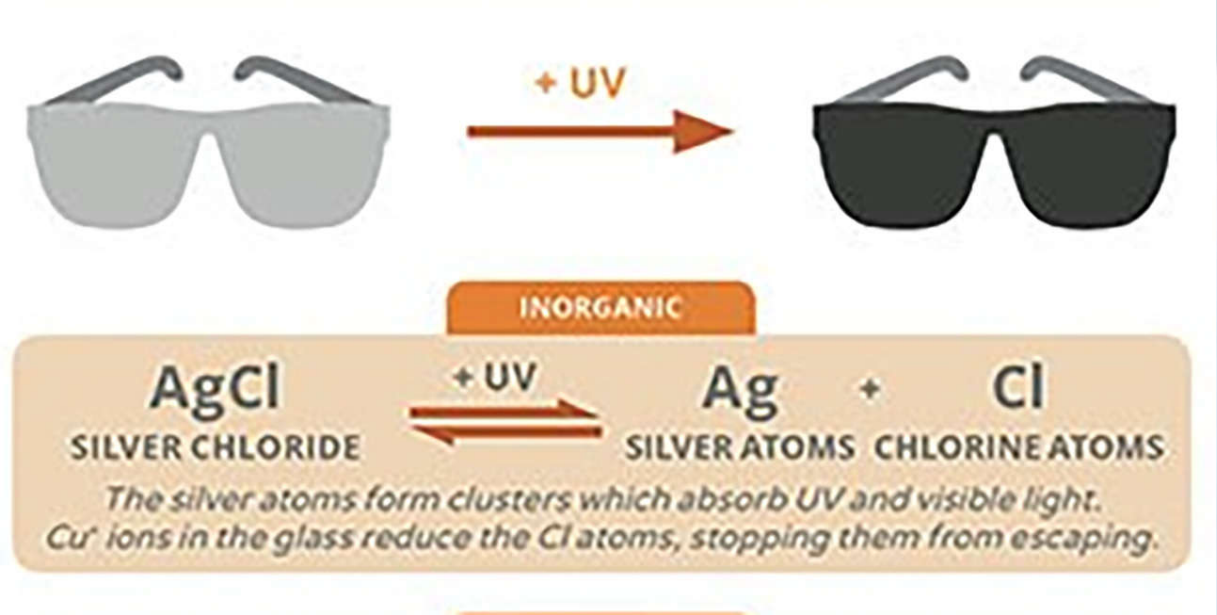
Photochromic materials:

Photochromic materials are those that show a reversible change in optical properties (color) through the action of light, i.e., electromagnetic radiation. They belong, therefore, to the chromogenic class of materials.



In particular, silver chloride is extensively used in the manufacture of photochromic lenses. Other silver and zinc halides are also photochromic. Yttrium oxyhydride is another inorganic material with photochromic properties.

Traditional photochromic eyeglasses are generally alkali boroaluminosilicates with 0.01 to 0.1 percent silver halide and a small amount of copper. Upon absorption of light, the silver ion reduces to metallic silver, which nucleates to form colloids about 120 angstroms in size.

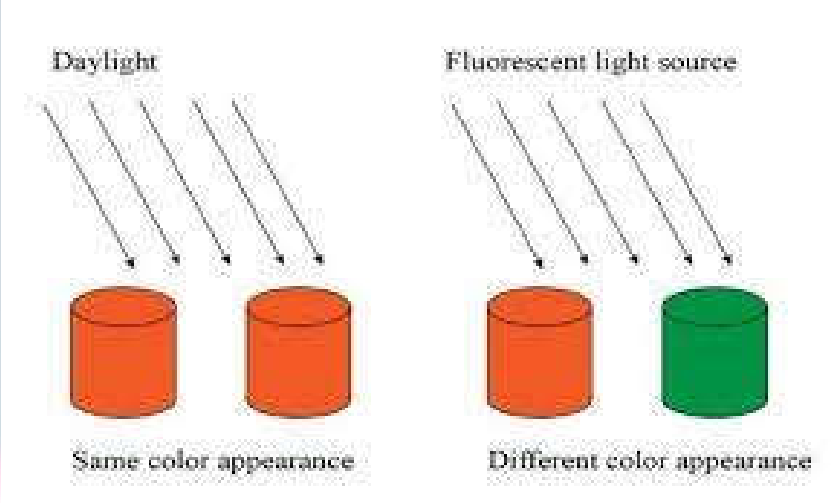


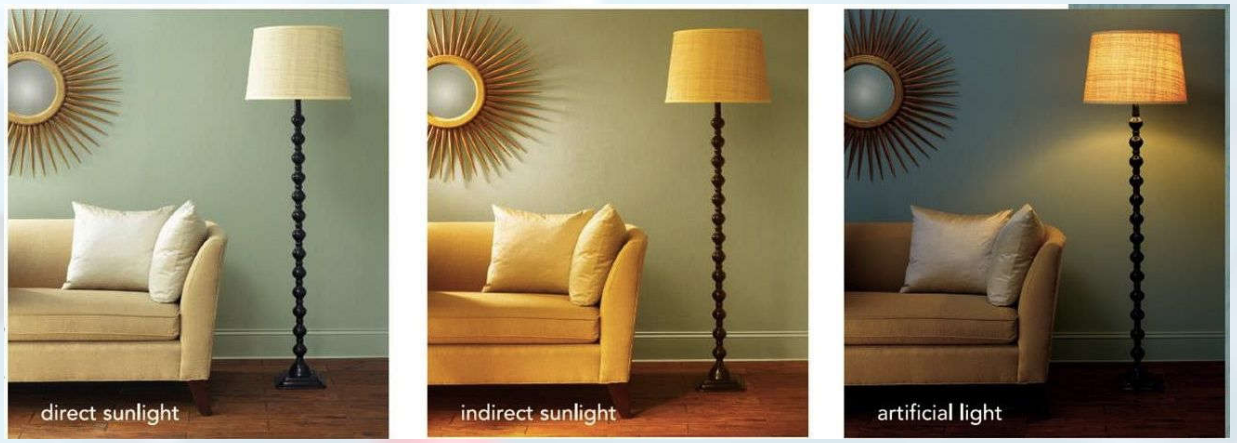
Optical whiteners:

Or optical brighteners are a type of chemical used to enhance the white or bright appearance of fabrics. They're often used during the manufacturing process of new white or lightly colored fabrics, and are commonly added to laundry detergents to maintain the appearance of brightness after successive washes.

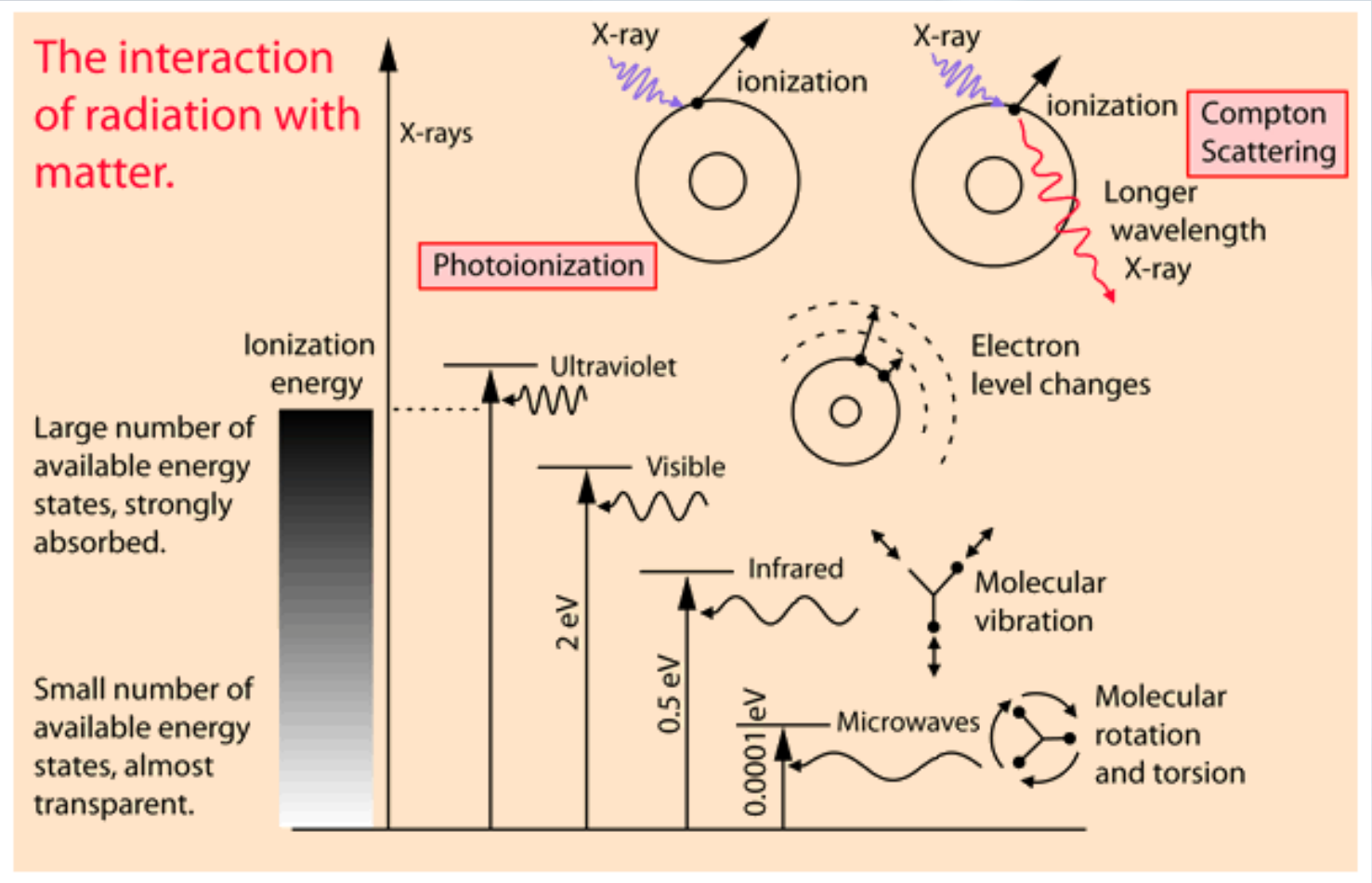
'Optical brighteners' is a general term for a group of chemicals, also known by other names such as 'Fluorescent Whitening Agents (FWAs)'. They're used in several industries, including fabrics, laundry detergents, paper, plastics and some cosmetics, and are derived from non-renewable sources such as pyrene (from coal tar). Optical brighteners can be considered as a type of dye, and they work by absorbing UV (ultraviolet) light and reflecting blue light. This makes materials look less yellow to the human eye, and thus appear whiter, brighter and 'cleaner'.

