Chapter one

1.0 Introduction and basic concepts

1.1 *Introduction*

In the last few years, semiconductors compounds have received a great deal of attention because of their importance in some technological applications. Organic semiconductors are used due to fabrication of active and passive solid state devices, the structural flexibility and good optical properties offered by thin films of organic semiconductors.

The study of thin films is very large interesting subject for its wide applications. Thin film techniques provide an advanced approach for reducing the size and weight of electronic assemblies. They have been used for many years in many applications such as mirror surfaces, but their use increased because of the industrial demand for reliable thin film microelectronic devices

Thin films have been used for variety of purposes. They can act as device, when sandwiched between two electrodes forming a capacitor and become active device when sufficient high voltage is applied to thin layers of low conductivity semiconductors in switching phenomena.

One of the important semiconducting compounds with respect to their technological applications is (II-VI) compounds; they are based on the elements in combination with sulfur, and other compounds. It has smaller band gaps and attracted considerable interest for optical applications.

Manganese sulfide (MnS) is important compound of amorphous semiconductors, MnS is a wide band gap ($E_g = 3.1$ eV) semiconductor with potential interest in short-wavelength optoelectronic applications such as in solar selective coatings, solar cells, photoconductors, optical mass memories and dilute magnetic semiconductor [1, 2].

Preparation of MnS has been carried out by different methods such as, thermal evaporation and other methods [3, 4].

In this study, the optical properties of manganese sulfide films that were deposited by the physical vapor deposition technique were investigated. The optical constants of the film were determined from Spectrophotometric measurements of transmittance. The present thesis is devoted to investigate the optical properties of manganese sulfide.

1.2 Importance of the Study:

Who are concerned with the those field of optical properties of thin films, and the problems associated with them, shows that the most popular and important way to prepare thin films are the ones which depends on chemical and physical evaporation. The optical properties of the samples which are obtained by studying the interaction of them with light can be utilized to make these films acts as filters beside other applications.

1.3The aim of the study:

The aim of this study is to investigate the following aspects concerning the MnS thin films:

1. The effects of thermal treatment of MnS thin films and its optical properties which substrates by Physical Vapor deposition.
2. Characterization (Transmission and Absorption) of MnS thin films, using Ultraviolet-Visible spectrometer and Michelson interferometer.
3. To find the thickness of manganese sulfide thin films.

1.4 Procedures of the study

This study is based on analytical and experimental technique to determine the optical properties of manganese Sulfide, so as to see their applications which employed in the production of multitude products and many others in electro optical field.

1.5 Sample study:

The samples are selected especially so as to do some tests and experiments to determine their properties which can be applied in different areas.

1.6 Thesis out line:

This study includes five chapters,chapter one includes the introduction, research plan and basic concepts of the work.Chapter two deals with theoretical background of the study, and thin film deposition techniques. Chapter three deals with thin films semiconductors , optical and mechanical properties of thin films characterizations and some application of thin films. Chapter four concerns with apparatus experiment procedure, sample study and experiment, methods of thickness measurements Setup and deposition of MnS films.

Finally chapter five discusses result of sample experiments, conclusion and future work.

1.7 Basic concepts:

The study of optical components requires knowledge of two disciplines, the physics of light and the physics of matter (mostly solid-state). The study of light is not new. In antiquity, light intrigued many cultures and religions, and at least one ancient religion worshiped light. However some ancient scientists realized that although light had wonderful and unexplained properties, particularly as it passed through colorful crystals, these properties are not caused by divine intervention, but they are real and therefore they could be scientifically explained. This curiosity finally demystified the properties of light. Perhaps the mythological story of Prometheus is an attempt to convey in lay language the message that light is for people to use and understand [5,6].

1. 7.1 the nature of light:

Light is just one portion of the various electromagnetic waves flying through space. The electromagnetic spectrum covers an extremely broad range, from radio waves with wavelengths of a meter or more, down to x-rays with wavelengths of less than a billionth of a meter. Optical radiation lies between radio waves and x-rays on the spectrum, exhibiting a unique mix of ray, wave, and quantum properties. The surprising dual nature of light is a couple, one nature is (electromagnetic) wave and the other nature is particles [6, 7].

1. 7.2 the Wave Nature of Light:

The wave nature of light is the same as that of radio waves and X-ray waves. As such, it is subject to reflection, refraction, diffraction, interference, polarization, fading, loss, and so on. Thus, being an electromagnetic wave, light interacts with any charges that may be present in the neighboring space. Therefore, to measure the force (magnitude and direction) of the electric field of light at any point in space, a theoretical positive charge is introduced at that point. Similarly, to measure the force (magnitude and direction) of the magnetic field, a theoretical elemental magnetic dipole is introduced at that point.

An electromagnetic wave, and thus light, is characterized by frequency and wavelength, as well as by phase and propagation speed with respect to a reference point.

Frequency is the number of peak waves in a second, and wavelength is the traveled distance of a complete wave (e.g., peak-to-peak) in free space or in a medium. The unit for frequency is cycles per second or hertz, and the unit for wavelength is nanometer (nm) or micrometer (mm). An older unit that is also encountered is the angstrom; one angstrom is equal to 10^{-10} meters.

Phase with respect to a reference point is the phase angle difference between the peaks of the wave with that point.

Propagation speed is the distance traveled by a peak of a wave within the unit of time.

Monochromatic light, or single color light, is light that consists of waves that are all of exactly the same "single" frequency. Waves that propagate in space have a spherical front. However, to simplify the mathematical analysis, electromagnetic waves are considered planar. Thus, light is described by the Maxwell's electromagnetic plane wave equations:

$$\nabla^2 E = \left({}^{1}\!/_{\upsilon^2} \right)\left({}^{\eta^2 E}\!/_{\eta t^2} \right) \qquad (1.1)$$

$$\nabla^2 H = \left({}^{1}\!/_{\upsilon^2} \right)\left({}^{\eta^2 H}\!/_{\eta t^2} \right) \qquad (1.2)$$

$$\nabla D = \rho \qquad (1.3)$$

And $$\nabla B = 0 \qquad (1.4)$$

Where ∇ is the Laplacian operator, υ is speed of wave in a medium, E and H are the electric and magnetic fields, respectively, D is the electric displacement vector (its gradient is the charge density p), and B is the magnetic induction vector. These four vectors are interrelated as

$$D = \varepsilon_0 E + \rho \qquad (1.5)$$

$$B = \mu_0 H_0 + M \qquad (1.6)$$

Where ε_0 and μ_0 are the dielectric permittivity and permeability, respectively, both constants of free space, and P and M are the electric polarization and the magnetic polarization of the wave, respectively.

When an electromagnetic wave propagates in a linear (e.g., noncrystalline) medium, the electric polarization is expressed as

$$\rho = \varepsilon_0 \chi E \qquad (1.7)$$

Where χ is the electric susceptibility of the medium (in a nonlinear medium, this is expressed as a tensor); note that in a nonlinear medium, the latter relationship includes higher-order terms.

