**(2-3) Optical Absorption Spectroscopy**

The change is the energy of a molecule upon absorption of electromagnetic radiation is given by [62]

(2.7)

where is the spacing between allowed electronic energy levels, is the spacing between allowed vibrational energy levels,( values are generally about 10 times less than values) , is the spacing between allowed rotational energy levels( values are generally about 10 or 100 times less than values) and is thespacing between allowed translational energy levels( values areextremely small and are unimportant in apsorption spectroscopy).

The rotational spectrum of a molecule is associated with changes in its rotational states without simultaneous changes in the vibrational and electronic states. The separation of the rotational energy levels is of the order of a few hundredth of one eV, and this results in absorption in the far infrared spectrum(nm) [63].

The vibration and vibration-rotation spectrum of a molecule is associated with the changes which occur in the vibrational states if the molecule without simultaneous changes in the electronic states but generally are accompanied by changes in rotational states. The spacing of vibrational energy levels is of the order of a few tenth of one eV and vibrational spectra occure in the near and middle infrared regions.

Electronic spectra arise from transitions between electronic states. Sush transitions are accompanied with simultaneous changes in the vibrational and rotational state. The molecular electronic spectra usually occur in the ultraviolet and visible regions.

Very few pure polymers absorb radiation in the visible spectrum ,that is, roughly between 380 and 760 nm. Thus most polymers are colorless. The absorption of light by macromolecules occurs only if the difference between two energy levels is exactly equal to the energy of a quantum:

(2.8)

where h is planck’s constant, v is the photon frequency, and are the energies of a single macromolecule in the final and initial states respectively.

**(2-3-1) Beer lambert law**

In spectrophotometric practice, qualitative analysis is based on the application of the beer lambert law, which is given by[64]:

( 2.9 )

where is the incident radiation intensity, is the transmitted intensity, T is the transmittance, is the molar absorptivity(molar absorption coefficient), c is the sample concentration and x is the thickness of the absorbing cell. The term log (I/I0) is called absorbency (A) of the sample also called the optical density (D) or extinction coefficient (E). The absorbency (extinction) is an accumulative property for a mixture of two or more components:

(2.9)

**(2-4) Optical Transitions in Amorphous Solids**

The study of the optical transitions of the materials is interesting for many reasons. Firstly, the use of these materials in optical application requires accurate knowledge of their optical constants over a wide range of wavelength, secondly analyzing the absorption edges provides valuable information about the electronic band structure of these materials.

According to Tauc [65] it is possible to isolate three distinct regions in the absorption adge spectrum in amorphous solids, as shown in Fig.(2- 6): the weak absorption tail(A) which originates from defects and impurities, the exponential edge region (B) which is strongly related to the structural randomness of the system, and the high absorption region(C)which determines the optical energy gap.

In the part(A),below the exponential part(where cm-1),the absorption is very weak and its strength and shape were found to depend on the preparation, purity and thermal history of the material even if the material is in the bulk form rather than as a thin film. It is difficult to study the week absorption tail in thin films because of the low absorption levels.

In the exponential region of the absorption edge(part B: where cm-1),the absorbance coefficient can be described by the following relation[66] :

(2.11)

Where is the pre-exponential factor, hv is the energy of the incident photon and characterizes the slope of the exponential edge region.Plotting the dependence of ln() vs E should gives the width of the localized states tails at the band gap.

In the high absorption region (part C: where cm-1), the absoption constant () has the following frequency dependence:

(2.12)

where B is a constant, is the optical band gap of the spectrum and n is an index which has a value of 2,31/2 and 3/2[67] depending on the nature of electronic transition for the absorption.

In the high absorption region, the optical absorption in amorphous materilals behaves in the same way as of crystalline materials. In this region the fundamental absorption takes place when one electron is excited, by absorption of a photon, from its location in the valance band to the conduction band. The location in k-space of the maximum valence band energy (Ev) may or may not correspond to the location in k-space of the minimum conduction band energy (Ec). When such a coincidence does occur(at the center of the zone or elsewhere) the solids is said to have a direct intrinsic gap. The significance of the term "direct gap"is that a photon of the special energy hv= Eg= (Ec - Ev) can excite an electron from the top of the filled band directly to one of the states at the very bottom of the conduction band, in a transition which is vertical in k-space as shown in Fig.(2-7.a). Any photon with energy somewhat larger than Eg can participate in a direct (vertical) transition such as those shown as dashed arrows in Fig.(2-7.a). The optical absorption coefficient () would have the spectral dependence of the frequency (v) in this case by the relation[67],

(2.13)

Where C is a constant proportional to the joint density of states in the valance band and conduction band and is dependent on the details of the band structure.