*A manufacturer sewed them using fabric from different suppliers. Although they appear to be the same color white in daylight, as soon as the ultraviolet light is flipped on you can see they are quite different. This is a phenomenon called "**metamerism**" – when two things appear to match under one light source, but no longer match when you change the lighting.*





Interaction of electromagnetic radiation with matter:

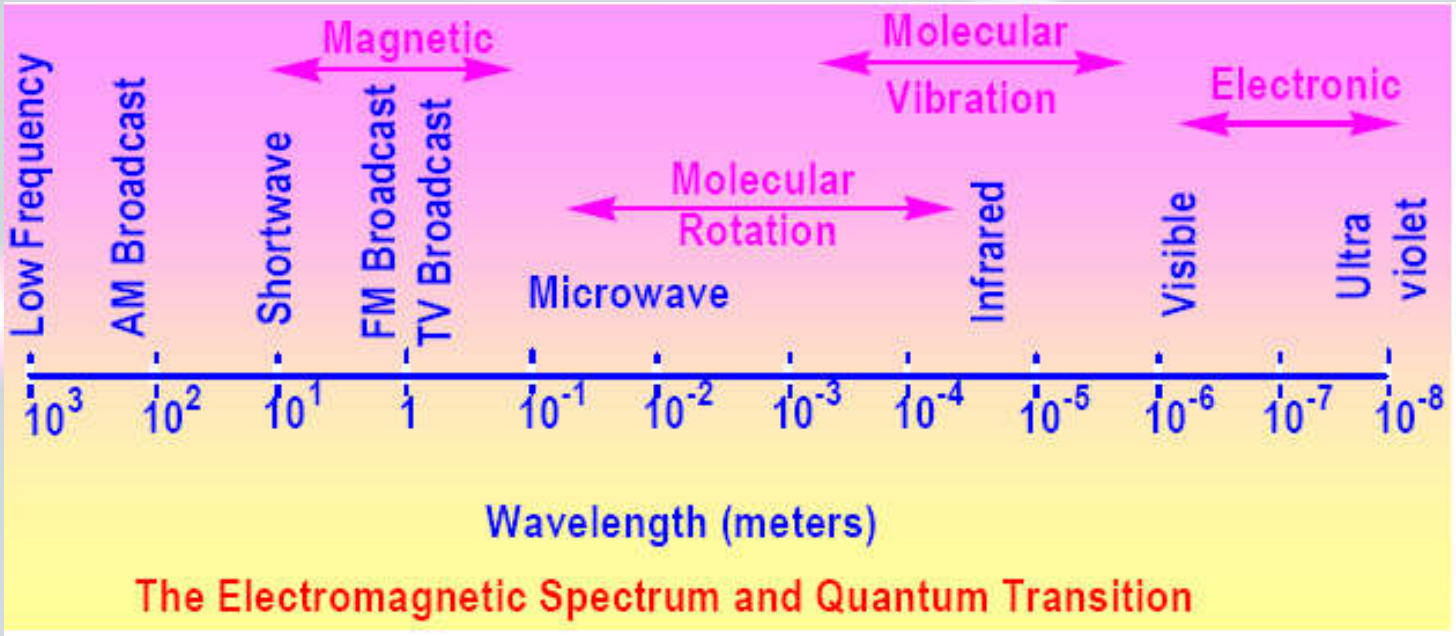


Microwave Interactions:

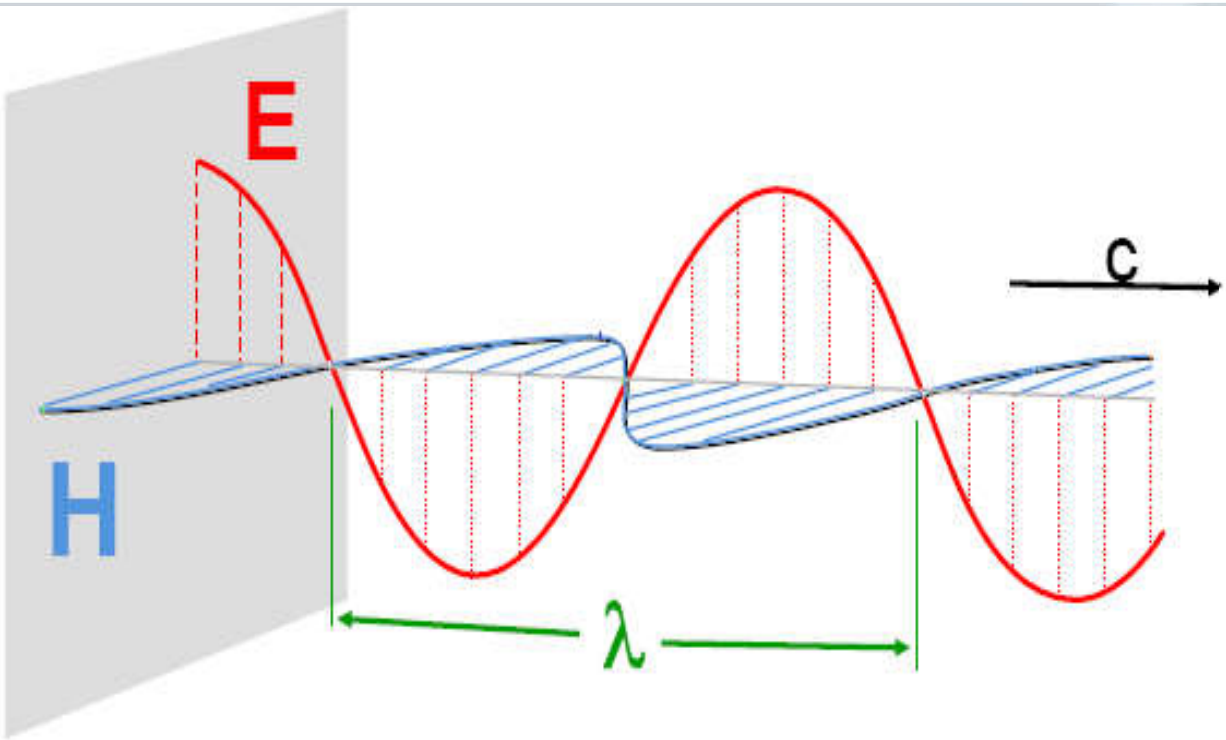
The quantum energy of microwave photons is in the range 0.00001 to 0.001 eV which is in the range of energies separating the quantum states of molecular rotation and torsion. The interaction of microwaves with matter other than metallic conductors will be to rotate molecules and produce heat as result of that molecular motion.

MW heating reduces the processing time and energy cost and has been known in the food industry for over half a century; its use in chemistry, however, started only since 1986.

Microwave irradiation plays an important role in fast and simple synthesis of nanocrystals. It has been observed that significantly different results can be obtained by conventional heating and microwave heating.



