Photochemistry: الكيمياء الضوئيه

It's a branch of physical chemistry, it deals with interaction of light (hv) with the matter. Solar spectrum (**sunlight**) is the main source of light in our world, even it seems to be white in its color, but in fact it is composing of different colors. Human eye can see only white light (visible light its wavelength 400-800 nm). Solar light can be analyzed to its components using simple prism and also it can see on rainbow in humidity sky after raining.

Figure 1: analyzing of solar spectrum with prism

Electromagnetic spectrum of light

Generally, radiation(light) or its called electromagnetic radiation composed of waves of two components (one is electrical component and the other magnetic component each of them is perpendicular on the other).

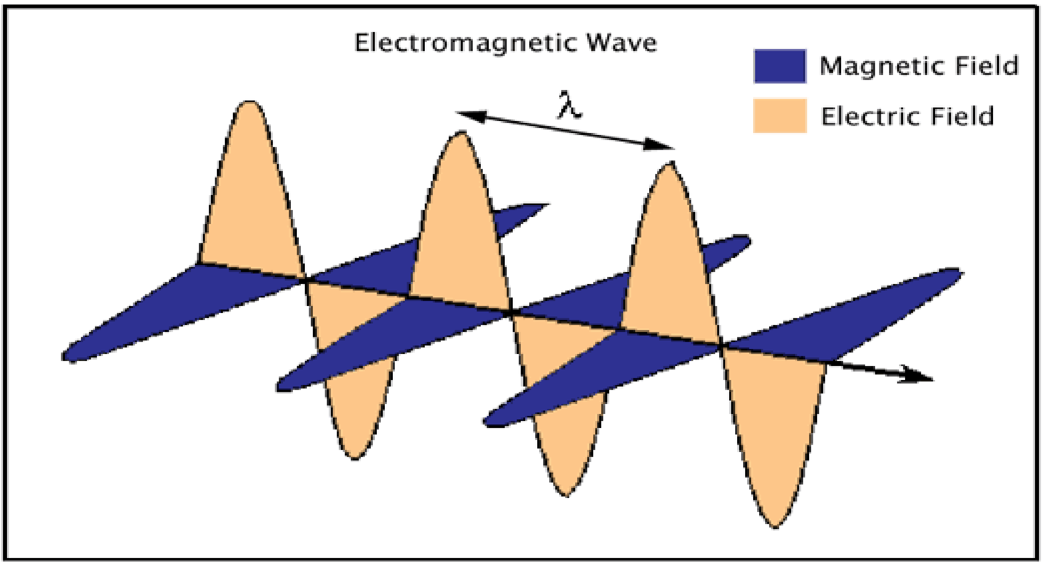

Figure 2: Electromagnetic spectrum

Changing electric fields induce a magnetic field (this is how electromagnets work), and changing magnetic fields induce an electric field (this is how the charger on your electric toothbrush works). The result is that if one oscillates, so will the other, and they will continually induce each other.

Components of electromagnetic spectrum

Electromagnetic spectrum composed of some regions and we cant see them directly but we can see only white light(visible). These regions are different in their wavelengths and their energies. Block diagram of solar spectrum is shown below:

