PART - II

INVESTIGATION ON THE SEMICONDUCTIVE PROPERTIES OF SOME ORGANIC COMPOUNDS

CHAPTER 1

INTRODUCTION

1.1 General

Interest in the electrical conduction processes in organic compounds has steadily increased in the past two decades. The major lines of investigation have fairly clear origins. For example, studies of the temperature dependence of the conductivity of aromatic and polymeric solids have been stimulated in part by the suggestion of Szent-Györgyi[1,2] that perhaps the motion of electrons in living systems may be associated with semiconduction process. Since that time, a great many papers have dealt[3,4] with the application of solid state concepts to biological and biochemical phenomena. However, Szent-Györgyi later suggested[5] that, as a general proposition, this idea cannot be accepted because the energy gap commonly encountered in proteins is far too wide; there is simply not enough energy available, generally, in biological systems to raise an electron across a gap of the order of 2.3 eV. However, these concepts have been applied successfully to processes like photosynthesis[6-22] and vision[23-30] for which relatively energetic quanta are indeed available. Moreover, quite a few biochemically important semiconductors have been found[31] which do have substantially lower values of energy gap, notably the carotenes, chlorophylls and at least some amino acids. In fact, most significant contribution which the study of organic semiconductors may bring to the progress of science in general may well be in the broad field of " bioenergetics ".

The biological importance of vitamin A and other long chain polyenes is well known. These compounds are thought[32-35] to be involved in some biological processes like photosynthesis, vision, bacterial respiration and olfactory transduction etc. A significant feature of these compounds is their conjugated chain structure of alternating single and double bonds. Possibly this may allow them to function as electron mediators in the biological processes. Such conjugation may also manifest itself in semiconduction and superconduction effects. The present investigation is concerned with the semiconductive properties of some linear conjugated polyenes. There has been considerable interest in the electrical conductivity of biologically important semiconductors in recent years[14,15,35-41]. Our interest is centered particularly on two rather remarkable properties, (1) effect of adsorption of gases or vapours on the electrical conductivity and (2) the "compensation behaviour"[39-46] namely a linear relationship between the logarithm of the pre-exponential factor (σ_0) [in the standard[39,40] expression $\sigma(T) = \sigma_0 \exp(-E/2kT)$ for specific conductivity] and the semiconduction activation energy (E).

Adequate interpretation of the semiconduction data of the polyene compounds rests on modern theories of solid state physics. The band theory of solids, the theory of semiconductors, tunneling and hopping model of charge transport and the theory of polaron conduction in solids - all aided to understand the electrical conduction in the conjugated polyene compounds. In the following sections of this chapter, outlines of the relevant parts of these theories are discussed.

1.2 Band Theory of Molecular Crystals

The band theory originally developed for metals, ionic and valence crystals has been applied with some success to molecular crystals[46-49] as well.

In one electron approximation, the wave function for a single electron can be written[50,51] as

$$\Psi_K = \phi_K(\vec{r}) \exp i\vec{K}\cdot\vec{r} \tag{1.1}$$

where $\vec{K}$ is the wave number vector of the electron; $|\vec{K}| = \frac{2\pi}{\lambda}$, where λ is the associated wavelength; and $\vec{r}$ is the position vector of the electron in the crystal; ϕ_K is a function which has the translational periodicity of the crystal lattice.

If $\phi_K(\vec{r})$ is constant throughout the crystal, then Ψ_K becomes a function which describes a free electron[51]. So this is precisely the type of function which is applicable in metals. The field in which the electrons move is the sum of three components and can be expressed in terms of the operators of the Hartree-Fock type[52-54] operating on ϕ, as

$$V = V' + V'' + V''' \tag{1.2}$$

where

$$V'' \equiv \int \left\{ \left[\sum_j \phi_j^*(\vec{r}_2)\, \phi_j(\vec{r}_2) \right] / r_{12} \right\} dV_2$$

and

$$V''' \equiv -\left\{ \int \left[\sum_j \phi_j^*(\vec{r}_2)\, \phi_j(\vec{r}_1) \right] \phi_i(\vec{r}_2) / r_{12}\, dV_2 \right\} / \phi_i(\vec{r}_1)$$