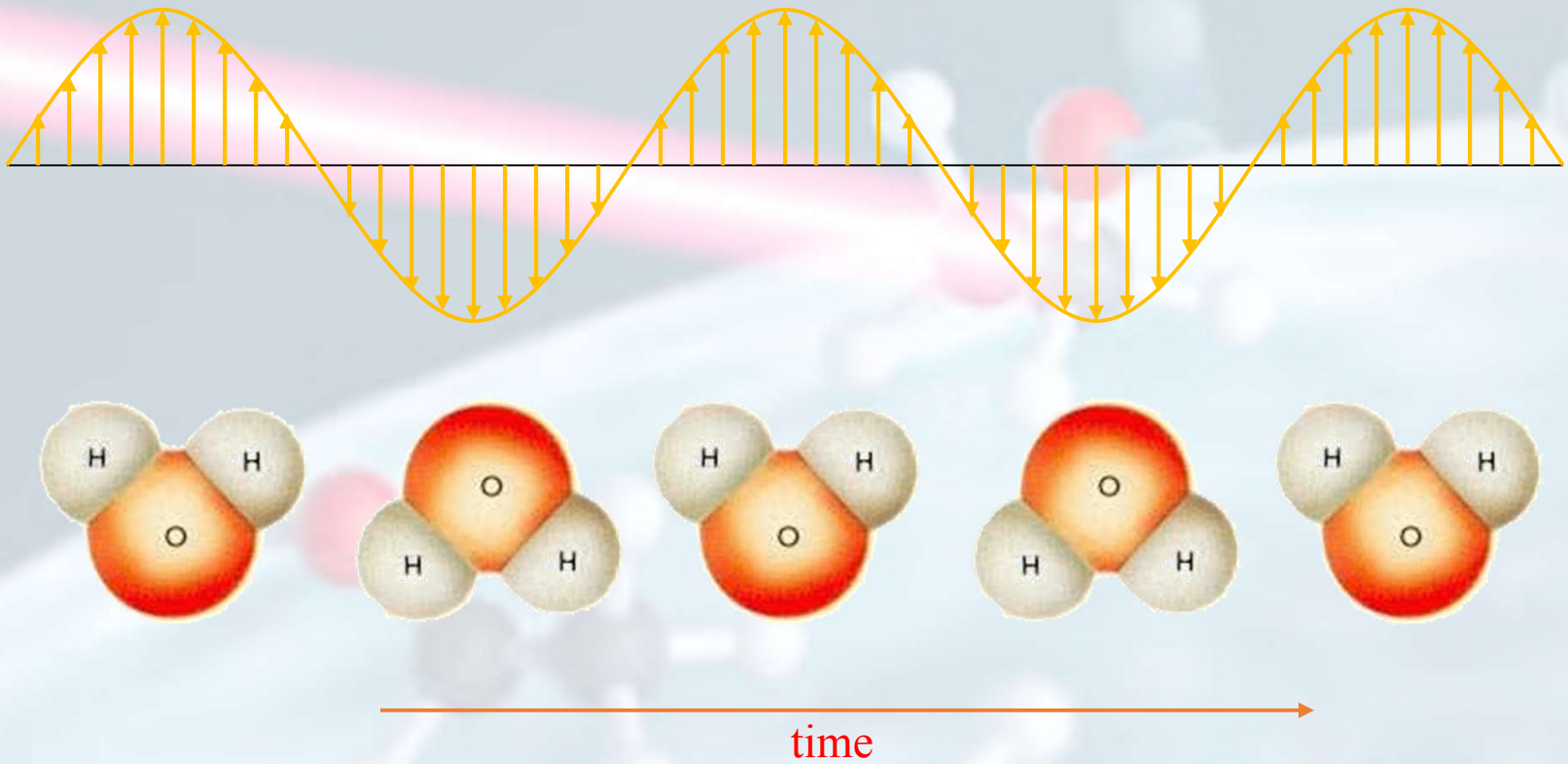
MW reactors operate at 2.45 GHz.



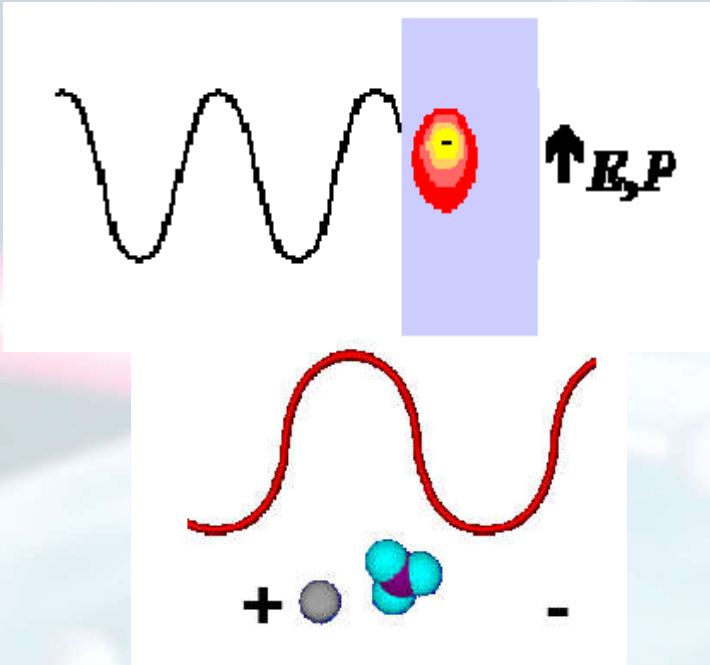
for 2450 MHz)
)0 km/s)

1946: Original patent (P. L. Spencer)
1947: First commercial oven
1955: Home models
1967: Desktop model
1975: U.S. sales exceed gas ranges
1976: 60% of U.S. households have microwave ovens

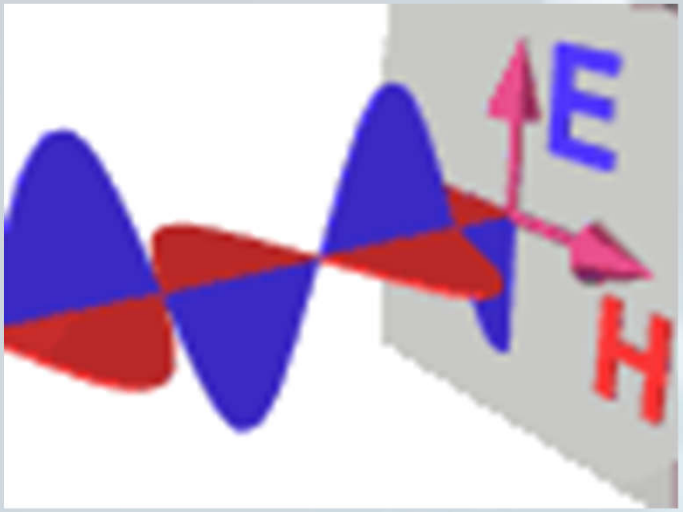
Dipolar Polarization Mechanism



Conduction Mechanism



Ions in solution will move by the applied electric field



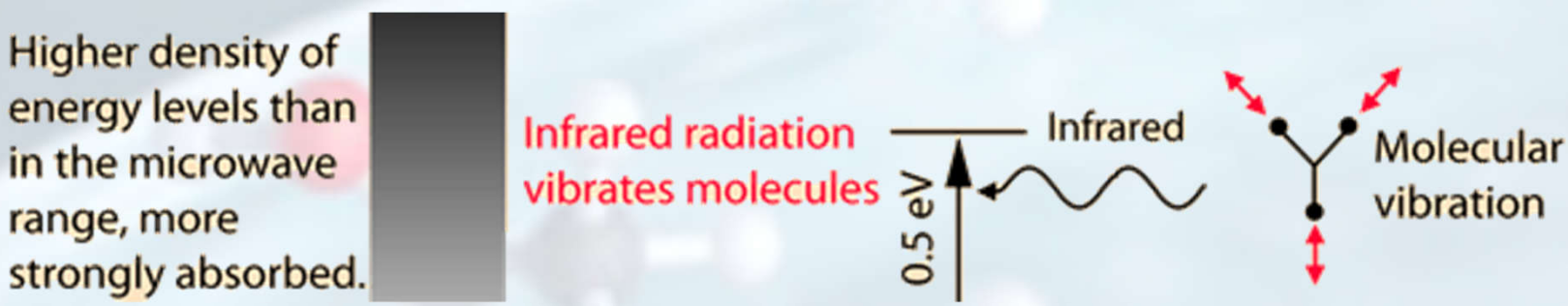
The ability of a solvent molecule to absorb microwave energy and pass it on in the form of heat to other molecules partly depends on the dissipation factor (tanδ) defined as the ratio of the dielectric loss (ε″) to the dielectric constant (ε′) of the solvent. Thus a study of the effect of solvents with different dielectric constants on microwave method is of great importance.

