

# Charge carrier transport in organic molecular crystals

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Received 7 November 1994, accepted 13 April 1995

**Abstract** : Charge carrier transport (drift mobilities) in homo-molecular crystals (organic semiconductors) have been covered in the review, Experimental results have been described in brief. Experimental results have been collected. Attention has been paid to mobility measurements over a wide range of temperature where almost temperature independent mobility (ATIM) has been observed. Low temperature results have been described and discussed. Trapped unperturbed time-of-flight (TOF) transits for naphthalene and perylene observed by Karl have been described. Also the electric field dependent mobility for anthracene has been discussed. Various theories for charge carrier transport in organic molecular crystals have been reviewed. Band structure calculations done at IIT Delhi, have been used to discuss the experimental data on drift mobilities. Small polaron transport mechanism have been critically examined. Various theories proposed to explain ATIM have been described. Besides Sumi's liberational phonon theory, Reineker *et al* presented the Liouville-equation approach for understanding the electron mobilities in naphthalene. Anderson *et al* used Boltzmann equation treatment below 100 K in all crystallographic direction of naphthalene. Silbey and Munn have considered a polaronic approach. Kenkre *et al* has presented unified quantitative explanation of the temperature dependence of drift mobilities of photo-injected carriers.

**Keywords** : Organic semiconductors, transport phenomena, mobility measurements.

**PACS Nos.** : 72.20.Fr, 72.80.Le

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#### 1. Introduction

Electrical properties of organic solids have been drawing considerable attention of scientists and technologists from many disciplines. This is because these solids challenge the traditional solid state physics concepts—the concepts that were proved to be successful in understanding inorganic semiconductors. On the practical side, these materials hold great promise because many organic solids having a variety of physical properties are known and a possibility exists of fabricating new ones having desired structure.

The materials that qualify as organic semiconductors contain an appreciable number of carbon-carbon bonds representing a high degree of conjugation and exhibit electrical conductivity which follows an Arrhenius temperature dependence [1-5]. Thus, we can classify organic semiconductors into various classes to include aromatic molecular solids, charge transfer complexes, neutral free radicals, ionic organic solids, polymers, wools, proteins and various other biological materials.

The central problem in the study of organic semiconductors is to understand as to how electric charge enters and is transported through a molecular and often highly disordered solid over distances which are very large on an atomic or molecular scale. Efforts by a good number of scientists are yet to help us in properly understanding the physics of electrical conduction in these solids. A complete understanding of the electrical conduction mechanism in organic solids requires a knowledge of the following :

- (i) Energy level diagram of the crystal,
- (ii) Carrier generation mechanism in both the dark and the light,
- (iii) Carrier recombination and trapping,
- (iv) Mechanism of charge carrier transport.

A lot of theoretical and experimental work exists in the literature on the above aspects. It is beyond the scope of this article to review all the data. Several good books and review articles are available on organic semiconductors. This article concentrates only on charge

carrier transport (drift mobilities) in homo-molecular crystals. No attempt has been made at exhaustive coverage of the literature.

## 2. Experimental techniques

Understanding the charge carrier transport requires the study of conductivity and carrier mobility. The mobility of carriers is more fundamental parameter than conductivity. The study of mobility anisotropy and dependence of mobility on temperature are very important for understanding the mechanism of charge carrier transport. A pulsed photoconductivity technique developed independently by Keplar [6] and LeBlanc [7] for determining the drift mobility of carriers in anthracene, has been extensively used for organic semiconductors. Some workers have used electron pulses instead of light pulse. All these techniques fall under the group called 'Transient Charge Technique'. These have been reviewed by Martini and Choi [8]. Drift mobility must be distinguished from microscopic mobility. The later refers to the motion of carriers between traps. Drift mobility depends on the extent of trapping. Thus, the drift mobility will be equal to microscopic mobility only for ideal trap free crystals.

### 2.1. Transient photoconductivity technique for drift mobility measurements (Time-of-flight Technique) :

It is a very useful and important technique for measuring drift mobility of high resistance solids such as organic solids. It has been used by many workers for a variety of crystals. A schematic diagram of the measurement circuit and measurement cell are illustrated in figures 1(a) and 1(b). The crystal is cut in the form of a disc with faces perpendicular to the