Here, V' is the field acting on electron 1 that arises from all the nuclei; V'' is the coulomb potential of the electronic charge distribution and V''' gives rise to a term known as the "exchange" term. In these equations, atomic units of charge are used; volume elements include the spin; ϕ_j is a one-electron function including the spin; $\vec{r}_1$ is the position vector of electron 1; r_{12} is the distance between electrons 1 and 2. V is almost same for all electrons. If V is nearly constant as in most metals, the energy $\varepsilon(\vec{k})$ of an electron with a given value of $\vec{k}$ is given by[51]

$$\varepsilon(\vec{k}) = \left(\frac{\hbar^2}{2m}\right)\vec{k}^2 \tag{1.3}$$

Due to the fact that the values of $\vec{k}$ are very closely spaced, $\varepsilon(\vec{k})$ is almost a continuous function of $\vec{k}$ and separated bands of permissible $\varepsilon(\vec{k})$ values are not observed. If $\phi_k(\vec{r})$ varies greatly within a unit cell and falls to zero between adjacent cells, then the motion obtained is the opposite extreme of free-electron motion, known as the "tight-binding" condition.[51,52,55] This "tight-binding" is a characteristic of molecular crystals. Under this approximation the one-electron crystal wave functions ψ_k are constructed[56,57] from linear combinations of one-electron molecular wave functions χ_n:

$$\psi_k(\vec{r}) = N^{-\frac{1}{2}} \sum_{n=1}^{N} \exp\left(i\vec{k}\cdot\vec{r}_n\right)\chi_n\left(\vec{r}-\vec{r}_n\right) \tag{1.4}$$

Here $\vec{r}_n$ locates the geometrical centre of molecule n, and the sum extends over the N molecules in the crystal. The molecular wave function χ_n is oriented in the crystal in the same way as molecule n i.e., χ_n is the same function for all n. It is assumed that the integrals $\int \chi_m^* \chi_n \, d\tau = 0$ if $m \neq n$.

Applying the periodic boundary conditions[68] an elementary cell in $\vec{K}$ space can be defined whose volume is given by the conditions

$$-\pi < \vec{K}\cdot\vec{\alpha}, \quad \vec{K}\cdot\vec{\beta}, \quad \vec{K}\cdot\vec{c} \leq +\pi \tag{1.5}$$

where $\vec{a}$, $\vec{b}$, and $\vec{c}$ are unit cell vectors in a monoclinic lattice with two molecules in unit cell situated at (0,0,0) and at (a/2, b/2, 0) $\vec{\alpha}$ and $\vec{\beta}$ are defined by $\vec{\alpha} = \frac{1}{2}(\vec{a}+\vec{b})$ and $\vec{\beta} = \frac{1}{2}(-\vec{a}+\vec{b})$; $\vec{\alpha}$, $\vec{\beta}$ and $\vec{c}$ connect the centers of nearest neighbour molecules. The conditions represented by equation (1.5) define a zone in $\vec{K}$ space which is not identical with the conventional Brillouin zone[51,52,55]. There is a one-to-one correspondence between the points in the Brillouin zone and the points in the elementary cell defined by equation (1.5). Since the Brillouin zone is extremely complex in shape, the equation (1.5) is generally used to set the limits on $\vec{K}$.

The crystalline field is approximated by

$$V(\vec{r}) = \sum_{n} V_n(\vec{r} - \vec{r}_n) \tag{1.6}$$

where V_n is the Hartree potential of an isolated neutral molecule. The eigenvalue of Ψ_n is written[68] as

$$\mathcal{E}'(\vec{K}) = \mathcal{E}_0 + \mathcal{E}_1 + 2 \sum_{s}{}' \mathcal{E}_s \cos \vec{K}\cdot\vec{r}_s \tag{1.7}$$

where,
$$\varepsilon_0 = \int \chi_n \left[-(h^2 \Delta / 2m) - eV_n \right] \chi_n \, d\tau \tag{1.8}$$

$$\varepsilon_1 = \sum_s{}' \int |\chi_n|^2 V_{n+s} \, d\tau , \qquad s \neq 0 \tag{1.9}$$

$$\varepsilon_s = \int \chi_{n+s} V_{n+s} \chi_n \, d\tau \tag{1.10}$$

and the lattice vectors $\vec{r_s}$ and $-\vec{r_s}$ are counted as one in the sum (eqn. 1.7). The prime sign on $\sum$ indicates that the term with $\vec{r_s} = 0$ is omitted from the summation. The eigenfunctions obtained from equation (1.4) are for a fictional triclinic lattice. These are single valued functions of $\vec{K}$ in a Brillouin zone defined by the conditions in equation (1.6) and can be transformed to the proper notation for the monoclinic space group by choosing a Brillouin zone half as big :