$$\tan\delta = \frac{\varepsilon''}{\varepsilon'}$$

Solvent (bp °C)	Dielectric Constant (ε′)	Solvent	Tan δ	Solvent	Dielectric Loss (ε″)
Water (100)	80.4	Ethylene Glycol	1.350	Ethylene Glycol	49.950
Formic Acid (100)	58.5	Ethanol	.941	Formic Acid	42.237
DMSO (189)	45.0	DMSO	.825	DMSO	37.125
DMF (153)	37.7	2-Propanol	.799	Ethanol	22.866
Acetonitrile (82)	37.5	1-Propanol	.757	Methanol	21.483
Ethylene Glycol (197)	37.0	Formic Acid	.722	Nitrobenzene	20.497
Nitromethane (101)	36.0	Methanol	.659	1-Propanol	15.216
Nitrobenzene (202)	34.8	Nitrobenzene	.589	2-Propanol	14.622
Methanol (65)	32.6	1-Butanol	.571	Water	9.889
NMP (215)	32.2	Isobutanol	.522	1-Butanol	9.764
Ethanol (78)	24.3	2-Butanol	.447	NMP	8.855
Acetone (56)	20.7	2-Methoxyethanol	.410	Isobutanol	8.248
1-Propanol (97)	20.1	o-Dichlorobenzene	.280	2-Butanol	7.063
MEK (80)	18.5	NMP	.275	2-Methoxyethanol	6.929
2-Propanol (82)	18.3	Acetic Acid	.174	DMF	6.070
1-Butanol (118)	17.1	DMF	.161	o-Dichlorobenzene	2.772
2-Methoxyethanol (124)	16.9	1,2-Dichloroethane	.127	Acetonitrile	2.325
2-Butanol (100)	15.8	Water	.123	Nitromethane	2.304
Isobutanol (108)	15.8	Chlorobenzene	.101	MEK	1.462
1,2-Dichloroethane (83)	10.4	Chloroform	.091	1,2-Dichloroethane	1.321
o-Dichlorobenzene (180)	9.9	MEK	.079	Acetone	1.118
Dichloromethane (40)	9.1	Nitromethane	.064	Acetic Acid	1.079
THF (66)	7.4	Acetonitrile	.062	Chloroform	0.437
Acetic Acid (113)	6.2	Ethyl Acetate	.059	Dichloromethane	0.382
Ethyl Acetate (77)	6.0	Acetone	.054	Ethyl Acetate	0.354
Chloroform (61)	4.8	THF	.047	THF	0.348
Chlorobenzene (132)	2.6	Dichloromethane	.042	Chlorobenzene	0.263
o-Xylene (144)	2.6	Toluene	.040	Toluene	0.096
Toluene (111)	2.4	Hexane	.020	o-Xylene	0.047
Hexane (69)	1.9	o-Xylene	.018	Hexane	0.038

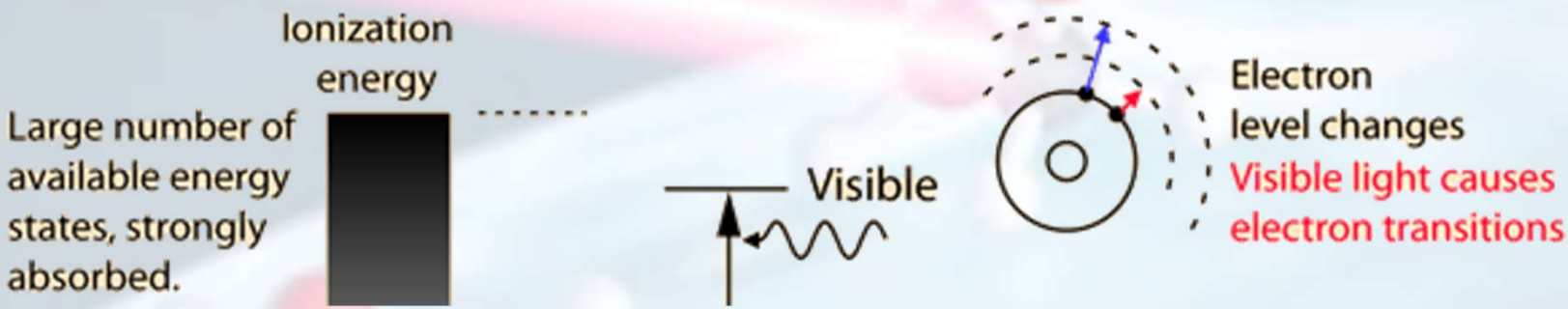
Infrared Interactions:

The quantum energy of infrared photons is in the range 0.001 to 1.7 eV which is in the range of energies separating the quantum states of molecular vibrations. Infrared is absorbed more strongly than microwaves, but less strongly than visible light. The result of infrared absorption is heating of the tissue since it increases molecular vibrational activity. Infrared radiation does penetrate the skin further than visible light and can thus be used for photographic imaging of subcutaneous blood vessels.

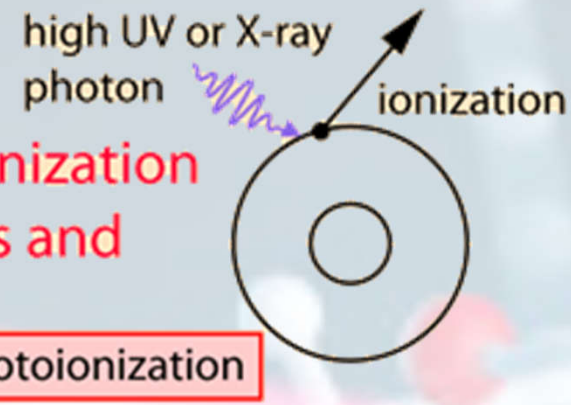


Visible Light Interactions:

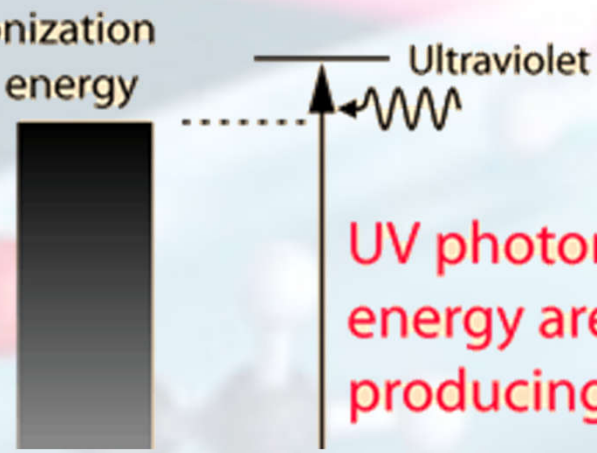
The primary mechanism for the absorption of visible light photons is the elevation of electrons to higher energy levels. There are many available states, so visible light is absorbed strongly.



Ultraviolet Interactions:



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



Large number of available energy states, strongly absorbed.

UV photons below the ionization energy are strongly absorbed in producing electron transitions.

Interaction of electromagnetic radiation UV-visible with matter/organic compounds:

- Transition from ground state to excited state
- Changes electronic distribution, geometry and uncoupling of electronic spin
- Electron moves from ground state energy level of a molecular to a higher level i.e. an unoccupied orbital of higher energy
- Energy level of a molecule are quantized

The amount of energy required to raise an electron in a given molecule from one level to a higher energy one is a fixed quantity i.e. $\Delta E = h\nu$ for one molecule and for n number of molecules it is $\Delta E = nh\nu$

X-Ray Interactions:

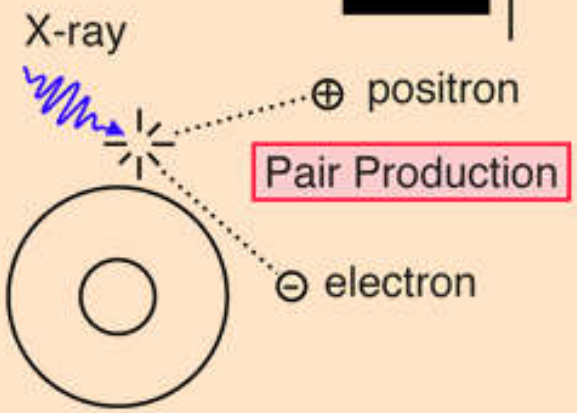
Since the quantum energies of x-ray photons are much too high to be absorbed in electron transitions between states for most atoms, they can interact with an electron only by knocking it completely out of the atom. That is, all x-rays are classified as ionizing radiation. This can occur by giving all of the energy to an electron (photoionization) or by giving part of the energy to the electron and the remainder to a lower energy photon (Compton scattering). At sufficiently high energies, the x-ray photon can create an electron positron pair.

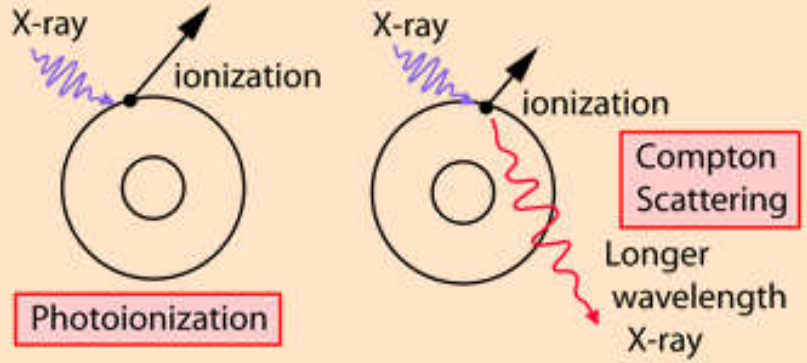
X-ray interactions

X-rays

X-ray photon energies are far above the ionization energies of atoms.