Moreover, the dielectric constant of the material, ε, is connected with the susceptibility as

$$\varepsilon = \varepsilon_0 (1+\chi) \qquad (1.8)$$

1. 7.3 The Particle Nature of light:

Like all particles, light exerts pressure and causes a wheel to spin (Compton’s experiment). Thus, light is described in terms of number of particles or photons, the smallest quantity of monochromatic light, described by the energy (E) equation:

$$E = h\upsilon \qquad (1.9)$$

Where h is Plank’s constant, 6.626755×10^{-34} (joule-second), and υ is the frequency of light. Visible light (light that human eye can see, such as light from an incandescent light bulb) consists of continuum of wave lengths that span (visible) spectrum from deep red (700nm) to deep violet-blue(400nm) as shown in figure(1.1). In free space, light (of all wavelengths) travels in straight path at constant maximum.

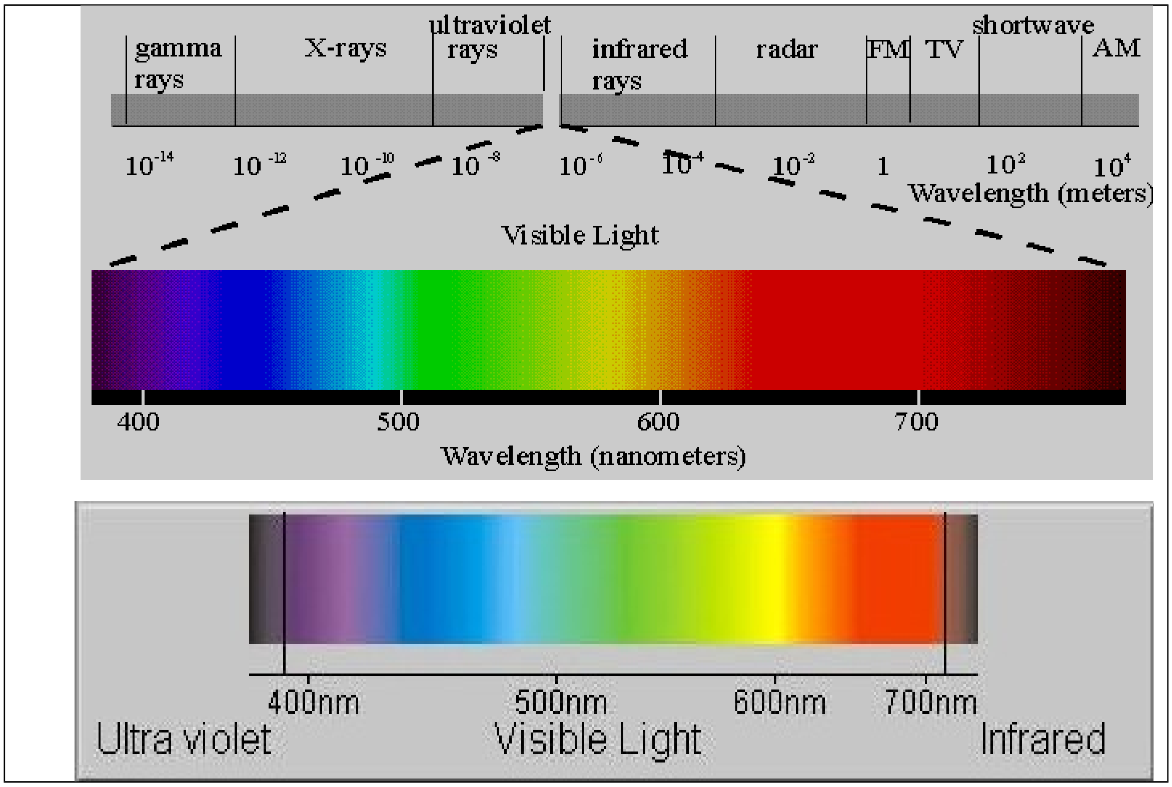


Figure 1.1 the Electromagnetic spectrum.

However, the speed of light changes when it travels in a medium, and this change is not the same for all media or for all wavelengths. By free space it is meant space that is free from matter (vacuum) and free form electromagnetic fields. When light is in the vicinity of a strong electromagnetic field, it interacts with it. From this interaction and other influences, its trajectory changes direction, In fact, in the presence of gravitational fields of cosmic proportions, the trajectory change of light causes a phenomenon known as gravitational Lansing, which is used in astrophysics to detect dark matter and distant galaxies[5].

1.7.4 Regions of the Electromagnetic Spectrum:

The following table gives approximate wavelengths, frequencies, and energies for selected regions of the electromagnetic spectrum; table (1) shows the spectrum of Electromagnetic radiation.

Table 1.1 spectrum of Electromagnetic radiation.

Region	Wavelength (Angstroms)	Wavelength (centimeters)	Frequency (Hz)	Energy (eV)
Radio	10^{9} <	10 <	x 10^{9} 3 >	10^{-5} >
Microwave	$10^{6} – 10^{9}$	0.01 - 10	x 10^{9} - 3 x 10^{12} 3	0.01 - 10^{-5}
Infrared	7000 – 10^{6}	x 10^{-5} 7 - 0.01	x 10^{12} - 4.3 x 10^{14} 3	2 – 0.01
Visible	4000 – 7000	7x10^{-5} - 4x10^{-5}	x10^{14} - 7.5x 10^{14} 4.3	3 – 2
Ultraviolet	10 – 4000	x 10^{-5} - 10^{-7} 4	x 10^{14} - 3 x 10^{17} 7.5	10^{3} - 3
X-Rays	0.1 - 10	10^{-9} - 10^{-7}	x 10^{17} - 3 x 10^{19} 3	10^{5} - 10^{3}
Gamma Rays	0.1 >	10^{-9} >	x 10^{19} 3 <	10^{5} <

1.7.5 The Power of Light:

In quantum theory the watt (W), the fundamental unit of optical power, is defined as a rate of energy of one joule (J) per second. Optical power is a function of both the number of photons and the wavelength. Each photon carries an energy that is described by Planck’s equation:

$$E = \frac{hc}{\lambda} \tag{1.11}$$

Where E is the photon energy (joules), h is Planck’s constant (6.623 x

10^{-34} J s), c is the speed of light (2.998×10^8 m s^{-1}), and λ is the wavelength of radiation (meters). All light measurement units are spectral, spatial, or temporal distributions of optical energy. Short wavelength ultraviolet light has much more energy per photon than either visible or long wavelength infrared [8].

1.7.6 Transparent and Opaque Matters:

Some matters and phonons allow most optical energy to propagate through it, and the matter in this case is called optically transparent. In contrast, some dense matters absorb light within the first few atomic layers and are called non-optically transparent or opaque matter ,they scatter and absorbs the photons: for example :compare clear glasses or water with a sheet of metal.