$$-\pi < \vec{K}\cdot\vec{a}, \ \vec{K}\cdot\vec{b}, \ \vec{K}\cdot\vec{c} \leq +\pi \tag{1.11}$$

and taking two eigen functions per $\vec{K}$,

$$\psi_K^{\pm} = \left(\frac{1}{N}\right)^{\frac{1}{2}} \sum_n \left[\left(\exp 2\vec{K}\cdot\vec{n_1}\right) \chi_{n_1} \pm \left(\exp 2\vec{K}\cdot\vec{n_2}\right) \chi_{n_2} \right] \tag{1.12}$$

where n_1 and n_2 are the two molecules in unit cell n. The eigen values in this notation are

$$\varepsilon^{\pm}(\vec{K}) = \varepsilon_0 + \varepsilon_1 + 2\sum_s{}' \varepsilon_s \cos \vec{K}\cdot\vec{r_s} \pm 2\sum_s \varepsilon_{s+\alpha} \cos\left[\vec{K}\cdot(\vec{r_s}+\vec{\alpha})\right] \tag{1.13}$$

The intermolecular resonance integrals ε_s determine the structure of the band. The resonance integrals fall off rapidly with intermolecular distance and only a few nearest neighbour interactions are found to be important. Functional forms for V_n and the appropriate χ_n are required to evaluate[56,57] ε_s. The band structure depends on the structure of the crystal lattice. In case of anthracene, the integral between molecules connected by $\vec{\alpha}$ is the same as that between molecules connected by $\vec{\beta}$ and we call them both ε_α. The other significant terms are $\varepsilon_b\,(\vec{r}_s = \vec{b})$ and $\varepsilon(\vec{r}_s = \vec{c}+\vec{\alpha}$ and $\vec{r}_s = \vec{c}-\vec{\beta})$. The integral between molecules connected by $\vec{c}$ is negligible, as is that between molecules connected by $\vec{a}$. The one-electron energy for each band, then, neglecting the constant energy terms ε_0 and ε_1, is given by

$$\varepsilon(\vec{K}) = 2\varepsilon_\alpha\left[\cos \vec{K}\cdot\vec{\alpha} + \cos \vec{K}\cdot\vec{\beta}\right] + 2\varepsilon_b \cos \vec{K}\cdot(\vec{\alpha}+\vec{\beta})$$

$$+\, 2\varepsilon_\gamma \cos \vec{K}\cdot(\vec{c}+\vec{\alpha}) + \cos \vec{K}\cdot(\vec{c}-\vec{\beta}) \tag{1.14}$$

1.3 The Conduction Equation

If n_i is the concentration of the ith species of charge carriers having mobility μ_i and total charge z_i times the electronic charge (e), the net conductivity of the medium for i different species of carriers is given by

$$\sigma = \sum_i \left[z_i e n_i \mu_i \right] \tag{1.15}$$

It is assumed that there is negligible interaction between different carrier species.

In case of semiconductors where the charge carriers are electrons and holes, the equation (1.15) can be written as

$$\sigma = n_c e \mu_e + n_h e \mu_h \tag{1.16}$$

Here n_c is the concentration of electrons in the conduction band, n_h is the concentration of holes in the valence band, μ_e is the mobility of electrons and μ_h is the mobility of holes.

The concentration of electrons in the conduction band, n_c, can be expressed by[51,55]

$$n_c = \int_{E_c}^{top} \rho(E)\, F(E)\, dE \tag{1.17}$$

where E_c represents the bottom of the conduction band, $\rho(E)$ is the density of states and F(E) is the Fermi-Distribution function. Integration of expression (1.17) with assumption[55] $(E_c - E_F) \geqslant 4kT$, gives

$$n_c = 2(2\pi m_e^* kT/h^2)^{3/2} \exp(E_F - E_c)/kT \tag{1.18}$$

where m_e^* is the effective mass of the electron near E_c and E_F is the Fermi-Energy.