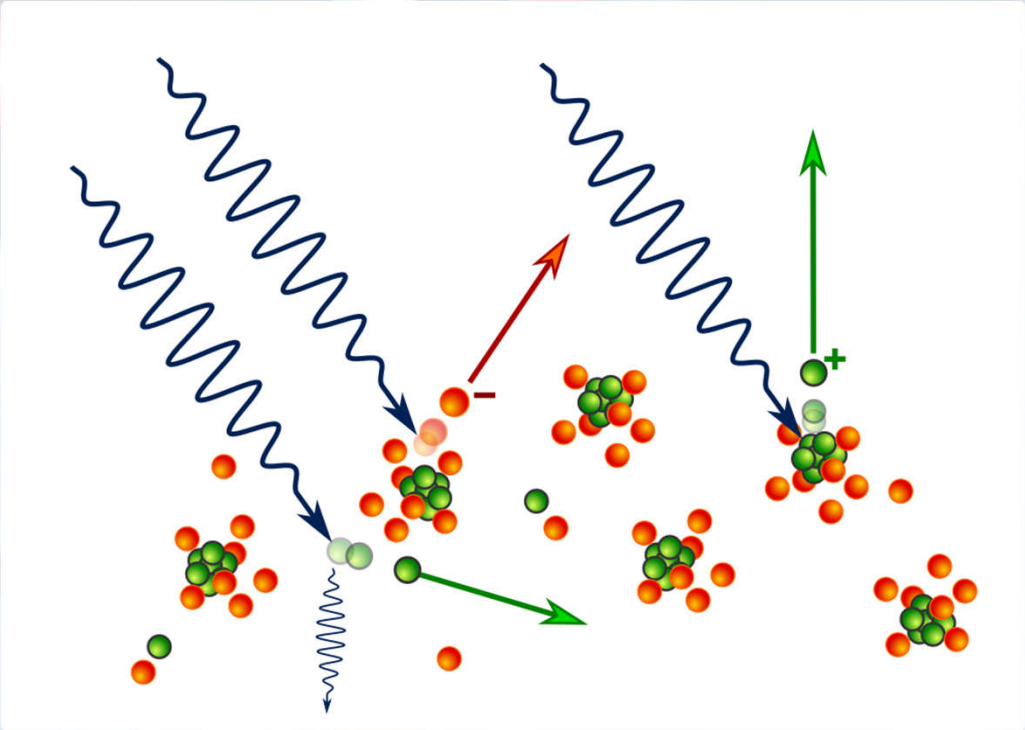
Ionization energy

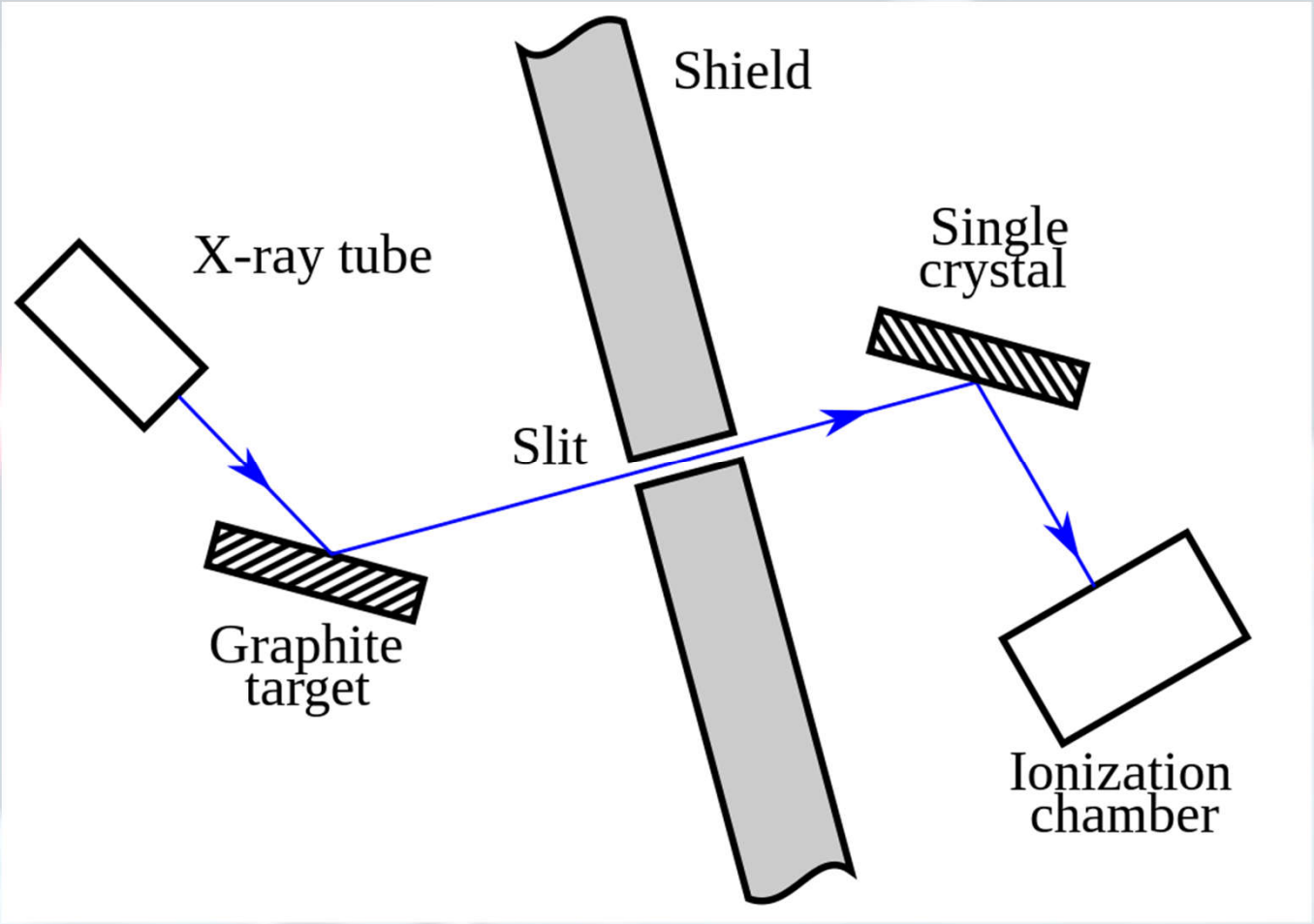


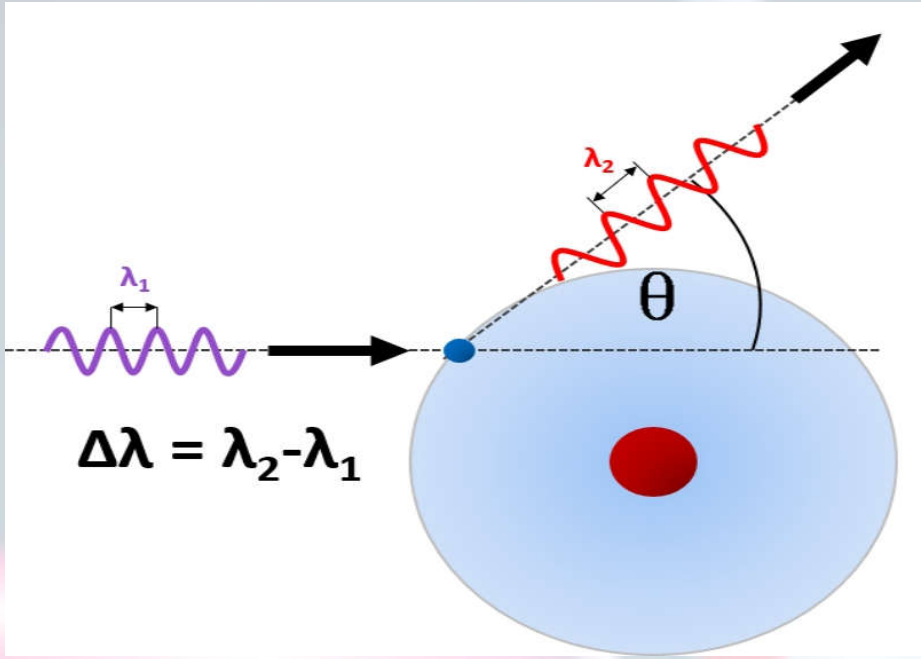


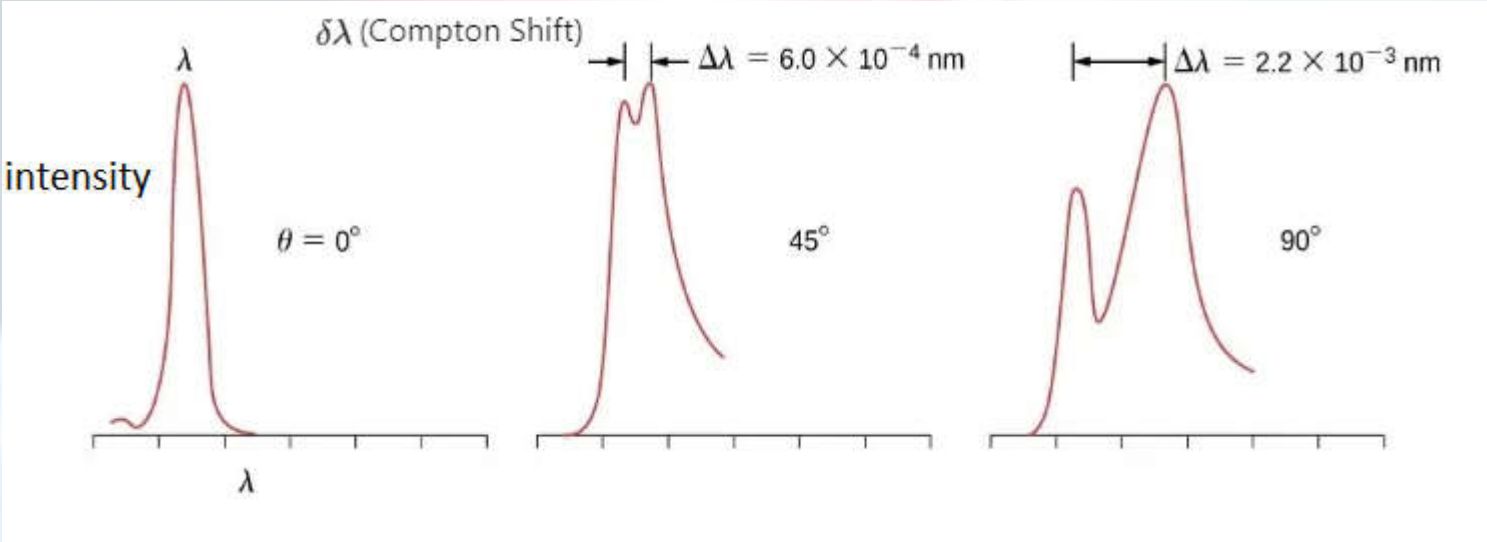
Compton scattering:

Compton scattering (or the Compton effect) is the quantum theory of high frequency photons scattering following an interaction with a charged particle, usually an electron. Specifically, when the photon hits electrons, it releases loosely bound electrons from the outer valence shells of atoms or molecules.



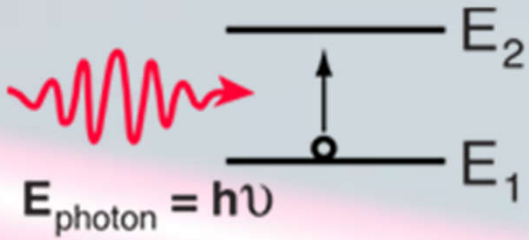

Shield
X-ray tube
Single
crystal
Slit
Graphite
target
Ionization
chamber


λ1
λ2
θ
Δλ = λ2-λ1


δλ (Compton Shift)
Δλ = 6.0 × 10⁻⁴ nm
Δλ = 2.2 × 10⁻³ nm
intensity
λ
θ = 0°
45°
90°
λ

Quantum Properties of Light:

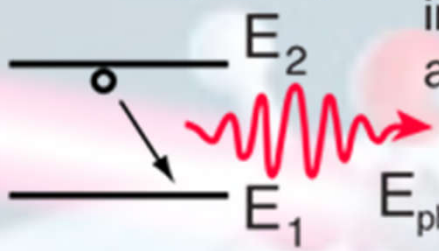
Quantum properties dominate the fields of atomic and molecular physics. Radiation is quantized such that for a given frequency of radiation, there can be only one value of quantum energy for the photons of that radiation. The energy levels of atoms and