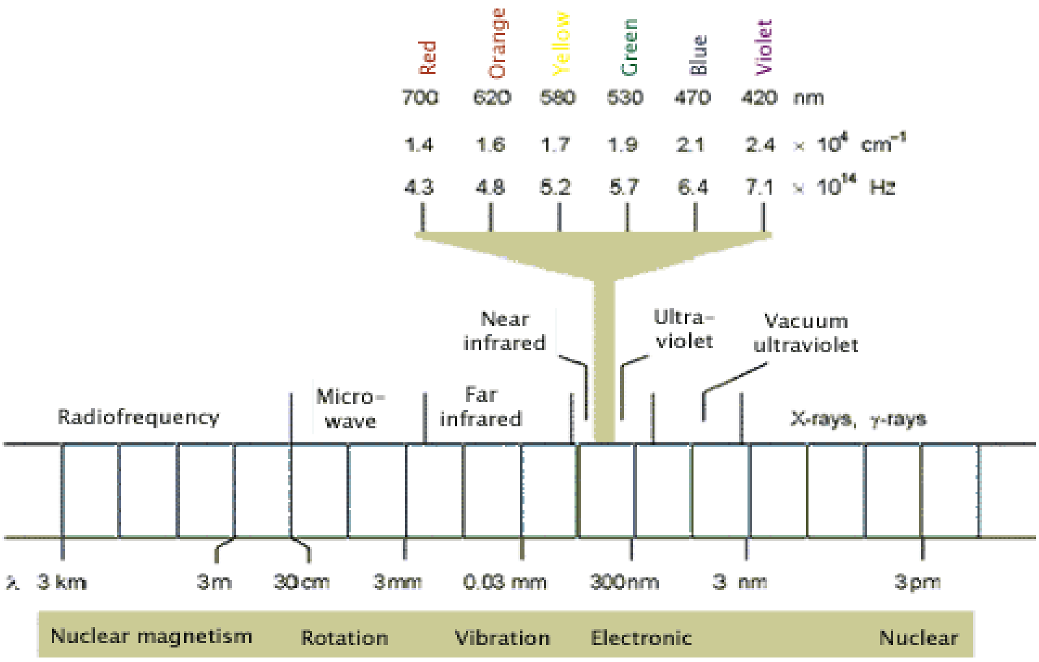

Figure 3: Reigon of solar spectrum

Regions of the solar spectrum

The types of electromagnetic radiation are broadly classified into the following classes:

1. Gamma radiation
2. X-ray radiation
3. Ultraviolet radiation
4. Visible radiation
5. Infrared radiation
6. Microwave radiation
7. Radio wave

Properties of electromagnetic radiation

Electromagnetic radiation composed of a stream of particles called (photons). Energy of each photon (hv), h, is Blank constant and v is the frequency of radiation. All types of electromagnetic spectrum travelled in space with speed of (3 x10 ^{8} m/sec). Also all types of Electromagnetic radiation has two types of properties, wave and particle properties.

A-wave properties of electromagnetic radiation:

Electromagnetic radiation is a sine vibrational wave that is composed of two type of components, electrical component and magnetic component.

1-wavelength (λ)

It is the average distance that is traveled by wave between two successive crest in the same wave. Wavelength usually measured in nanometer (1 nm=1 $x10^{-9}$ m). There is inverse proportionality between (λ and E), (Eα 1/λ). So that energy of light would increase with decease of its wavelength.

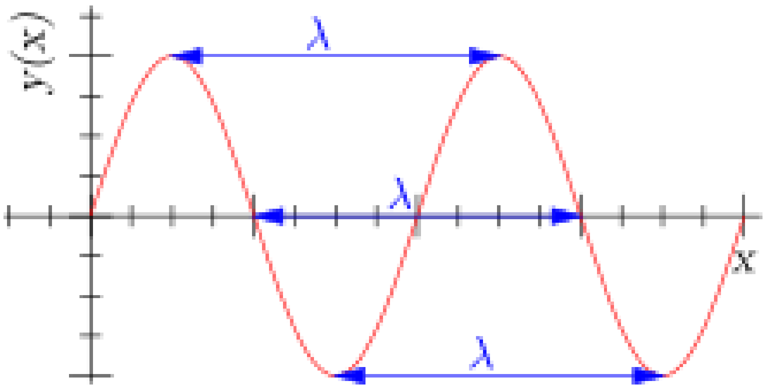

Figure 4: wavelength of light

2- Frequency of light(v):

It is a number of periods that is travelled by wave in one second (wave/second). Frequency measured in Hertz (number of cycle per second (CPS). CPS=Hz.

There is direct proportionality between (v) and the energy of light. (Eαv). The relation between wavelength and frequency is given by:

(v= c/λ): v=frequency, c, speed of light, 3 $x10^{8}$ m/sec,

Eα v, Eα 1/λ,

The energy of photon:

$E=hv=hc/\lambda$

3- wavenumber(v^{-}):

Its number of waves per one centimeter and it is measured in (cm^{-1}). Wavenumber is directly proportional with the wavenumber of light.($E\alpha\ v^{-}$). Mathematically wavenumber is the inverse of wavelength in cm unit:

($v^{-}= 1/\lambda$ in cm) [1 nm= $1x\ 10^{-9}$ m, 1 nm=$1x10^{-7}$ cm]

$E= h.\ v=h.\ c/\lambda= h.c.v^{-}$

For example v^{-}=100 cm^{-1}, meaning it has a hundred wave in one cm,

80 cm^{-1}, has 80 wave in cm and so on.