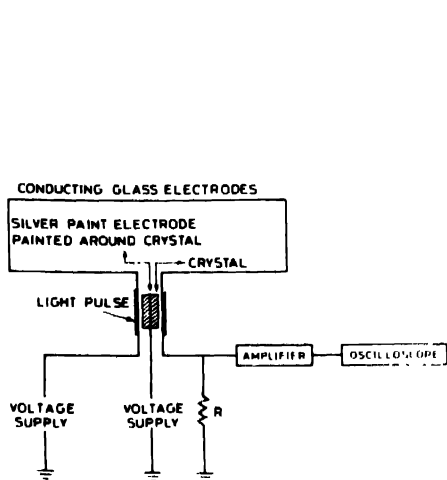


Figure 1(a). Drift mobility measurements circuit

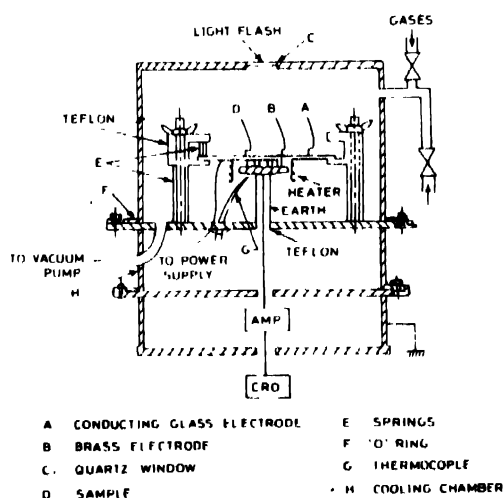


Figure 1(b). Drift mobility measurements cell.

crystallographic direction along which mobility is to be measured. The sample is sandwiched between two planar electrodes. The front electrode is a semi-transparent and conducting glass electrode and the back electrode is of copper.

The carriers are injected by shining a strongly absorbed flash of light for 1-2 microseconds. The photocarriers drift under the influence of the applied field. Depending on the polarity of the electrodes, either the electrons or the holes drift across the sample. The current pulse is detected by measuring a voltage drop across a resistor ( $R$ ) connected in series

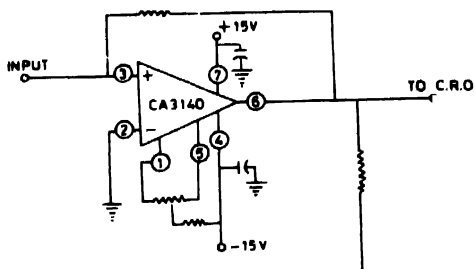


Figure 2. Pre-amplifier

with the crystal. The resulting voltage pulse is amplified by a high input impedance pre-amplifier (Figure 2) and then recorded in a storage oscilloscope. The transit time ( $\tau_t$ ) of the carrier is measured from the recorded pulse and the mobility of the carriers is calculated from

$$\mu = \frac{d^2}{V \cdot \tau_t} \quad (1)$$

where  $d$  is the thickness of the sample and  $V$  is the applied voltage. For different applied voltages, one measures the transit time and the mobility is calculated from the slope of  $1/\tau_t$  vs  $V$  plot. The transit time can be measured by two methods :

- (a) Differential method.
- (b) Integration method.

These methods have been nicely discussed by Meier [9] and Ravindra Nath [10].

A good source of available experimental data is the books by Gutmann and Lyons [11] and its update [12]. They have also described various variations used by different workers.

### 3. Experimental results

A complete list of mobilities of organic molecular crystals was published by Schein [13] in 1977 and later updated in 1982 by Schein and Brown [14]. Besides these lists, the mobilities of charge carriers in organic molecular crystals can be found in some of the reviews [15-32].

The magnitude and temperature dependence of the mobilities of anthracene and naphthalene have attracted much attention. Anthracene has been regarded a prototype of organic molecular crystals in general and hydrocarbons in particular. It is interesting to note that the magnitude and temperature dependence of mobilities  $\mu$  exhibit a remarkable trend, independent of the particular material [14]. The mobilities of both the electrons and holes are

$\mu = 1 \text{ cm}^2/\text{V}\cdot\text{sec.}$  within an order of magnitude at room temperature, and  $\mu$  is almost always weakly temperature dependent as given by

$$\mu \propto T^{-n} \quad (2)$$

Values of  $n$  in the range 1 to 1.5 have frequently been found, but values upto 2.5 have also been reported.

An exception to this general trend is shown by the electron mobility in the  $c'$  direction of anthracene (perpendicular to the crystallographic  $ab$  plane). A number of authors confirm that this mobility is smaller than in other directions and increases gently with increasing temperature [6,7,33-37]. However, Schein [38] on the basis of his mobility measurements over a wide range of temperature from 100 K to about 500 K, has shown that in  $c'$  direction of anthracene, we have almost temperature independent mobility (ATIM).

For naphthalene, Schein *et al* [39] extended the measurement below 77 K (54 K to 324 K). Their measurements show that we have ATIM in the  $c'$  direction of naphthalene but it rises dramatically from its high temperature value as  $T$  is decreased below 100 K. These results show that there are three distinct regions. From 150 K to 324 K, the mobility is essentially independent of temperature, similar to the behaviour of the electrons in the  $c'$  direction of anthracene [24,38,40] with  $\mu \propto T^{0.1 \pm 0.1}$ . Below 150 K, the mobility initially decreases by about 10%. At lower temperatures upto 54 K, the mobility increases exponentially with decrease in temperature.