molecules can have only certain quantized values. Transitions between these quantized states occur by the photon processes absorption, emission, and stimulated emission. All of these processes require that the photon energy given by the Planck relationship is equal to the energy separation of the participating pair of quantum energy states.



Absorption can occur only when

$$\Delta E = h\upsilon = E_2 - E_1$$

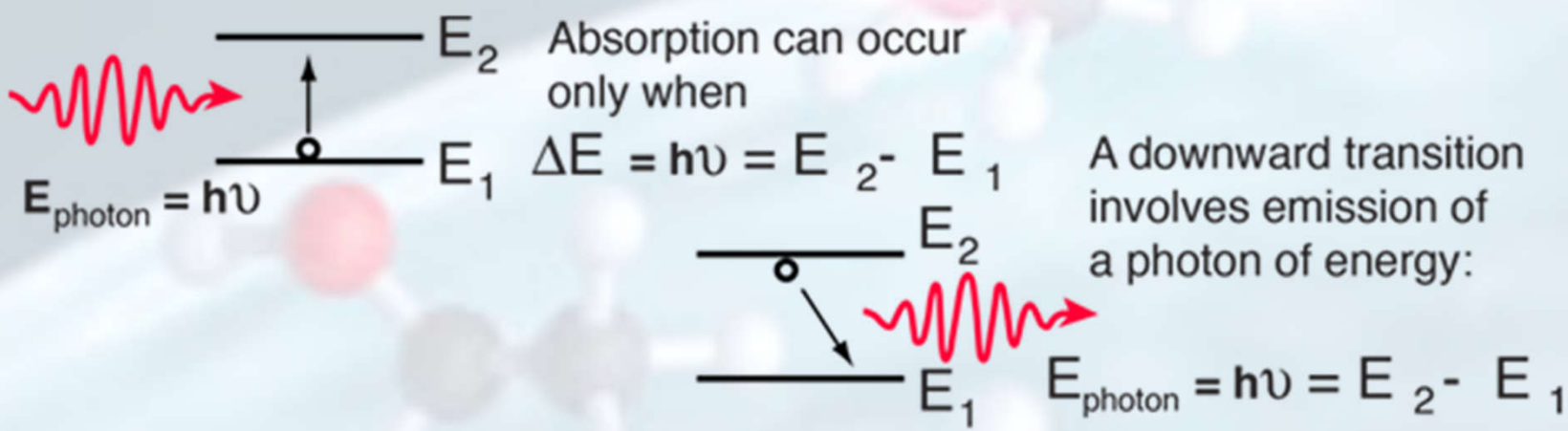
A downward transition involves emission of a photon of energy:



$$E_{photon} = h\upsilon = E_2 - E_1$$

Absorption and Emission:

Taking the electron transitions associated with visible and ultraviolet interactions with matter as an example, absorption of a photon will occur only when the quantum energy of the photon precisely matches the energy gap between the initial and final states. In the interaction of radiation with matter, if there is no pair of energy states such that the photon energy can elevate the system from the lower to the upper state, then the matter will be transparent to that radiation.