Some matters passes a portion of optical energy through it and absorb 50%, and is called semitransparent matter. Such matter attenuates the optical power of light and may be used in optical devices known as optical attenuators. Like most of transparent matters, semitransparent mirrors. Some matters allow selected frequencies to propagate through and is called an optical filter. Like: red, green, yellow, or blue glass. Some matters in an ionized state absorb selected frequencies and pass all others. Example: most transparent matter, semitransparent mirrors. Some matters permit rays with certain polarization to propagate through and absorb or reflect the others; it is called a polarizing filter. For example: polarizing sunglasses.

Some matters emit photons when it is illuminated with light of another shorter wavelength. Example: most minerals under UV light; fluorescent substance, erbium, and so on.

1.7.7 Homogeneity and Heterogeneity:

A homogeneous optically transparent medium has the same consistency (chemical, mechanical, electrical, magnetic, or crystallographic) throughout its volume and in all directions.

A heterogeneous optically transparent medium does not have the same consistency (chemical, mechanical, electrical, magnetic, or crystallographic) through out its volume [5].

1. 7.8 Organic Materials:

Besides inorganic compounds such as traditional crystals and oxides, there is a growing interest in organic compounds. Organics promise components that can be easily manufacturable in large quantities and thus at low cost. Certain compounds can be deposited to virtually any type of other material such as glass, plastic, and treated paper. For example, consider organic compounds that can be made into optical organic thin films (OTF). Based on fluorescence properties, when a voltage excites their molecular state, they emit light of a specific wavelength, known as exciton. The duration of light emission of such compounds is on the order of many microseconds. Among these compounds is perylene, which emits blue light; and other compounds that emit different colors. These compounds have high luminescent efficiency at a wide angle.

Thus, optical organic thin films may find several optoelectric applications, Such as flat thin displays with transparent electrical contacts made of titanium oxides or indium tin oxide (ITO) by deposition.

Other organic compounds, such as pentacene, have electrical properties that are suitable for producing field-effect transistors. Pentacene is a simple molecule made of five connected benzene rings that form crystals. These compounds may be applicable to portable devices, communications, electronic identification, and others.

In a different endeavor, organic matter is used to extract compounds that can be used in optical and semiconductor fields. For example, corn is used to extract compounds that can be turned into plastic films. Rice hull or coconuts are rich in silicon dioxide, or silica, which can be used for semiconductors or in devices with specific properties. Obviously, the world of organics holds many secrets for the near future [5, 8].

1. 7.9 Interaction of Light with matter:

When light meets matter, its electromagnetic field interacts with the near fields of ions and electrons, and depending on consistency and the structural details of matter interactions take place that may affect the light properties, the material properties, or both. In fact, in many cases light affects matter, which in turn affects light [8, 10].

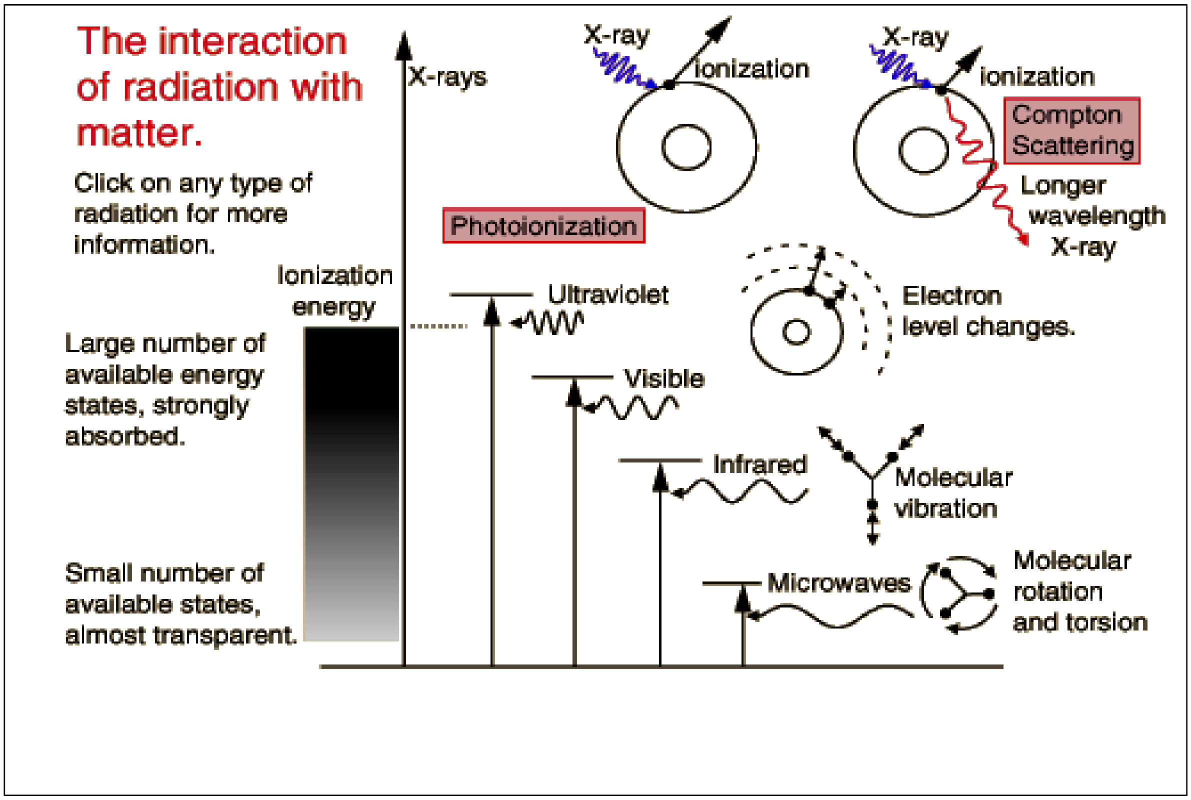


Figure 1.2 the interaction of radiation with matter.

1. 7.10: 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 the molecular rotation and torsion. The interaction of microwaves with matter other than metallic conductors will be to rotate molecules and produce heat as a result of that molecular motion as shown in figure 1.3. Conductors will cause electric currents which will heat the material. Most matter, including the human body, is largely transparent to microwaves. High intensity microwaves, as in microwave oven where they pass back and forth through the food millions of times, will heat the material by producing molecular rotations and torsions. Since the quantum energies are a million time slower than those of x-rays, they cannot produce ionization and the characteristic types of radiation damage associated with ionizing radiation.