Wave properties can be connected as follows:

$v^{-}= 1/\lambda$ in cm, $\nu= c/\lambda$, $c=\nu.\lambda$

B-particle properties of electromagnetic radiation

A light is a stream of particles called photon with energy (E=hv). Avogadro's number of photons is called Einstein and energy of Einstein (E=Nhv), N , is Avogadro's number(6.02 $x10^{23}$), h is blank constant (6.62 x 10^{-34} J.sec). in addition to above wave properties (v, v-, and λ), it has particle properties as it has classical momentum and energy and according to Max-Blank theory:

P=m. c   (momentum of photon)

P=N. m. c (momentum of Einstein)

E=hv   (energy of photon),

E=Nhv   (energy of Einstein)

$E=N.h.c/\lambda$

Example 1: calculate energy of photon with a wavelength of 450 nm?

Solution:

$E=hv= hc/\lambda= (6.62 \times 10^{-34}$ J.sec.)(3x 10^{8} m/sec)/ 450 x 10^{-9}

$E = 0.044 \times 10^{-7}$ J,

$E= 4.4 \times 10^{-9}$ J

Example 2: Calculate energy in kJ for five Einstein of a light of wavelength of 450 nm?

Solution:

$E=Nhv=Nhc/\lambda$

$E= 5Nhc/\lambda$

$E=5 \times 6.02 \times 10^{23} \times 6.62 \times 10^{-34} \times 3 \times 10^{8} / 450 \times 10^{-9}$

$E= 1.328 \times 10^{6}$ J

$E= 1.328 \times 10^{3}$ kJ

Basic of photochemistry

The Basic Laws of Photochemistry

Grotthuss–Draper law (1st law)

Photoexcitation is the first step in a photochemical process where the reactant is elevated to a state of higher energy, an excited state. The first law of photochemistry, known as the Grotthuss–Draper law (for chemists 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**].

$$A \xrightarrow[\text{absorption of light}]{hv} P$$

$$A \xrightarrow[\text{no absorption of light}]{} \text{no reaction}$$

The Second Law of Photochemistry (Stark-Einstein law, or it is called photochemical equivalent):

states that for each photon of light absorbed by a chemical system, only one molecule is activated for a photochemical reaction. This law is true for ordinary light intensities, however, with high-powered lasers, two-photon reactions can occur, i.e., the molecule is raised to a higher energy state than produced by single-photon absorption. According to this law only one photon is absorbed by a particle:

(photon: particle)

$$A + 1\,hv \longrightarrow A^{*} \quad (1:1)$$

There are some exception for 2nd law of photochemistry as in Laser, in this case one particle may absorb more than one photon:

$$A + 2hv \longrightarrow A^{**} \quad (1:2)$$

Interaction of light with the matter

1-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 lead to rotate molecules and produce heat as result of that molecular motion. Conductors will strongly absorb microwaves and any lower frequencies because they will cause electric currents which will heat the material. .

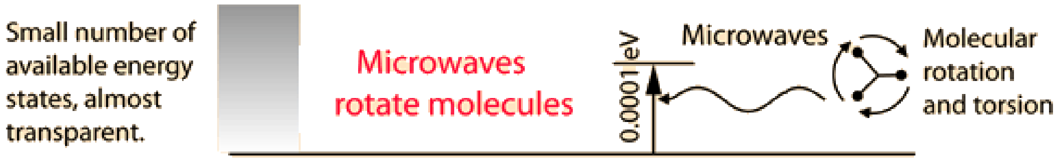

Figure 5: Interaction of microwave radiation with matter

2-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 and it leads to vibrate the bonds of absorbed species. (vibration bonds results from attraction and repulsion) between electrons and nucleus.