The concentration of holes, n_h, in the valence band may be written as[51,55]

$$n_h = \int_{bottom}^{E_v} \rho(E)\left[1 - F(E)\right] dE \tag{1.19}$$

where the integration extends over the valence band; E_v is the energy corresponding to the top of the valence band. If it is assumed[55] that the Fermi-level lies more than about $4kT$ above E_v, then $1-F(E) \approx \exp(E-E_F)/kT$ and integration of (1.19) gives

$$n_h = 2(2\pi m_h^* 2k/h^2)^{3/2} \exp(E_v - E_F)/kT \qquad (1.20)$$

where m_h^* represents the effective mass of a hole near the top of the valence band. Employing the fact that $n_c = n_h$ one can get from (1.18) and (1.20)

$$E_F = (E_c + E_v)/2 + \frac{3}{4} kT \log(m_h^*/m_e^*) \qquad (1.21)$$

Substitution of this value of E_F in (1.18), yields

$$n_c = n_h = 2(2\pi kT/h^2)^{3/2} (m_e^* m_h^*)^{3/4} \exp(-E/2kT) \qquad (1.22)$$

where E represents the energy gap between the valence and the conduction bands. This is applicable only to an intrinsic semiconductor in thermal equilibrium. Thus, from equation (1.16) the conductivity of an intrinsic semiconductor is given by

$$\sigma = \sigma_0 \exp(-E/2kT) \qquad (1.23)$$

where,

$$\sigma_0 = 2e(2\pi kT/h^2)^{3/2} (m_e^* m_h^*)^{3/4} . (\mu_e + \mu_h) \qquad (1.24)$$

The effective mass m^* of an electron or a hole is a concept which is much used in band theory. It is defined[51,55] by the equation

$$m^* = \hbar^2 / \frac{d^2\epsilon}{dk^2} \qquad (1.25)$$

where ϵ is the energy of an electron with wavenumber $\vec{k}$ ($k = 2\pi/\lambda$, where λ is the de Broglie wavelength). A large value of the effective mass corresponds to a low mobility; both are determined by the width of the band. The mobility μ in general is a tensor μ_{ij} and is thus anisotropic[56]. The velocity $\vec{v}(\vec{K})$ associated with an electron in a level characterized by the wavenumber vector $\vec{K}$, which has the energy $\varepsilon(\vec{k})$ is given[51,59] by

$$\vec{v}(\vec{K}) = \left(\frac{2\pi}{h}\right)\left(\frac{\partial\varepsilon(\vec{k})}{\partial\vec{k}}\right) \tag{1.26}$$

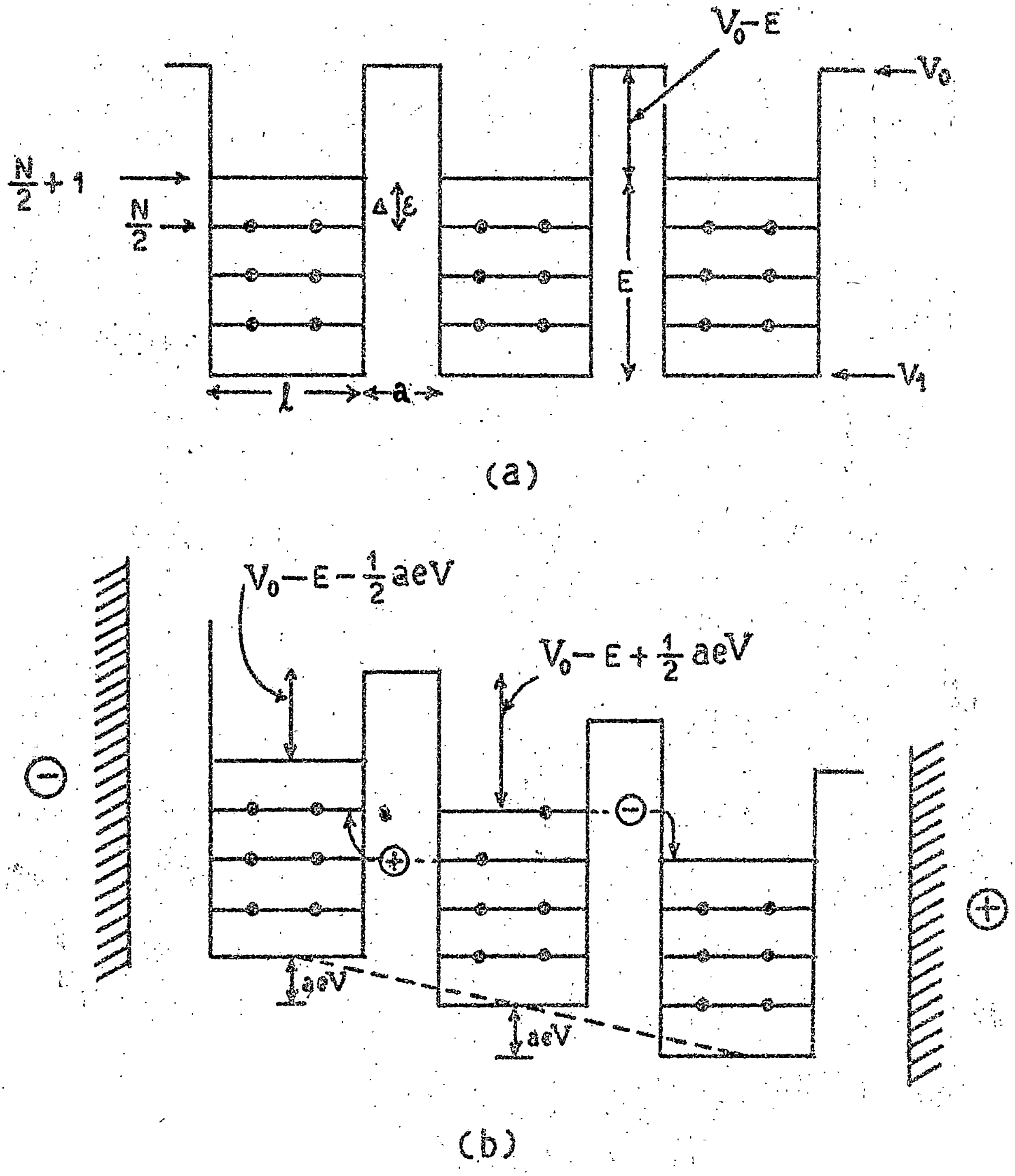
The mobility can be expressed in terms of the components of the velocity and of a function which depends on the scattering of the electrons as they move through the lattice.