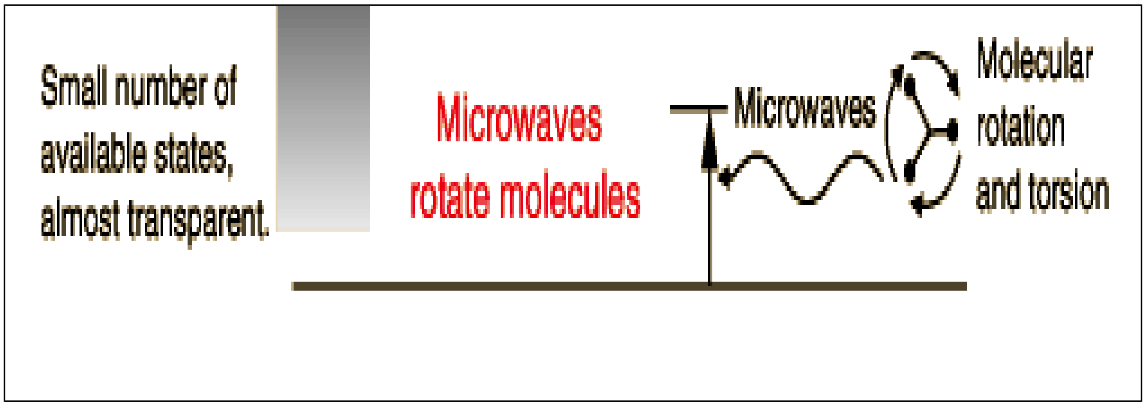


Figure 1.3 Microwaves interactions.

1. 7.11: Infrared interaction:

The quantum energy of infrared photons is in the range 0.001 to 1.7eV 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 tissue since it increases molecular vibration activity. Infrared radiation dose penetrate the skin further than visible light and can thus be used for photographic imaging of subcutaneous blood vessels [5, 6].

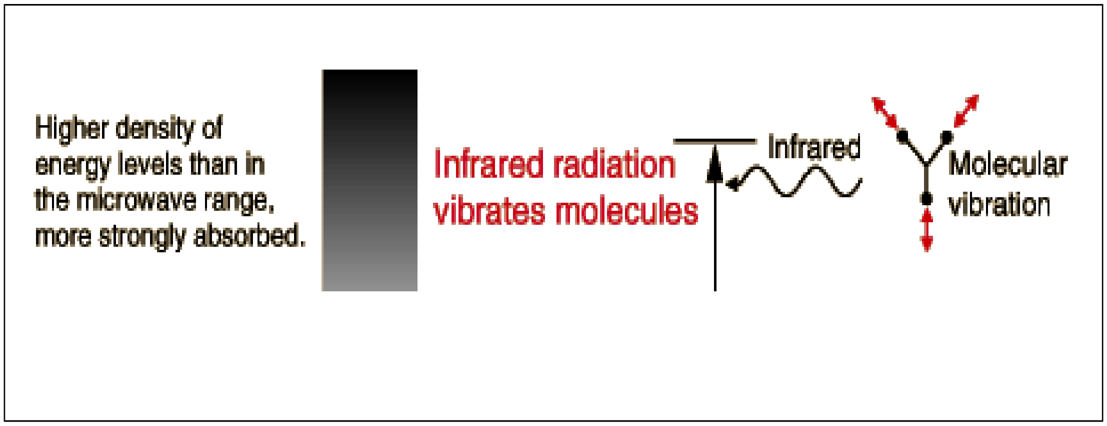


Figure 1.4: Infrared interaction.

1. 7.12 Visible light interactions:

Primary mechanism for the absorption visible light photons is the elevation of electrons to higher energy levels. There are many available states, so visible light is absorbed strongly. With a strong light source, red light can be transmitted through the hand or a fold of skin, showing that the red end of the spectrum is not absorbed as strongly as the violet end. While exposure to visible light causes heating, it does not cause ionization with its risks you may be heated by the sun through a car windshield, but you will not be sunburned-that is an effect of the higher frequency UV part of sunlight which is blocked by the glass of windshields [5, 6].

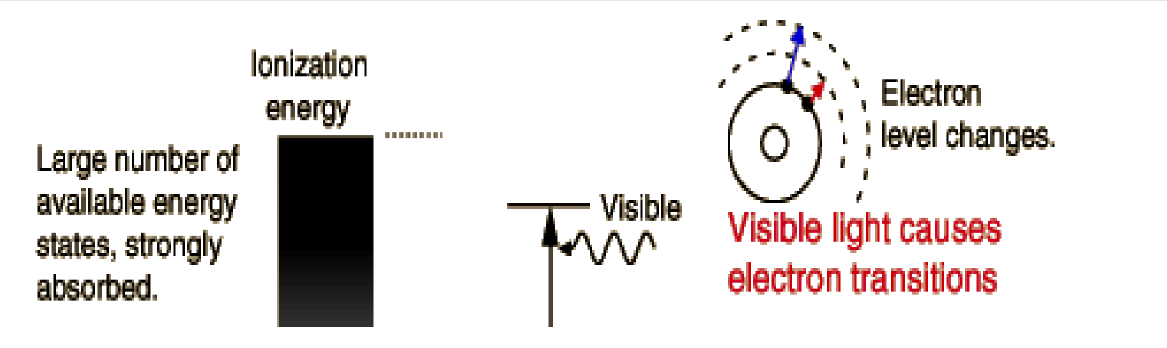


Figure 1.5 Visible interactions.

1. 7.13 Ultraviolet interactions:

The near ultraviolet is absorbed very strongly in the surface layer of skin by electron transition. As you go to higher energies, the ionization energies for many molecules are reached and the more dangerous photo ionization processes take place. Sunburn is primarily an effect of UV, and ionization produces the risk of skin cancer.

The ozone layer in the upper atmosphere is important for human health because it absorbs most the harmful ultraviolet radiation from the sun before it reaches the surface. The higher frequencies in the ultraviolet are ionizing radiation and can produce harmful physiological effects ranging from sunburn to skin cancer.

Health conveners' for UV exposure are mostly for the range 290-330nm in wave length, the range called UVB. According to Scotto, et al, the most effective biological wavelength for producing skin burns is

297nm.Their research indicates that the biological effects increase logarithmically within the UVB range, with 330nm being only 0.1% as effects as 297nm for biological effects. So it is clearly important to control exposure to UVB [9, 10].