Non –direct transition can occur in amorphous solid for which the highest valence band energy does not occur at the same place in k-space as the lowest conduction band energy as shown in Fig.(2-7.b). If the incident photon energy exceeds ED-EV, the electron-hole pairs of the minimum creation energy cannot be produced in one-step (direct) optical process. However, as suggested by Bardeen et at.[68], non-direct transition can occur in such cases via an intermediate virtual state, whereby photonabsorption is accompanied by either the creation of or annihilation of a lattice vibrational phonon . This model requires a minimum photon energy of (Eg+k0 ) for non-direct transition which creates a hole electron pair and a phonon of energy (k0 ) and momentum h(kC-kV). An alternative process,in which a photon is absorbed and a phonon is also absorbed in pair creation, can proceed from the lower threshold energy (Eg- EV).According to this model the absorption coefficient() can be given by the relation[68],

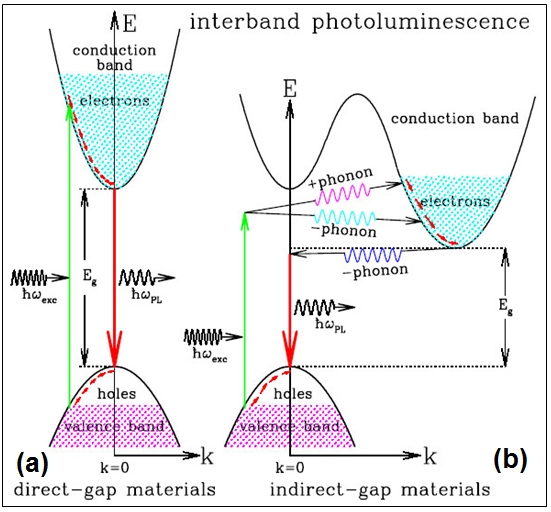
(2.14)

**(2-5) Jablonski Diagram**

When a molecule absorbs energy in the form of electromagnetic radiation, an electron is excited to a higher energy level (S1 or S2), it can return to the ground state (S0) by a number of routes with emission of light. This process is known as luminescence. Luminescence can be schematically illustrated with the classical Jablonskidiagram (Fig.(2-8), which was firstly proposed by Alexander Jablonskiin 1935[69].

There are three main types of luminescence described below:

1. Fluorescence: This occurs if the electron decays immediately from S1 to S0. An electron in the excited state is paired anti–parallel with an electron in a ground state so the return of this electron is spin allowed and hence the emission of a photon is very rapid. The time scale for fluorescence is 10-9-10-7 sec.

**Fig.(2-7): Energy versus wave vector for,**

1. **Direct transition (b) Non direct transition**
2. Phosphorescence: Occurs when the electron in the excited state S1undergoes a spin conversion and jumps to a forbidden triplet excited state T1 (intersystem crossing) then emission from the excited triplet state occurs with lower energy (longer wavelength) relative to fluorescence. It is a forbidden transition hence the time scale is longer as compared to fluorescence (10-3-102 sec).
3. Delayed Fluorescence: Occurs when the electron first decays into the triplet state and then crosses back over into the lowest singlet excited state before returning to the ground state.

Most organic molecules that emit light, including π-conjugated ligands, do so from singlet excited states; therefore the emission is a spin allowed process termed fluorescence. The d6 and d8 second and third row transition metal ions [Re(I), Ru(II), Os(II), Rh(III), Ir(III), and Pt(II)] can induce intersystem crossing by strong spin-orbit coupling, which means the excited states are a hybrid of singlet (spin allowed) and triplet (spin forbidden) states that leads to the relaxation of spin selection rules. The presence of some triplet contribution leads to slower emission and consequently prolongs the emissive lifetimes. The long lived emission allows time resolved detection methods of analysis to be employed, which gets round the problem of background interference from other fluorescent bio-molecules and also offers the potential for lifetime based sensing and imaging [70].

**(2-6) Photoluminescence Spectroscopy**

Photoluminescence is a radiative emission process from the lowest excited single state (s1) to the single ground state (so) as shown in Fig.(2- 8) . In the following molecular processes, which may compete with Photoluminescence.

**(2-6-1) Fluorescence Quantum Yield**

The ratio of the number of photons emitted by S1 to the number of photons absorbed by So is known as the fluorescence quantum yield, φf .