1.4. Tunneling Model of Dark Conduction

Tunneling is a quantum mechanical phenomenon in which a particle such as an electron passes through a potential energy barrier without acquiring enough energy to pass over the top of the barrier.

The tunneling mechanism generally considered was proposed by Eley and Willis[60] is illustrated in Fig. 1.1. Here three adjacent similar molecules are shown : (a) in the absence of an applied voltage gradient V (volts cm^{-1}); and (b) after application of V and after the excitation of an electron in the central molecule. The diagram is schematic and the energy levels in a molecule are shown as equally spaced which is not observed in real molecules. After excitation of the electron from the $\left(\frac{N}{2}\right)$ th level to the $\left(\frac{N}{2}+1\right)$ th level both the electron and the hole can tunnel as shown in Fig. 1.1(b)

FIG. 1.1 : Tunnel model[60] of an organic semiconductor


$V_0 - E$
V_0
$\frac{N}{2}+1$
$\frac{N}{2}$
$\Delta\varepsilon$
E
V_1
l
a
$V_0 - E - \frac{1}{2}aeV$
$V_0 - E + \frac{1}{2}aeV$
$-$
$+$
aeV
aeV

(a)

(b)

FIG.1·1

The total energy change for transferring the electron is

$$\Delta E = I_G - A_G - aeV - \left(\frac{e^2}{\epsilon r}\right) \tag{1.27}$$

where I_G, A_G are the ionization energy and electron affinity of the organic molecule; 'a' the barrier width; aeV, the energy change caused by the applied field V indicated in Fig. 1.1 (b) by a vertical displacement of a potential well relative to its neighbour. The term $e^2/\epsilon r$ expresses the coulombic interaction of the opposite charges separated by a distance r. The effective permittivity ϵ for the region between the charges is generally high because of the polarizability of surrounding π-electrons. Since the ion pair will polarize the surrounding medium, a correction term should be applied to the formula (1.27).

The number of times an electron penetrates an intermolecular barrier gives a measure of its drift velocity. It is proportional to the product of the number of times it strikes the barrier and the probability of penetration. The electron in the $\left(\frac{N}{2}+1\right)$ th level is regarded as moving between the potential walls with a velocity v_e given by

$$v_e = \left(\frac{N}{2}+1\right)\frac{h}{2lm_e^*} \tag{1.28}$$

where l is the distance across the well and m_e^*, the effective mass of the electron. If P_f and P_r represent the probability of penetrating the barrier of width 'a' in the direction of the field and in the reverse direction respectively, the drift velocity v_{de} of the electron in the field is

$$v_{de} = \left(\frac{v_e}{2l}\right)(a+l)(P_f - P_r)$$

$$= \left[\left(\frac{N}{2}\right)+1\right]\left(h/4l^2 m_e^*\right)(a+l)(P_f - P_r) \qquad (1.29)$$

and the current density is given by

$$i = n e v_{de} \qquad (1.30)$$

In the equation (1.29) it is assumed that the net displacement of the electron upon going through the barrier is $(a+l)$.