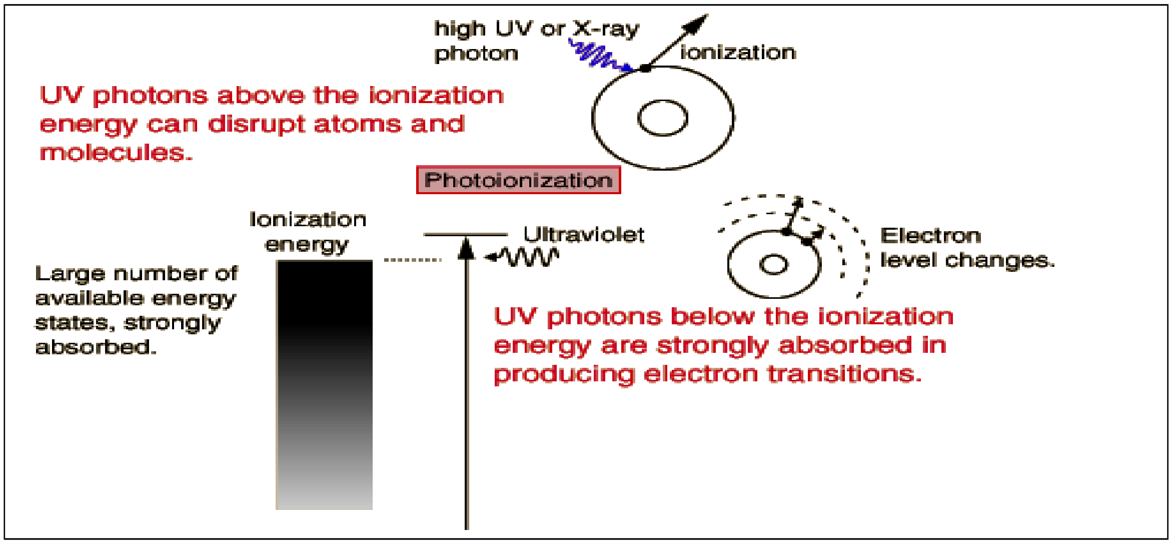


Figure 1.6: Ultraviolet interactions.

1. 7.14 X-ray interactions:

Since the quantum energies of x-ray photons are 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-ray are classified as ionizing radiation. This can occur by giving all of the energy to an electron 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 [9, 10].

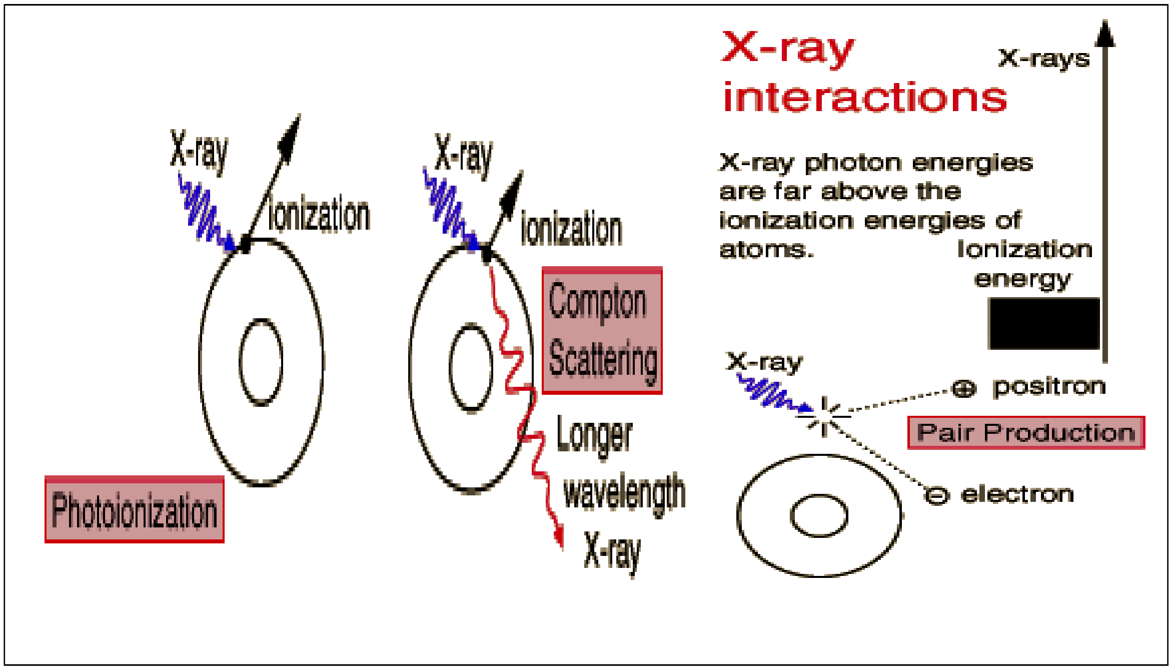


Figure 1.7 X-ray interactions.

1.7.15 Absorption:

Absorption is the processes by which incident radiant flux is converted to another form of energy, usually heat. Absorbance is the fraction of the incident flux that is absorbed. An absorption coefficient (α) in (cm^{-1}) is often used in the expression

$$\tau_i = e^{-\alpha x} \qquad (1.12)$$

Where τ_i internal transmittance and (x) is path length (cm).
In most Cases, absorbance is not directly measured, but is interfered from transmission measurement, with appropriate correction for reflection losses. These corrections can be calculated from the Fresnel equation if the surfaces are polished and the index of reflection is known. For materials

where the absorption is extremely small, this method is unsatisfactory, as the uncertainties are dominated by the reflection contribution [11].

1.7.15 .1 Beers-Lambert law:

In beers-Lambert law, absorption is observed as decrease of the photons in the beam while transmitting in the material. In linear optics the incremental decrease of the intensity *I*, and when absorption coefficient (α) measured in cm^{-1}:

$$I = I_0 e^{(-\alpha x)} \qquad (1.13)$$

$$A = -\log \frac{I}{I_0} \qquad (1.14)$$

And $\alpha = (h\nu - E_g)^{\frac{1}{2}}$ (1.15)

$$\alpha = \frac{1}{x} \ln(T) \qquad (1.16)$$

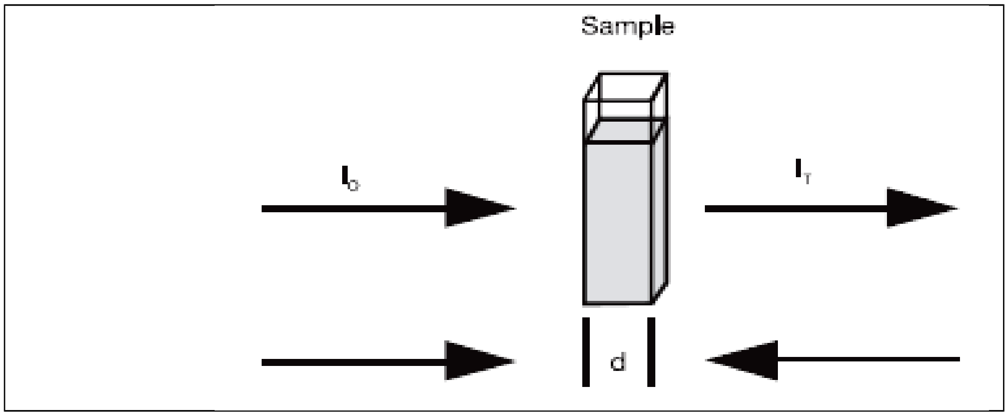


Figure 1.8: Linear absorption of light in a sample of thickness.
In this figure the sample, (d) represent the thickness x.