φF = Number of photons emitted by S1/Number of photons absorbed by So

φf = Rate of emission of photons by S1 /Rate of absorption of

photons by So

The fluorescence quantum yield of a compound may be determined by comparing the area under its fluorescence spectrum with the area under the fluorescence spectrum of a reference compound whose fluorescence quantum yield is known. The spectra of both compounds must be determined under the same conditions in very dilute solution using a spectrometer incorporating a ‘ corrected spectrum ’ capability, in order to overcome any variation in detector sensitivity with wavelength.

Because of Kasha’s rule, the probability of an excited molecule ending up in the lowest vibrational energy level of S1 is very high,irrespective of the energy of the exciting light used. Thus the fluorescence quantum yield is independent of the wavelength of the exciting light ( Vavilov’s rule ).

When a molecule is in the S1 (v = 0) state, fluorescence emission is only one of the several competing physical processes by which the molecule can return to the ground state. A molecule in S1 (v = 0) can undergo fluorescence, intersystem crossing or internal conversion, which have rate quantum yields φf , φisc and φic , respectively and:

φf+φisc +φic =1 (2.15)

If the only process occurring from S1 (v = 0) is fluorescence then φf will be equal to 1, whereas if no fluorescence occurs from S1 (v = 0) then φf will be equal to 0. Thus the fluorescence quantum yield has values between 0 and 1.

In general, because of the relatively large energy gap between S0 and S1, φic is much smaller than φfand φisc ,which implies that φf + φisc≈1 ( Ermolev’s rule ) [71].

**(2-6-2) Stokes Shift**

An examination of the Jablonski diagram reveals the fact that the energy of the emitted photon is generally smaller than the energy of the absorbed photon. This phenomenon was first observed by G. G. Stokes in 1852 [72].

The energy of electronic transition is equal to the energy difference between the starting energy level and the final level. Therefore, the transition energy E (J mol−1) is:

E = hν = hc/λ (2.16)

where h is the Planck constant (h = 6.63×10−34 J · s), ν is the light frequency (s−1 or Hertz, Hz), c is the light velocity, and λ is the wavelength (nm).

The energy absorbed by a fluorophore is more important than the energy of an emitted photon. Referring to Equation (2.16), the absorption energy is

Ea = hc/λa (2.17)

and emission energy is

Eem = hc/λem (2.18)

Since

Eem<Ea

λem>λa

λa and λem are absorption and emission spectra peaks.Thus, the emission spectrum has its maximum shifted to longer wavelengths compared to the maximum of absorption spectrum [Fig.(2-9)]. Sir George Stokes observed this shift for the first time in 1852 and since this time it is called the Stokes shift. When absorption and/or the emission spectra of a fluorophore possess two or more bands, the Stokes shift is equal to the difference that separates the two most intense bands of the two spectra.

The stokes shift( ) is equal to [73]:

= (2.19)

Energy losses between absorption and emission are always observed in fluorescent molecules in solution. They are mainly due to the rapid decay of the singlet S1 to its lowest vibrational level. Also fluorescence transitions generally end up in higher vibrational levels of So, reducing further the absorption energy.Further Stokes shifts may be due to solvent effects, excited state reactions and energy transfer [72].

**(2-6-3)The Fluorescence Intensity**

The fluorescence intensity (If) from the solution can be calculated from the Beer-Lambert law[64]:

(2.20)

Where is the is the fluorescence intensity, is the geometrical factor which is determined by the solid angle of the fluorescing radiation subtended by the detector and defines the efficiency of the detector as of the fluorescent wavelength incident on it. Equation (2.20) can be simplified to,

(2.21)

where is the intensity of the incident light, is the molar absorptivity (molecularextinction coefficient ), c is concentration of solute, x is thepath length of the sample and is the quantum yield of fluorescence.

The fluorescence intensity decay after withdrawal of the exciting source according to a first-order rate equation,

(2.22)

where is the initial fluorescence intensity at time t=0, is the fluorescence intensity at some later time (t), is the mean lifetime (unimolecular lifetime) of the excited single state.