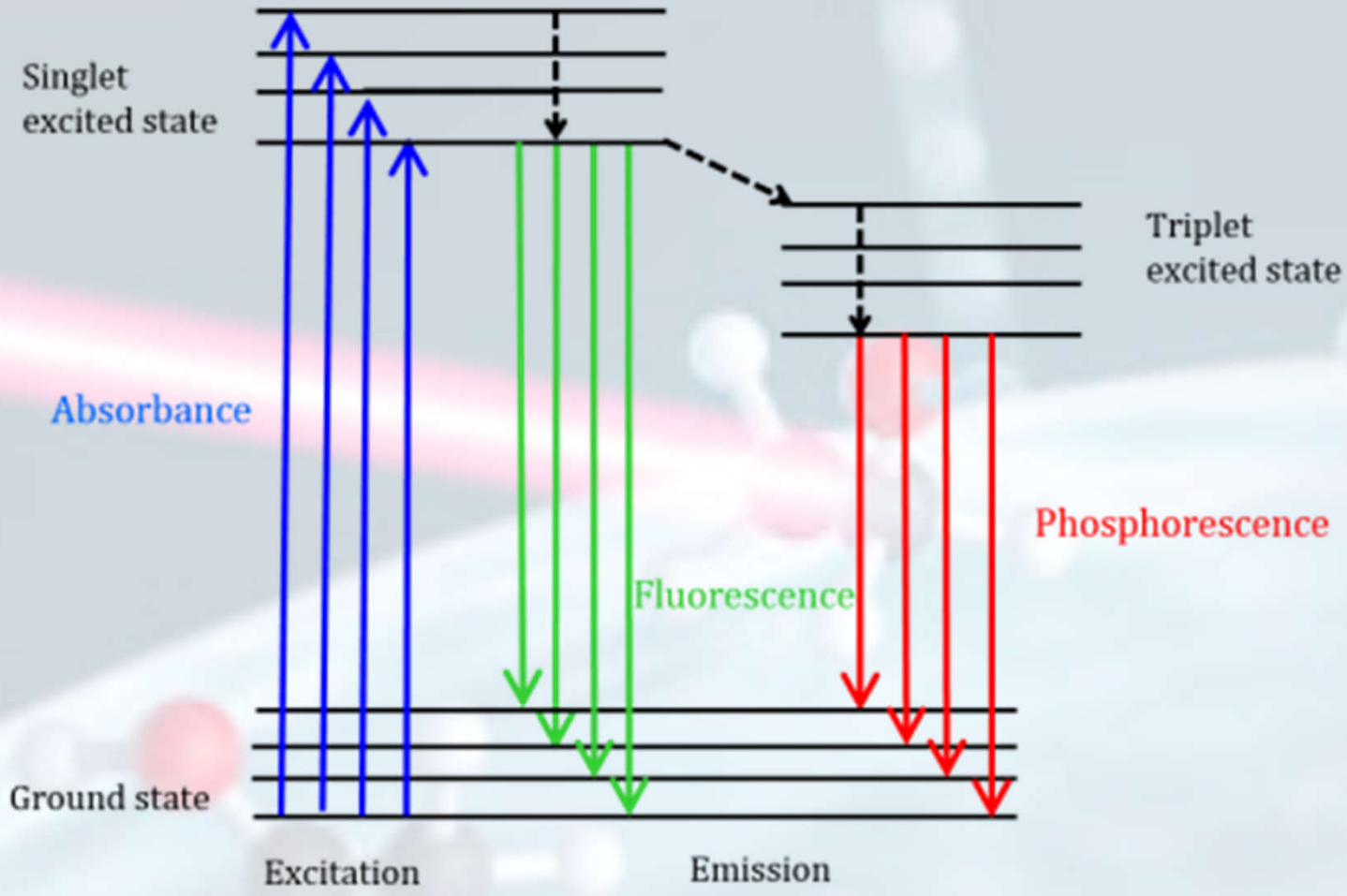


Fluorescence:

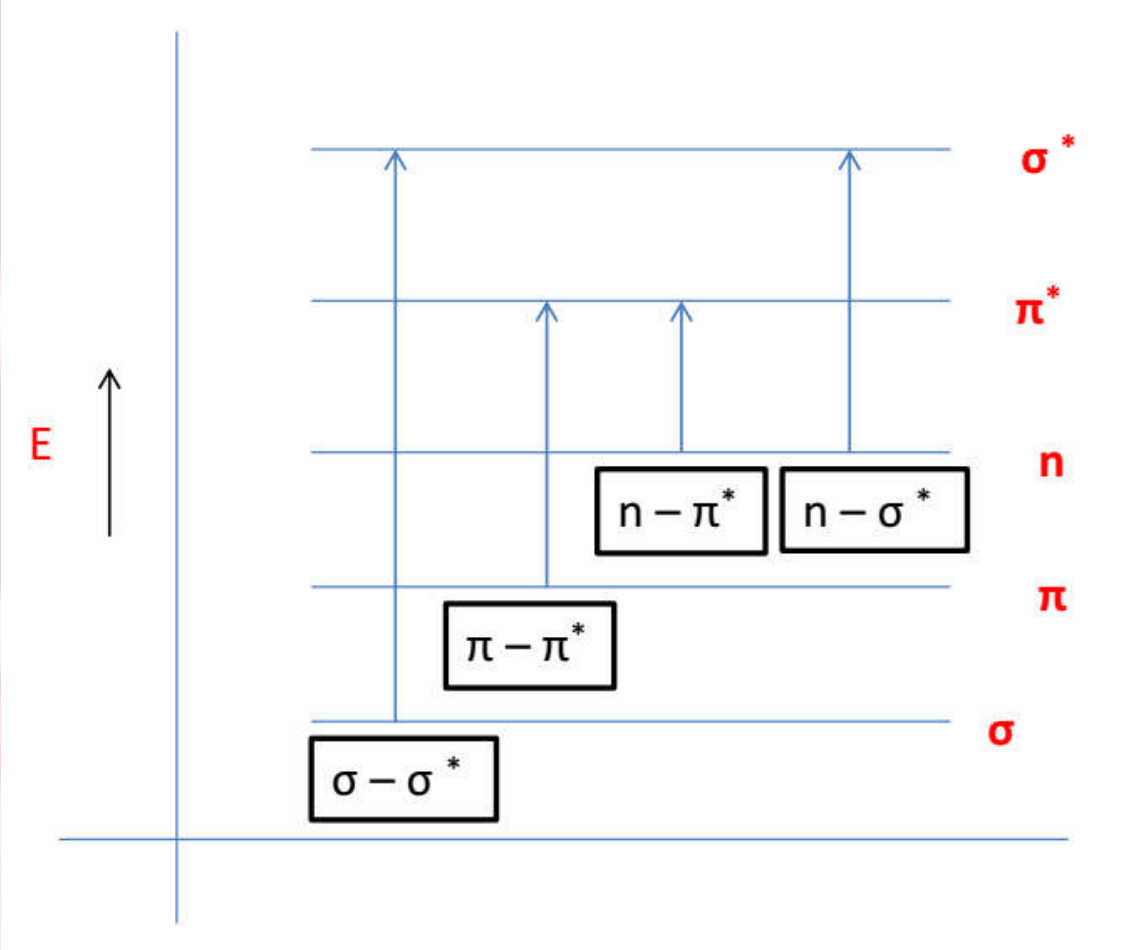
Fluorescence, a type of luminescence, occurs in gas, liquid or solid chemical systems. Fluorescence is brought about by absorption of photons in the singlet ground state promoted to a singlet excited state. The spin of the electron is still paired with the ground state electron, unlike phosphorescence.

Phosphorescence:

Phosphorescence is a type of photoluminescence related to fluorescence. When exposed to light of a shorter wavelength, a phosphorescent substance will glow, absorbing the light and reemitting it at a longer wavelength. Unlike fluorescence, a phosphorescent material does not immediately reemit the radiation it absorbs.


Singlet
excited state
Triplet
excited state
Absorbance
Phosphorescence
Fluorescence
Ground state
Excitation
Emission

Types of excitations:



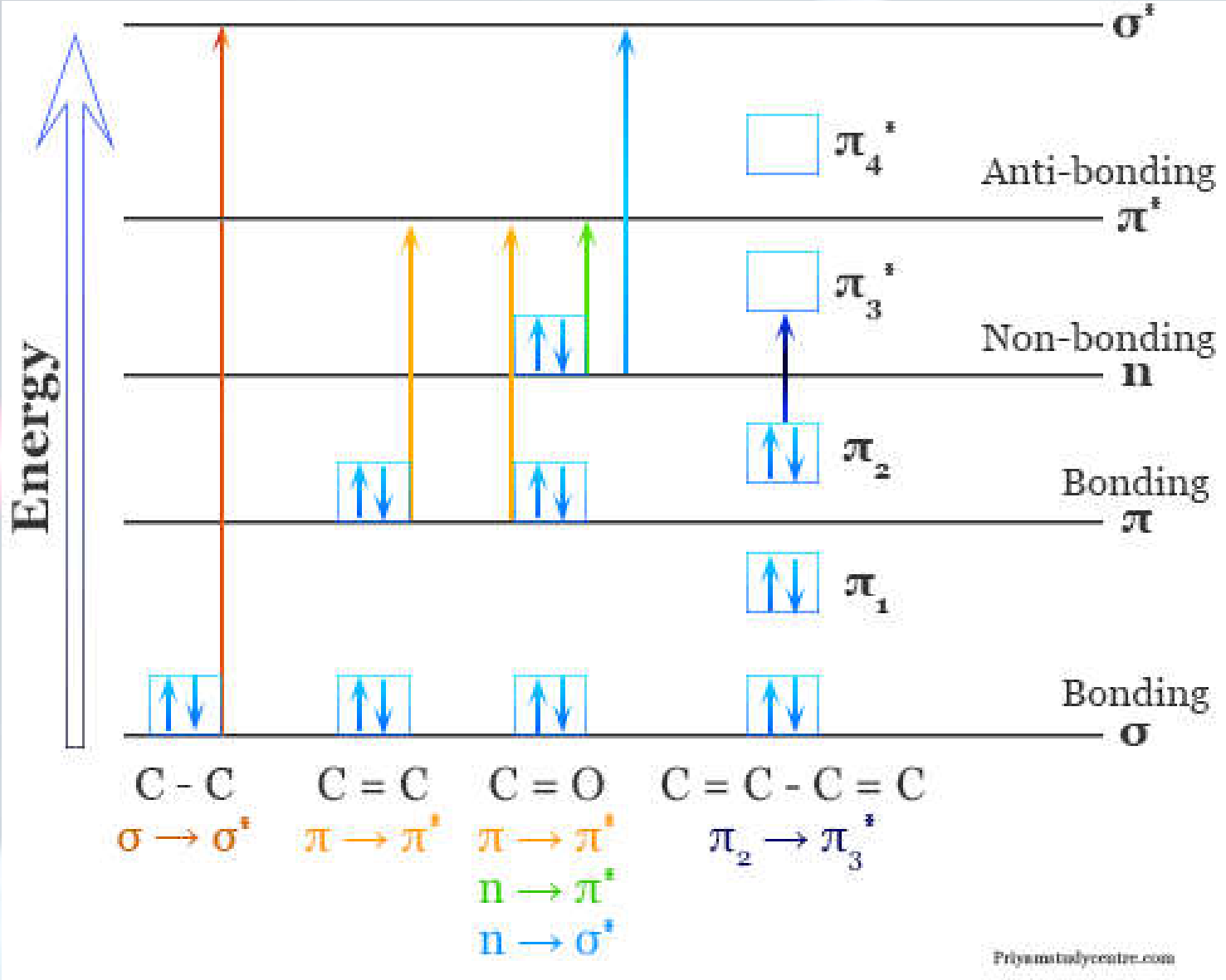
1. $\sigma - \sigma^*$ ⟶ alkanes (no n or pi electrons)
2. $n - \sigma^*$ ⟶ alcohols, amines , ethers etc
3. $\pi - \pi^*$ ⟶ aldehydes, carboxylic esters, alkenes etc.
4. $n - \pi^*$ ⟶ aldehydes, ketones,carboxylic esters(can undergo above three transitions also)