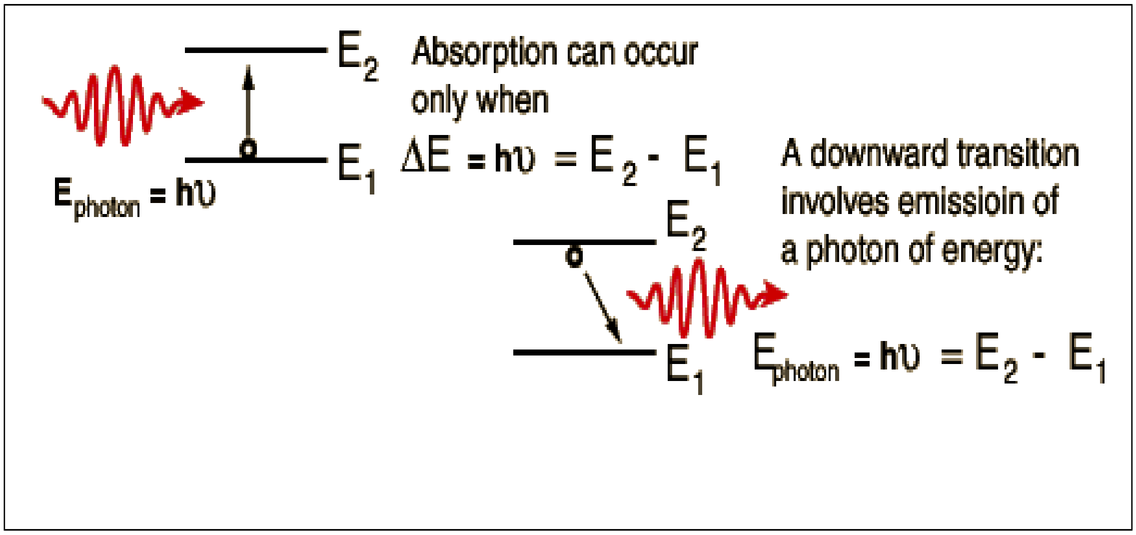


Figure 1.9: Schematic diagram as illustration absorption coefficient of light.

For determining, the incident intensity (I_o), and the transmitted intensity (I) have be measured. The quotient of these is the transmission or transmittance T:

$$T = \frac{I}{I_o} \qquad (1.17)$$

It can be shown that for absorption or emission of phonons, the material has to perform a transition between two eigen-states E_m and E_p of the material and thus the photon energy has to fulfill the resonance condition as below:

$$E_{photon} = h\nu_{photon} = \left(E_p = E_m\right) \quad E_{photon} \qquad (1.18)$$

1. 7.16 Emittance:

Emittance is the ratio of the radiance of an object or surface to the radiance of a black body at the same temperature. It is therefore dimensionless and can assume values between 0 and 1for thermal radiators at equilibrium. Spectral emitance ε (λ) is the emittance at a given wavelength. If a radiance is natural with respect to wavelength, with a constant spectral emittance less than unity, it is called a gray-body.

$$\varepsilon = \frac{L}{L^{bb}} , \varepsilon(\lambda) = \frac{L_\lambda}{L_\lambda^{bb}} \qquad (1.19)$$

Where: L is radiance of object or surface. And L^{bb} is radiance of black body. If the body is non–gray, its emittance is dependent upon temperature in as much as the integral must be weighted by the source (Planck) function[11].

1. 7.17 Emission Spectra:

The emission of radiation is also governed by the F.Condon principle since what is probable for absorption must be probable for emission. In case of atoms or simple molecules at very low pressures where coalitional perturbation are absent, the excited species may return to the ground state directly by emitting the same frequency of radiation as it has absorbed. This is known as resonance radiation, the mercury resonance radiation at 253 nm in due to such transitions [12].

For polyatomic molecules and molecules in the condensed state, the excess vibrational energy gained in vibration-coupled electronic transition, is quickly lost to the surrounding in a time period=10^{-34} s. The molecule comes to stay at the zero vibration level of the first excited state for about 10^{-8}s for an allowed transition and more for a partially forbidden transition. If it's permitted to return to the ground state by radiative transition, fluorescence emission is observed. On the return transition, it again follows the Franck-Condon principle and arrives at a higher vibrational level of the ground state. Because of the nature of wave function in v=0 state and the Boltzmann distribution of energy in the excited state, there is distribution of frequencies around the most probable transition. The most probable transition again depends of on the inter- nuclear equilibrium geometries of the molecules in the two states.

1.7.18 The relation between transmittance, reflectance,and absorbance:

Radiant flux incident upon surface or medium undergoes transmission, reflection, and absorption. Application of conservation of the energy leads to the statement that the sum of the transmission, reflection and absorption of the incident flux is equal to unity, or:

$$\alpha+\tau+\rho=1 \qquad (1.20)$$

In the absence of nonlinear effects:

$$\alpha(\lambda)+\tau(\lambda)+\rho(\lambda)=1 \qquad (1.21)$$

If the situation is such that one of the above relations is applicable, then emittance ε may be substituted for absoptance (α) in the previous equations, or;[9]

$$\varepsilon = 1 - \tau - p \quad , \varepsilon(\lambda) = 1 - \tau(\lambda) - p(\lambda)$$

(1.22)

1.7.19 Reflection and refraction: Snell's law:

When a ray impinges on an angle the planar interface of two homogeneous transparent media (free space and glass), apportion of it will be reflected and the remainder will be refracted as shown in figure 1.10

The index of refraction of a transparent medium (n_{med}) is defined as the ratio of the speed of monochromatic light in a medium (υ_{med}):

$$n_{med} = \frac{c}{v_{med}} \qquad (1.21)$$

Then, betwee*n* two mediums, the relationship is true:

$$\frac{n_2}{n_1} = \frac{v_1}{v_2} \qquad (1.23)$$

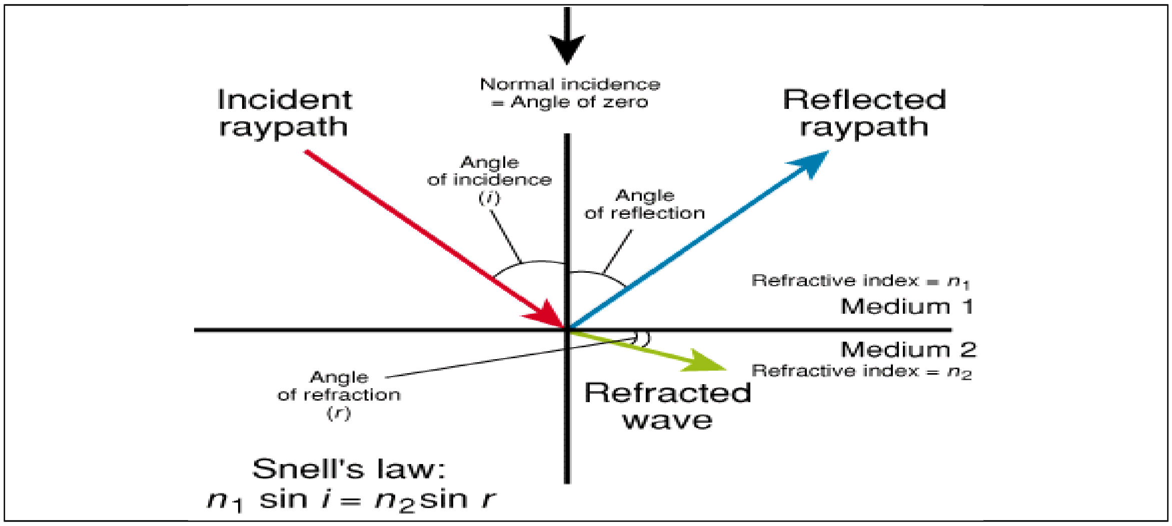


Figure 1.10 Reflection and refraction of normal incidence.