**(2-7) Dielectric properties of polymer**

**(2-7-1) Definitions**

Dielectrics are materials possessing high electrical resistivities. A good dielectric is therefore a good insulator but the reverse is by no means true. Electrically, dielectrics are called upon to perform functions in ac circuits other than simple isolation of components. It is the electric dipole (positive and negative charges separated by a distance) structure they possess intrinsically, or assume in direct and alternating electric fields, that is the key to understanding their nature and use. A capacitor consisting of two parallel conducting plates of area A, separated a distance L by a vacuum space, is a good place to start. The ratio of the charge, Q (coulombs, C), stored on the plates to the voltage, V, across them is defined as the capacitance, C (farads, F):

(2.23)

However, the ability to store charge depends on the geometry of the plates and the filling between them (Fig.2-10.A). For a vacuum capacitor,

, (2.24)

where is the permittivity of free space { = 8.85 x 10-12 F/m). If a dielectric is now inserted, keeping the voltage constant, it is observed that more charge (Q') can be stored on the plates. This effect can be interpreted as signifying a higher capacitance which can be accounted for in Eq.(2.24) by substituting for , where is the permittivity of the dielectric.

Dielectric properties of different materials are compared via the *relative permittivity* or **dielectric constant**, defined as[74]:

(2.25)

**(2-7-2) Polarization**

**(2-7-2-1)Macroscopic Polarization**

Internal dipole moment alignment, or **polarization** in the presence of the electric field, is the reason dielectrics enhance capacitance. Polarization can arise, for example, because positive and negative ions or charge centers within molecules and atoms separate and assume the direction of the applied field. Although all of the dipoles within the dielectric align, it is those dipoles immediately facing the plates that effectively have uncompensated charges, as seen in Fig.(2-18.B). This polarization charge on the dielectric surface attracts additional opposite charge from the battery. An increased charge density on the capacitor plates is the result. How the polarization charge density, P, is related to the plate charge densities, with and without the dielectric, is developed in basic physics courses. From electrostatics we know that in a given electric field(ξ=*V/d*inV/m),the surface charge density, D, on capacitors filled with vacuum and dielectric are [74]:

(2.26)

and

(2.27)

respectively. The difference between the two is defined as the polarization,

P = D – Do = ( R (2.28)

a quantity that increases linearly with the magnitude of the electric field.

**(2-7-2-2)Microscopic Polarization**

As already noted, dipoles within the dielectric are responsible for the polarization. There are two kinds of dipoles in materials (those that are **induced** and those that are permanent) and both cause polarization or charge separation. A measure of the latter is the dipole moment, , defined as ,where Q is the magnitude of the charge and *d* is the distance separating the pair of opposite charges. The connection between the macroscopic polarization and microscopic dipole moments is given by

, (2.29)

where the sum over the number of moments per unit volume (Vo) of solid is carried out vectorially.

Dielectrics are good insulators so that charge is not easily transported in them. This does not prevent the charge within atoms and molecules from responding to applied electric fields, however, by parting slightly from one another or even reorienting. When this happens the dielectric is polarizedrespectively. The difference between the two is defined as the polarization,

P = D – Do = ( R (2.28)

a quantity that increases linearly with the magnitude of the electric field [74].

**(2-7-2-3)source of Polarization**

Three basic types of polarization that contribute to the total magnitude of P in a material have been identified:

1. *Electronic*. At any instant, atomic electron charge clouds are displaced toward the positive end of an applied electric field while the positively charged nucleus is attracted to the negative end (Fig. 2-11.A). If the field reverses direction, the atomic charge reorients in concert but the magnitude of is preserved. If, however, the electric field is turned off, the polarization vanishes; clearly, electronic polarization is an induced effect. It can persist to extremely high electric field frequencies because electron standing waves within atoms have very high natural frequencies(1016 Hz). The electronic polarization (Pe) is proportional to the magnitude of in small electric fields, and can follow its oscillations at optical frequencies. Because of this, there is a very important connection between dielectric and optical properties. It will not be proved here but the refractive index is equal to the square root of the dielectric constant:

(2.30)

2. *Ionic*. Many dielectrics are ionic materials. Application of alternating

electric fields deform the cation and anion bonds, inducing net dipole moments (Fig.2-11.B) and an ionic polarization given by Pi . Again, thesedipoles can follow alternating electric fields but the ions are too heavy to oscillate in phase with them much beyond frequencies of about 1013 Hz.

*3.Orientational*. Dielectrics often possess microscopic permanent dipole moments. Examples include water and transformer oils, where one end of the molecule is effectively positive while the other end is negative (Fig. 2-11.C).Application of electric fields causes these molecular dipoles to orient; but they are also buffeted by the surrounding thermal vibrations which tend to randomize their orientations. The orientational polarization (Po) is larger the greater the electric field and the lower the temperature. By summing the individual contributions, the total polarization is obtained as [74] :

P = Pe + Pi + Po (2.31)

**2-7-2-4 )Frequency Response(interfacial polarizability)**

All three polarization mechanisms are operative at the lowest frequencies and, therefore, *s,* is high. As the frequency is raised, one polarization mechanism after another is frozen out. The first to stop contributing to is the orientational component, then the ionic, and lastly the electronic[15].