$$\sigma - \sigma^* > n - \sigma^* > \pi - \pi^* > n - \pi^*$$

⟶

Decreasing energy

- ✓ **However, the order may sometimes be altered in some solvents.**
- ✓ **More conjugation in a molecule, the more the absorption is displaced towards higher wavelengths.**


Energy
σ*
π4*
Anti-bonding
π*
π3*
Non-bonding
n
π2
Bonding
π
π1
Bonding
σ
C - C
σ → σ*
C = C
π → π*
C = O
π → π*
n → π*
n → σ*
C = C - C = C
π2 → π3*
Priyamstudycentre.com

Theory of Ultraviolet–Visible Absorption:

The UV-Visible spectroscopy principle is based on the absorption of ultraviolet light or visible light by chemical compounds. To occur a chemical reaction, the reacting molecules must be activated by acquiring activation energy.

In photochemical reactions, the activation energy is obtained by absorption of radiation or light energy. In order to study the mechanism of the photochemical reaction, we need to study the following types of electronic transition:

Sigma to sigma star transition ($\sigma \rightarrow \sigma*$)

n to sigma star transition ($n \rightarrow \sigma*$)

n to pi star transition ($n \rightarrow \pi*$)

Pi to pi star transition ($\pi \rightarrow \pi*$)

Absorption peaks (λmax) and molar absorptivity (∈max) and possible electronic transition of some common compounds are given below the table:

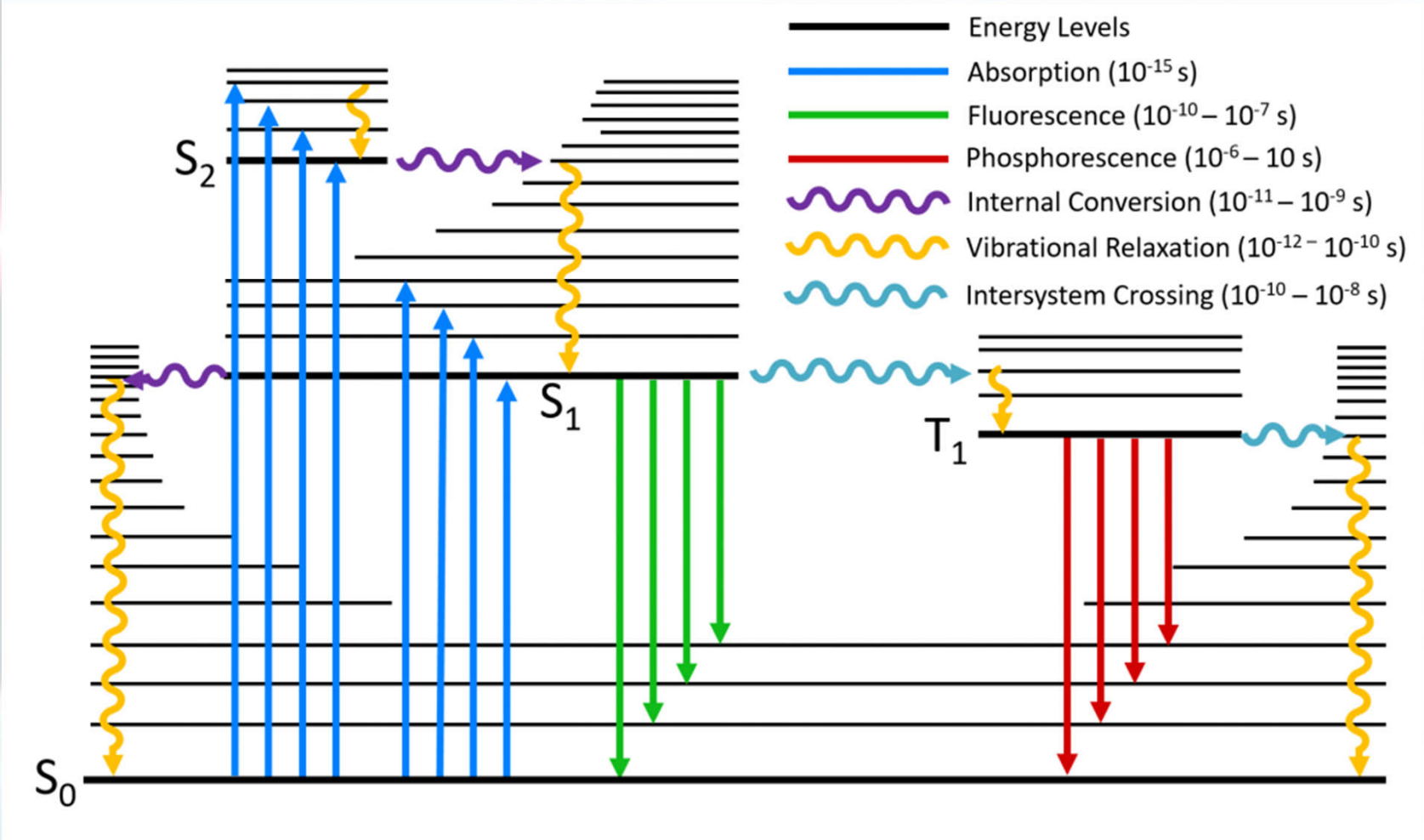
Compounds	λ_{max} (nm)	ϵ_{max} (L/cm/mol)	Electronic transition
Alkenes	177	1.3×10^4	$n \rightarrow \pi^*$
Alkyne	178 – 225	10×10^3 – 150	$n \rightarrow \pi^*$
Carbonyl	186 – 280	1.0×10^3 – 16	$n \rightarrow \pi^*$
Carboxyl	204	41	$n \rightarrow \pi^*$
Amide	214	60	$n \rightarrow \pi^*$
Azo	339	5	$n \rightarrow \pi^*$
Nitro	280	22	$n \rightarrow \pi^*$
Ketone	282	27	$n \rightarrow \pi^*$
Water	167	1.48×10^3	$n \rightarrow \sigma^*$
Methyl alcohol	184	15	$n \rightarrow \sigma^*$
Benzene	204	7.9×10^3	$n \rightarrow \sigma^*$

Jablonski Diagram:

The Jablonski diagram, typically used to illustrate fluorescence in molecular spectroscopy, demonstrates the excited states of a molecule along with the radiative and non-radiative transitions that can occur between them.

Aleksander Jablonski was a Polish academic who devoted his life to the study of molecular absorbance and emission of light. He developed a written representation that generally shows a portion of the possible consequences of applying photons from the visible spectrum of light to a particular molecule.

Jablonski Diagram



The naming of the electronic states is based on the spin angular momentum configuration of each state. Singlet states (a total spin angular momentum of zero) are denoted by an S and triplet states (a total spin angular momentum of one) by T:

S_0 is the singlet ground state of the molecule

S_1 is the first excited singlet state and S_n is the nth excited singlet state

T_1 is the first excited triplet state and T_n is the nth excited triplet state

Radiative & Non-Radiative Transitions:

The colored arrows represent the various transitions that can transfer energy between the molecular states and are split into radiative and non-radiative transitions.

Radiative transitions are transitions between two molecular states where the energy difference is emitted or absorbed by photons and are represented in a Jablonski diagram by straight arrows.

Non-radiative transitions are transitions between two molecular states without the absorption or emission of photons and are represented in a Jablonski diagram by undulating arrows.