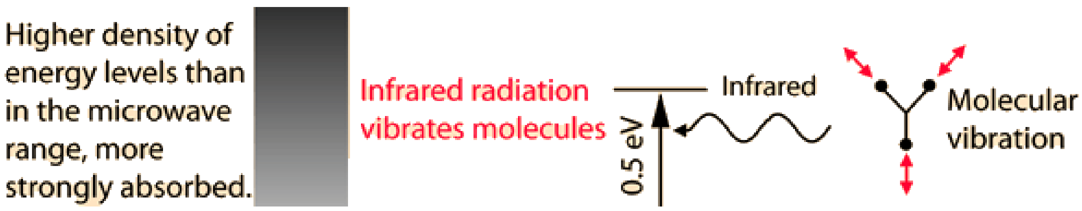

Figure 6: Interaction of IR radiation with matter

3-Visible Light Interactions

The primary mechanism for the absorption of visible light photons (400-800)nm, is the elevation of electrons to higher energy levels. There are many available states, so visible light is absorbed strongly and leads to electronic transitions within the molecule or atom itself..While exposure to visible light causes .heating, it does not cause ionization.

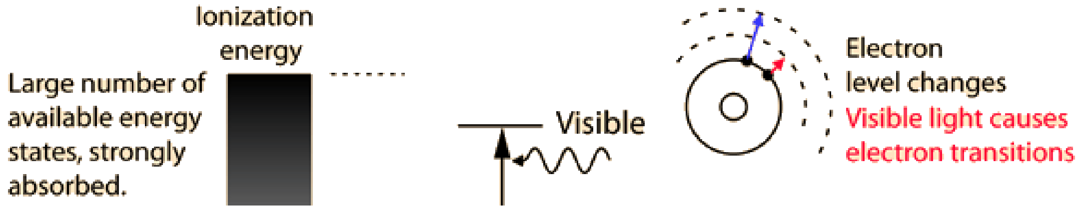

Figure 7: Interaction of visible radiation with matter

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4-Ultraviolet Interactions

The near ultraviolet is absorbed very strongly(200-400) nm in the surface layer of the skin by electron transitions. Absorption of UV light can cause ionization due to leave electron completely atom or molecule as it has high energy (low wavelenghth).

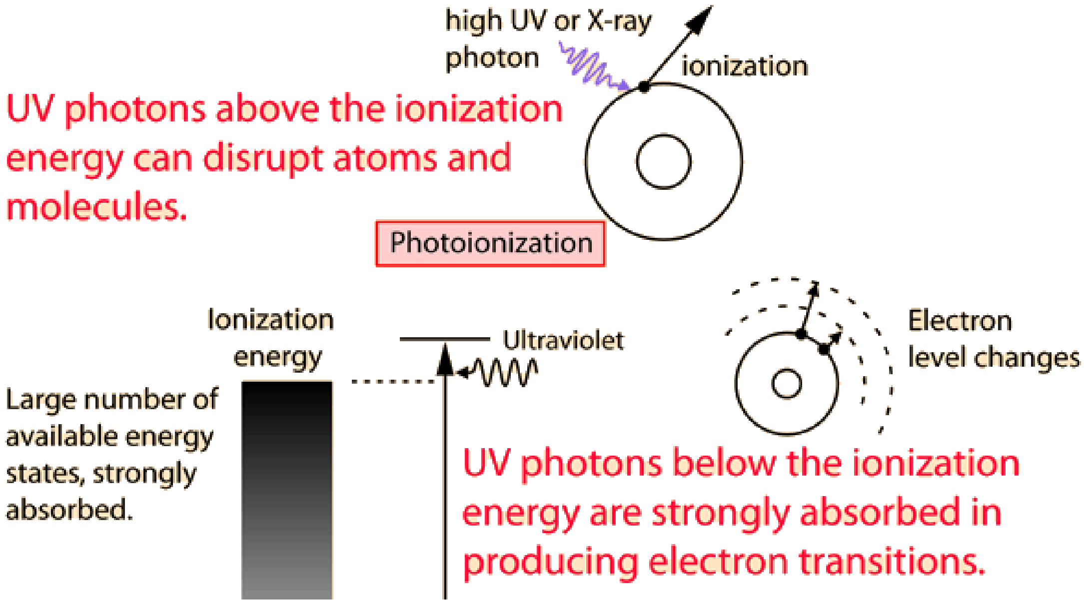

Figure 8: Interaction of UV radiation with matter

o S_o^V + heat$^-$ (ISC)