**(2-7-3) Dielectric Behavior of Ideal Polar Polymers**

Replacement of one or several hydrogen atoms in CH4 renders the molecule polar. As a rule the various characteristics like thermal stability, mechanical strength, etc. are achieved by suitable substitutions and the process inevitably imparts a dipole moment to the molecule.There are many more polar polymersthan non-polar. Polymers possess a dipole

moment due to the presence of one or several types of polar bonds located in the polymer structure in such a way that the dipole moment of the bonds do not neutralize each other. The polar group may be situated in the main chain, a side group or attached to an aromatic ring [75].

For polar polymers the changes in ac characteristics with frequency are much more complex than that of non-polar polymers. As indicated in Fig.(2-8), at very high frequencies crystalline barriers or viscosity of a glassy polymer will prevent the dipoles from moving at all in the very rapidly reversing electric field[76] . consequently, the dipole structure will not influence the ac characteristics at very high frequencies (and ).As the frequency decreases the dipoles will move to a limited extent accompanied by energy loss. The loss will increase as the frequency decreases and the dipole can more follow the reversals of the electric field.

Ultimately, the reversals become slow enough for the dipole to encounter less resistance to moving and the loss again decreases. At the lowest frequencies, all of the dipoles that will ever turn under the influence of the electric field will do so, and the dielectric contribution is considered. At the same low frequencies the loss dipole contribution is considered. At the same low frequencies the loss factor, , will reach a minimum. The dielectric relaxation time , is approximately the mean time required for the molecular dipole to turn 180o against viscous resistance in a supercooled glassy polymer or the time it stays in an orientational position in a crystal before it jumps over an energy barrier to another which is 180o opposed.The Debye model of dielectric relaxation is convenient to study relaxation process by measuring the real and imaginary components of the permittivity over a range of frequencies. As is well known, these relaxation processes are a function of the structure of the specimen, and may be used as the means of characterising materials. The frequency dependence of thereorientation process was the subject of extensive work by Debye (1945) [77]. Debye [78] expressed the curves of Fig.(2-13) in terms of a single relaxation time by the following relations,

(2.32)

and

(2.33)

where, is the dielectric constant, is the dielectric loss index at angular frequency , is the static (low frequency) dielectric constant, is the

infinite (high frequency) dielectric constant and is the dielectric relaxation time.

It is easy to show that

(2.34)

The values of at this value of are

(2.35)

(2.36)

The dissipation factor tan also increases with frequency, reaches a maximum, and for further increase in frequency, it decreases [75].The relationship between the complex permittivity , polarization P, filed frequency ,and relaxation time per mole of a polar gas is given by the equation [79],

(2.37)

where M is the molecular mass; d is the density; is the Avogadro's number; is the polarizability and is the permanent dipole moment.It is evident from equation (2.37) that only the orientation polarization (second term) depends on the field frequency and the relaxation time.At the second term of the equation becomes negligibly small(the dominator being very large). Then the total polarization equals the deformation polarization and where n is the refractive index. At the total polarization is given by the equation,

(2.38)

The permittivity then reaches its maximum static value at where an inflexion point appears on the vs. Log curve, and a maximum on (or tan ) vs. Log curve . The position of this maximum depends on the temperature and the applied frequency; the higher the temperature, the more is the maximum shifted towards high frequencies (and with increasing frequency towards higher temperatures).

The electromagnetic field energy dissipated as heat per unit volume of a polar dielectric is proportional to the loss factor ( tan ), squared field strength E2 and frequency of the applied field:

(2.39)

**(2-7-4) Dielectric Relaxation in Solid Polymers**

Prepechco and his Coworkers [12] have studied the mechanism of dielectric relaxation processes in polymers in detail. According to the terminology they proposed, two types of dielectric relaxations are possible in polymers, dipole segmental and dipole group. These processes give maxima on the temperature or frequency dependencies of and tan as shown in Fig.(2-14)**.** The dipole segmental is associated with orientation rotation of side chains or individual atomic groups ,e.g, polar substituent's and is often denoted by the -ralaxation peak where segmental movement is possible, i.e., in the rubber-like state (above the Tg of the polymer).

The dipole group is due to orientation of the polar groups themselves, losses of this kind may also occur below the Tg of the polymer, i.e., in the glassy state, and above Tg in the rubber-like state.