Thus considering the value of n as n_c obtained from equation (1.22), the equation for 'i' can be given by

$$i = \left[2\left(2\pi m_e^* kT\right)^{3/2}/h^3\right]\left[\exp(-E/2kT)\right]\left(\frac{N}{2}+1\right).$$
$$eh(a+l)(P_f - P_r)/4l^2 m_e^* \qquad (1.31)$$

which is an equation of the form

$$i = \sigma_0 V \exp(-E/2kT) \qquad (1.32)$$

An evaluation of P_f and P_r now enables σ_0 to be calculated. Here P_f and P_r depend on the shape of the barrier.

1.6 The Hopping Model for Dark Conduction

If two molecules are separated by a potential barrier, a carrier on one can move to the other by moving over the barrier via an activated state — the process is called hopping.

A simple hopping model has been applied by Pohl[61] and by Pohl and Opp[62] to the motion of carriers in an organic solid. The carriers are considered to move by hopping to neighbouring molecules in a manner which is random except for the anisotropy caused by the applied field (F). If the carriers are electrons, then

$$i = ne\mu F \tag{1.33}$$

where n is the concentration of electrons.
It can be shown that

$$\mu = \left[f a^2 e N_s (kT)^2 / (h^3 \nu^2) \right] \exp\left(-E_s/kT\right) \tag{1.34}$$

where f is the average angle of hopping with regard to the direction of F; a, the intermolecular distance; N_s, the number of neighbouring sites; ν, the frequency of vibration in the two directions normal to the direction of carrier motion across the barrier; E_s, the height of the barrier. The interaction of the carrier with vibration in the lattice[63] may also give hopping of charge carriers without having these to cross a potential barrier. Considering such electron-lattice interaction using the localized representation[64] the value of μ becomes

$$\mu = (ea^2/\hbar)\left[2\pi \beta_u^2 / (kT\hbar\omega_0)\right] \exp\left[-\gamma_u(2S+1)\right] \cdot I_0\left\{2\gamma_u\left[S(S+1)\right]^{\frac{1}{2}}\right\} \tag{1.35}$$

where β_u denotes the matrixelement connecting molecular functions on sites separated by a distance u ; ω_0 is Debye frequency for acoustic waves; γ is a dimensionless parameter and accounts for the electron-lattice interaction; S is given by

$$S = 1/\left[\exp(\hbar\omega_0/kT) - 1\right] \tag{1.36}$$

and I_0 denotes a Bessel function. For the hopping model to be valid not only $\hbar\omega_0$ is to be much greater than β, but the carrier must also remain on a lattice site much longer than the period of a vibration; that is, the relaxation time (τ_u) in which the electron hops from a site j to a site $j+u$ must be much greater than $2\pi/\omega_0$. Then the equation representing the mobility in case of hopping model i.e.,

$$\mu = (ea^2)/kT\,(1/\tau_u) \tag{1.37}$$

suggests that $\mu << (ea^2/\hbar)(\hbar\omega_0/kT) \approx 1\ \mathrm{cm^2\,volt^{-1}\,sec^{-1}}$.

Thus one criterion which arises for the validity of the hopping model is that the mobility should be less than about 1 $\mathrm{cm^2\ volt^{-1}\ sec^{-1}}$. The other criterion which has sometimes been quoted is that a positive temperature dependence of mobility indicates that a hopping model applies. However, Glerum[64] has shown that, although the mobility increases with temperature when the interaction between the carrier and the lattice is large, when $\gamma < 10$ the mobility either does not change or it decreases with increasing temperature.

1.6 Polarons in Molecular Crystals

In some circumstances the interaction of electrons and phonons can lead to the electrons being trapped in self-induced potential wells. The entity which then moves through the crystal is not an electron by itself, but an electron accompanied by a localized vibration, a combination which is called a polaron[63].