And $$n_1 \cos\beta = n_2 \cos\alpha \qquad (1.24)$$

Where n_1,v_1, and n_2,v_2 are the index of refraction and the speed of light in the two media, and α and β are the angle of incidence and the angle of refraction with respect to the surface of incidence, respectively.

When the angle of incident is very small, $\cos\alpha = 1 - \frac{\alpha_2}{2}$ and the cosine equation becomes:

$$n_1\left(1-\frac{\beta^2}{2}\right) = n_2\left(1-\frac{\alpha^2}{2}\right) \qquad (1.25)$$

The index of refraction, for free space has the numerical value of 1, whereas for other material it is typically between1and 2, and in some cases it is greater than 2or 3. The reflected portion of monochromatic light is known as Fresnel reflection. The amount of reflected power and the polarization state of the reflected light depend on the polarization state of the incident light, the angle of incident, and the refractive index difference. For normal equation

$$p = \frac{(n-1)^2}{(n+1)^2} \qquad (1.26)$$

if the absorption of the material over a length d is A, which is calculated from the absorption coefficient α, then the internal material transmittance, t_i, is defined as the inverse of the material absorption. For internal transmittance is given by

$$\tau = \left((1-p)^2 \tau_1\right) / \left(1 - p^2 \tau_1^2\right) \qquad (1.27)$$

The following basic relationships are also useful:

Speed of light in space: $c=\lambda f$

Speed of light in medium: $v_{med} = \lambda_{med} f$

Index of refraction:
$$\frac{n_1}{n_2} = \frac{\lambda_2}{\lambda_1} \qquad (1.28)$$

Where f is the frequency of light and λ is its wave length. Both the letter λ and the Greek ν are used for frequency. We use f to eliminate confusion between v (free speed) and ν (frequency).

Snell's law relates the ratio and of index of refraction with the angle of the incident and with the refracted rays [11].

$$\frac{n_2}{n_1} = \frac{\sin\theta_i}{\sin\theta_t} \qquad (1.29)$$

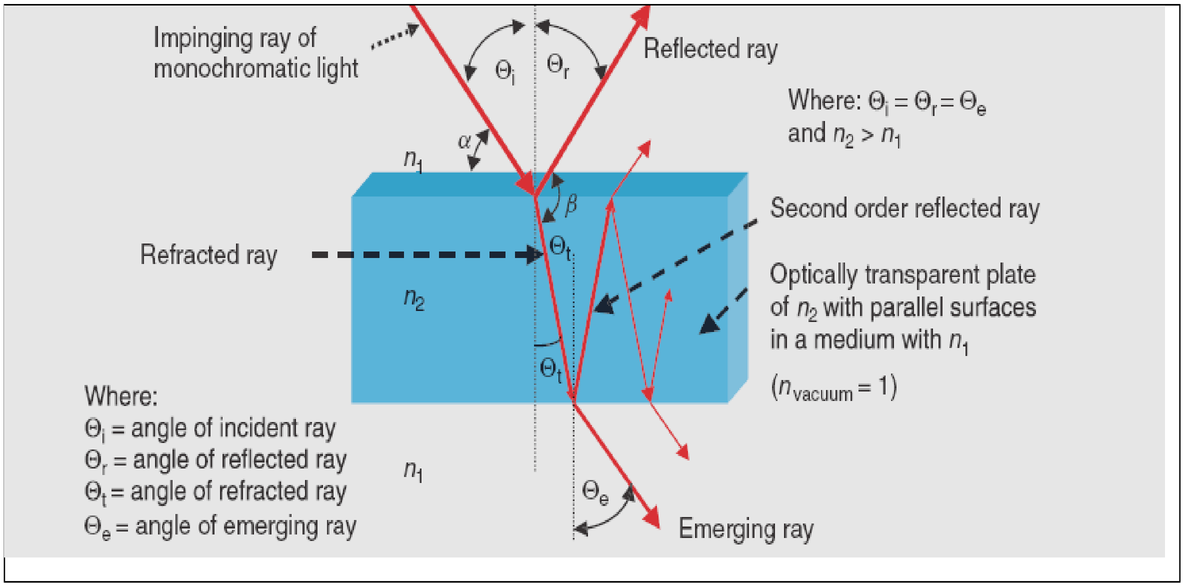


Figure 1.11 Reflection and refraction of monochromatic light.

1.7.20 Critical angle:

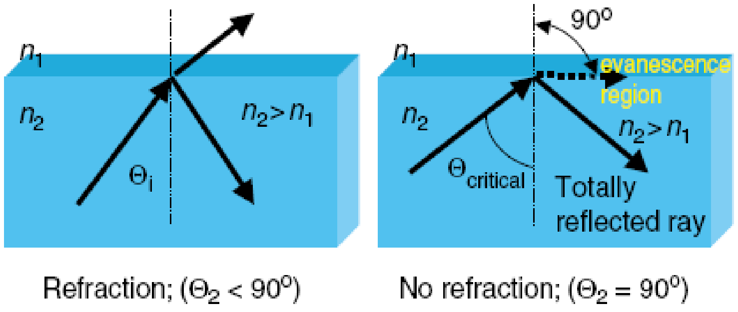
Critical angle $\Theta_{critical}$, is the maximum angle of incident of light from a material with high to low refractive index at which light stops being refracted and is totally reflected. As the angle incidence approaches the critical angle, the refracted ray becomes parallel to the surface without added phase shift, and is termed evanescent. Beyond that point, there is no refracted ray. The critical angle depends on the refractive index and the wave length of light.

In certain case, a gradual variation of refractive index may take place. When light rays enter from one side, rays are refracted such that they may emerge from one side; rays are refracted such that they may emerge from the entered. This is the case of the natural phenomenon known as a mirage

$$\text{Sin } \Theta_{critical} = \frac{n_2}{n_1} \qquad (1.30)$$

For n1 =1(air), then:

$$\text{Sin } \Theta_{critical} = \frac{1}{n_2} \qquad (1.31)$$



Refraction; ($\Theta_2 < 90^o$)

No refraction; ($\Theta_2 = 90^o$)

Figure 1.12 definition of critical angle.