Siebrand[65,66] has considered a molecular crystal with one excess electron. The half-width of the one-electron band in the tight binding approximation is given by

$$J_k = \sum_u \langle \chi^0_{j+u} | V_j | \chi^0_j \rangle \tag{1.38}$$

where $|\chi^0_j\rangle$ is a molecular ionic function centered at the lattice point j and unperturbed by nuclear motions. Intermolecular vibrations of the lattice which interact only weakly with carriers and which have a low velocity are neglected, but molecular vibrations, taken to be harmonic, are regarded as contributing to the formation of polarons. Considering these assumptions and writing the electron phonon interaction as linear in the vibrational co-ordinates one finds that the binding energy of the polaron is of the order

$$E_b \approx \frac{1}{2} \sum_q M_q^2 \, \omega_q \, (\Delta x_q)^2 \tag{1.39}$$

where M_q is the reduced mass of the qth oscillator; ω_q, the frequency; Δx_q, the difference between the equilibrium distances of molecule and ion.

The formation of Bloch-type bands from the polarons, by treating the electronic overlap as a perturbation, now becomes possible. Such bands are narrower than the corresponding electron band by a vibrational overlap factor. Their width, when the phonon velocity is small compared with that of the polaron, is given by

$$J_\sigma (v^0 + v) = J_K \langle v_j | v_j^0 \rangle^2 \tag{1.40}$$

where v^0 and v are vibrational quantum numbers of the neutral molecule and the ion; $|v_j\rangle$ and $|v_j^0\rangle$ are the corresponding ion and molecular vibrational wave functions at center j. Approximately then,

$$J_\sigma (v^0 + v) \approx J_K (E_b/\hbar\omega)^{v^0+v} [exp(-E_b/\hbar\omega)] \tag{1.41}$$

Thus there exists, below the electron band, a series of polaron bands with widths J_σ.

When the polarons are strongly bound, i.e., $E_b \gg J_K$ and $E_b \gg \hbar\omega \gg 2\pi J_\sigma$, a number of important conclusions can be drawn. At very low temperatures, the carriers will occupy the lowest-lying polaron band. They will have low mobilities which are limited by lattice phonon scattering, in which case $\mu \propto T^{-3/2}$ to T^{-1}. At higher temperatures, the higher energy bands will be populated, and the effective band width will increase exponentially with temperature. It follows that $d\mu/dT$ will gradually change sign. As T approaches E_b/k, the mobility is governed by the distribution between polaron bands and the electron band, so that transport becomes an activated hopping process. As T exceeds E_b/k, the distribution over the bands is approximately independent of T and again $\mu \propto T^{-3/2}$ to T^{-1}.

Another interesting conclusion regarding the effects of temperature arises from the condition that

$$\hbar\omega \gg 2\pi J_{\sigma} \tag{1.42}$$

which is itself a consequence of the uncertainty principle. It means that for polaron formation the time an electron remains on a lattice site should be long compared with the period of a vibration, $2\pi/\omega$. This is the reason why lattice phonons in molecular crystals generally are not expected to participate in the formation of polarons. Now let us consider the temperature T_t equal to E_b/k. Here the polaron will dissociate thermally, and the electron will move without an accompanying molecular vibration. When the width of a polaron band is such that $\hbar\omega \approx 2\pi J_{\alpha}$, the polaron can be said to dissociate kinetically, the electron not remaining on the lattice site longer than the period of a vibration. Siebrand applies this notion to the case in which the carrier moves by activated hopping from a polaron band to the electron band and has an effective band width J' at $T = T'$. For an activated hoping process,

$$\mu = ea^2/\tau k T' \tag{1.43}$$

Since $$\omega/2\pi = 1/\tau \geqslant J'/\hbar \tag{1.44}$$

also, it follows that $\mu < 1\,\mathrm{cm}^2\,\mathrm{volt}^{-1}\,\mathrm{sec}^{-1}$, if $a = 5$Å and $\hbar\omega = kT'$. This conclusion agrees with that of Glarum[64].

The polaron band structure, equation (1.41), having been determined, transport is discussed by assuming that the polarons interact weakly with lattice vibrations. The polarons thus are scattered in a way which gives rise to a relaxation time $\tau(\vec{k})$.

Then the band structure and carrier mobility are connected by well-known formulas

$$\vec{v}(\vec{K}) = \hbar^{-1} \vec{\nabla}_K \, \varepsilon(\vec{K})$$

$$D_{ij} = \langle v_i(\vec{K}) \, v_j(\vec{K}) \, \tau(\vec{K}) \rangle \qquad (1.45)$$

$$\mu_{ij} = e D_{ij} / kT$$

where $\vec{v}(\vec{K})$ is the velocity of a carrier in state $|\vec{K}\rangle$; $\varepsilon(\vec{K})$ is the energy of $|\vec{K}\rangle$; D_{ij} , μ_{ij} are components of the diffusivity and mobility tensors.

When the carriers interact strongly with molecular vibrations, this interaction should be included in the zeroth order carrier wave function. This implies that the complete wave function for the crystal no longer separates into electronic and vibrational parts. The electron-vibration interaction results in a narrower band widths.

The coupling criteria has been discussed by McRae and Siebrand[67]. These criteria can be generalised to three dimensions, as is done by Siebrand[68]. He uses the dimensionless parameters

$$\gamma \equiv - E_b / \hbar\omega \qquad (1.46)$$

and $$\beta \equiv |\vec{J}| / \hbar\omega \qquad (1.47)$$

for a one-dimensional array of one dimensional oscillators. When γ is large, the carriers are effectively localised. This theory assumes a simple form when the intermolecular coupling is either strong or weak, but is more complicated when coupling is intermediate.

1.6.1 The Tunneling and Hopping of Polarons

When an electron is surrounded by a cloud of phonons, a transition from site j to site j' results in the destruction of the cloud at j and the creation of a new cloud at j'. There is thus a large number of phonon emissions and absorptions accompanying the transition, and the electron is scattered many times during a single jump to a neighbouring site. The electron on a site is trapped in a potential well and has to pass a barrier of a height equal to the binding energy of the polaron in order to move to the neighbouring site. This passage[68] is a tunneling in molecular solids. Tunneling, which is analogous to a wave-like motion, applies when the vibrational states involve only a few quanta and are well separated; hopping applies when a large number of highly excited vibrational levels are crowded together and consists of randomly performed jumps. The translational symmetry of the lattice necessarily implies[69] wave-like motion. However, translational symmetry may be destroyed by thermal motion. If the phonon band width exceeds that of the polaron band, the dispersion of the lattice frequencies introduces enough randomness to annihilate the polaron band structure. The crystal may then, behave like a liquid with respect to carrier transport (hopping being the mechanism) and the mobility should not change much upon melting contrary to that generally observed.[70,71] Polaron tunneling is therefore thought to be the mechanism of carrier transport in molecular solids.

The probability P_{hj} that the electron jumps from a site h to a site $j = h \pm 1$ is calculated by time-dependent perturbation theory as[68]

$$P_{hj} = 4|\langle h|H_e'|j\rangle|^2 \sin^2(xt/2)\ \hbar^2 x^2 \qquad (1.48)$$

where $\hbar x = E_j - E_h$ and H_e' refers to that part of the Hamiltonian of which the eigenfunctions describe the motion of the electron between the molecules. In the matrix element $\langle h|H_e'|j\rangle$, h and j refer to molecular wave functions. Here P_{hj} can be expressed more explicitly as

$$P_{hj} = (2\pi/\hbar)\rho(0)\, t\, J^2 S_{00}^4 \ \exp\left[-4E_b \sum_\sigma v_\sigma (1-\cos\sigma)/N\hbar\omega(\sigma)\right] \qquad (1.49)$$

where N is the number of lattice sites; ω, the vibrational angular frequency; t, the time; σ, 2π times the phonon wave number; $\rho(0)$, a density of states at $x = 0$; J, the intermolecular electronic coupling between nearest neighbours; S_{00}, the vibrational overlap integral for zero values of the vibrational quantum numbers v.

A detailed treatment of equation (1.49) is given by Holstein[72]. The diffusivity D is given by

$$D = a^2 \bar{P}_{hj} / t \qquad (1.50)$$

where a is the lattice spacing and $\bar{P}_{hj}$ is the thermal average of P_{hj} obtained by substituting in equation (1.49), the thermal averages of v_σ denoted by $\overline{v_\sigma}$, where

$$\overline{v_\sigma} = N/\left\{\exp[\hbar\omega(\sigma)/kT] - 1\right\} \qquad (1.51)$$

For temperatures $T \gg \hbar\omega/k$, mobility is expected to increase exponentially as T increases. If $T \gg \hbar\omega/k$, Holstein has shown that

$$D \sim \exp(-E_a/kT) \qquad (1.52)$$

where E_a, the activation energy, is of the order of but smaller than $-E_b$.

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