Although to this day the index of refraction has been considered to be only positive and greater than +1, the value of vacuum, researches and theoreticians have been trying to learn, what would have happen to light if there where materials with negative values would solve several issues in optics and would find several important applications in the optics and photonic areas [5].

1. 7.21 Dispersion:

Dispersion corresponds to the phenomenon whereby the index of refraction of a medium is frequency dependent. All material media are dispersive, only vacuum is non-dispersive.

Maxwell’s theory treats substantial matter as continuous, representing its electric and magnetic responses to applied ($\vec{E}$) and ($\vec{B}$) fields in terms of constants,(ε) and (ε).To deal theoretically with dispersion, it’s necessary to incorporate the atomic nature of matter and to exploit some frequency-dependent aspect of that nature [8].

1. 7.22 Scattering:

Light scattering is a term referring to physical processes involving the interactions of light and matter. Due to this interaction light incident on an ensemble of particles –crystals, molecules, atoms etc. is partially deflected in directions deviating from the incident direction. Scattering of lights is generally rather complex. In order to facilitate the understanding of the processes involved simplified models are usually used to describe the specific effects of any regarded physical process. Scattering involves both the properties of the light and radiation and those of the matter encountered. Wavelength and polarization of the light and depending on the size and structure of the matter with diffraction, refraction or absorption and re-emission of light energy by an oscillator (matter).

There are several possibilities to classify the various scattering processes. Here the distinction between elastic and inelastic scattering is made.

1.7.22.1 Elastic scattering:

An elastic scattering process refers to an interaction without a permanent exchange of the energy between the light and the matter. This means after the matter in the same state of energy as before and the energy contained in the light leaving the point of interaction is equal to the energy of the incident light. This restriction of equal energy does not prohibit a change in direction, but according to Planck's low it dose prohibit a change in frequency (wavelength).

1.7.22.2 Inelastic Scattering:

An inelastic process, on the other hand, is connected with a permanent energy exchange. The energy content of the matter after the interaction is higher or lower than in the original state. Due to the conservation of total energy, the energy of the emitted radiation is changed as well, resulting in a change of frequency (wavelength).

The fluorescence and absorption are actually not real scattering processes. However, both methods are very closely connected to the scattering processes and are widely used in heat and mass transfer investigations. The only real inelastic scattering process that has received much attention in this field is Raman scattering [13].

1. 7.23 Bragg’s law:

The Bragg law is the cornerstone of XRD analysis. It allows us to make accurate quantification of the results of experiments carried out to determine crystal structure. It was formulated in 1912 by W L Bragg, in order to explain the observed phenomenon that crystals only reflected X-rays at certain angles of incidence.

An X-ray incident upon a sample will either be transmitted, in which case it will continue along its original direction, or it will be scattered by the electrons of the atoms in the material, see figure 1.1. All the atoms in the path of the X-ray beam scatter X-rays. In general, the scattered waves destructively interfere with each other, with the exception of special orientations at which Bragg's law is satisfied [8].

Consider a simple crystal such as that illustrated in figure 1.13, with lattice planes separated by a distance d_{hkl}. As illustrated above, the scattered X-rays from this crystal will travel in random directions. A Bragg condition is such that the scattered rays from two parallel planes interact with each other in such a way as to create constructive interference. For this to happen the extra distance travelled by ray B, figure 1.13, must be an exact multiple of the wavelength of the radiation. This means that the peaks of each wave are aligned with each other [14].

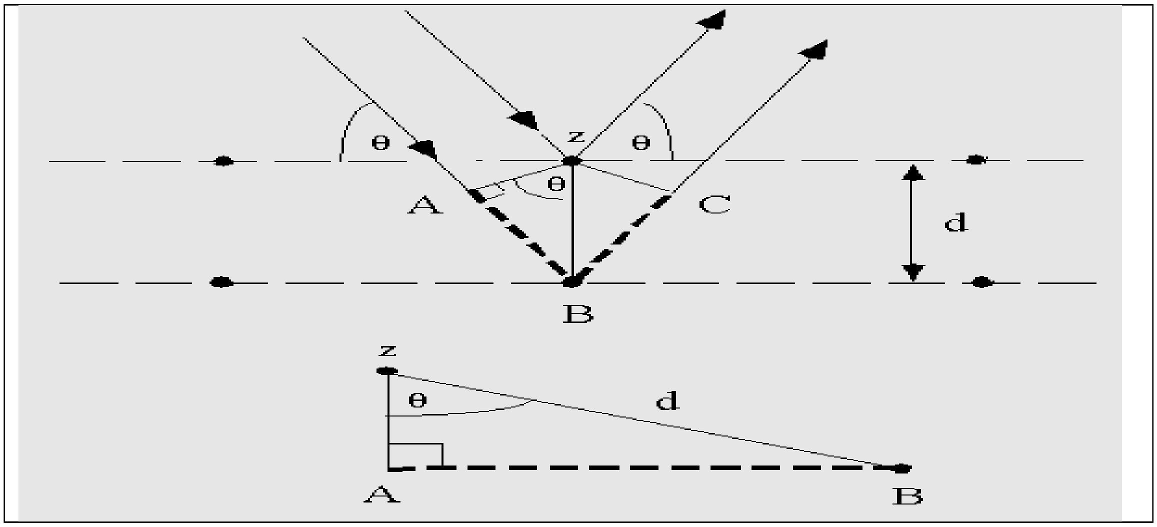


Figure 1.13 Schematic diagram as illustration to derive Bragg’s Law [7, 15].

The geometry of the Bragg condition is remarkably simple, and leads to the powerful result of the Bragg law. The extra distance that ray B must travel is the distance X-Y-Z. In order to consider the general case of hkl planes, the equation can be rewritten as:

$$n\lambda = 2d_{hkl}\sin\theta \qquad (1.32)$$

Since the d_{hkl} incorporates higher orders of diffraction i.e. *n* greater than 1. The angle between the transmitted and Bragg diffracted beams is always equal to 2Θ as a consequence of the geometry of the Bragg condition. This angle is readily obtainable in experimental situations and hence the results of X-ray diffraction are frequently given in terms of 2λ. However, it is very important to remember that the angle used in the Bragg equation must always be that corresponding to the angle between the incident radiation and the diffracting plane, i.e. 2d. The source of the X-rays incident on the sample, consists of an evacuated tube in which electrons are emitted from a heated tungsten filament, and accelerated by an electric potential (typically several tens of kilovolts) to impinge on a metal target.

The interaction between the electrons and the target leads to the emission of X-rays: Some was having a wavelength characteristic of the target, and some having a continuous distribution of wavelengths between about 0.05 nm and 0.5 nm (the so-called "white radiation"). For most experiments, characteristic radiation is selected (using a filter or Bragg reflection from a suitable crystal) because of its intensity and accurately known wavelength [7, 14].