Recently Karl *et al* [41] have reported observing trap-unperturbed time-of-flight (TOF) transits down to liquid helium temperature for naphthalene and perylene. With decreasing temperature, the electron and hole mobilities increase continuously over orders of magnitude (anisotropic power law). At high electric fields/low temperatures, the charge carrier velocities display sublinear deviations from Ohm's law and tend to saturate at approximately  $2 \times 10^6 \text{ cm/sec.}$  The highest measured mobility values ranged around  $400 \text{ cm}^2/\text{V}\cdot\text{sec.}$  Nakano and Maruyama [42] have reported an electric field dependent mobility for the electrons in anthracene along  $c'$  direction at 140 K:

In a series of papers, Burshtein and Williams [43-47] have reported drift mobility of charge carriers along different crystal directions and as a function of temperature in a number of molecular crystals. Mathur [48] has measured drift mobilities of photo-injected electrons and holes in biphenyl, *p*-terphenyl, pyrene and anthraquinone at room temperature and higher temperatures. For durene [47], very high charge carrier mobilities have been measured. In the crystal ( $a, b$ ) plane, both the hole and electron mobilities are isotropic which have values  $5 \text{ cm}^2/\text{V}\cdot\text{sec.}$  and  $8 \text{ cm}^2/\text{V}\cdot\text{sec.}$  respectively, at room temperature and follow a  $T^{-2.5}$  temperature dependence. In the  $c'$  direction, only the hole mobilities could be measured, which were  $0.15 \text{ cm}^2/\text{V}\cdot\text{sec.}$  at room temperature and followed a  $T^{-2.5}$  temperature dependence.

#### 4. Theories of charge carrier transport in organic molecular crystals

Theoretical attempts to explain the mechanism of charge transport in organic solids have been based on two different observables; dark conductivity  $\sigma$  and mobility  $\mu$ . Although drift mobility is a more fundamental property of a substance than its electrical conductivity, the earliest theories were directed towards an explanation of conductivity rather than mobility. In some of the transport processes like : tunnelling, hopping and band model, how charge carrier transfer takes place, is shown in Figure 3.

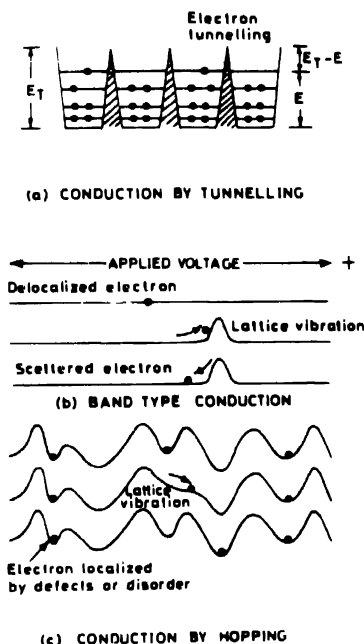


Figure 3. Transport mechanisms in solids.

##### 4.1. Tunnel model of conduction :

Eley and coworkers [49,50] for the first time, suggested a quantum mechanical tunnel model to explain how, in typical molecular crystals, a  $\pi$ -electron can pass from one molecule to a neighbouring molecule. In their model, the tunnelling of charge carriers takes place in two stages :

- (1) Excitation of a single molecule either thermally or optically to produce an electron in a normally unoccupied first excited  $\pi$ -orbital and a hole in HOMO (highest occupied molecule orbital) which normally contains two  $\pi$ -electrons.
- (2) Tunnelling of the charge carriers (electrons and holes) through the 'intermolecular' potential barrier to occupy corresponding orbital in the adjacent molecule.

Keller and Rast [51] modified the model to include the effect of temperature by allowing the intermolecular potential barrier to vary. As a result of lattice vibrations, this gives a temperature dependence of the mobility.

The tunnel model could predict the magnitude of carrier mobilities, explain the compensation law and the conductivity anisotropy. However, the model fails to satisfactorily explain the temperature dependence of mobility and the difference in the electron and hole mobilities.

#### 4.2. Energy band model :

The temperature dependence of carrier drift mobilities given by  $\mu \propto T^{-n}$  led to the use of band theory for understanding charge carrier transport in organic molecular crystals. The first band structure calculations for anthracene crystal were performed by LeBlanc [52]. He used tight binding approximation. One electron crystal wave functions  $\psi_k(\mathbf{r})$  were constructed from linear combination of one electron molecular orbitals.

$$\psi_k(\mathbf{r}) = N^{(-1/2)} \sum_{n=0}^{N-1} \exp(i\mathbf{k} \cdot \mathbf{r}_n) \phi_c(\mathbf{r} - \mathbf{r}_n), \quad (3)$$

where  $\mathbf{k}$  is the wave vector, index  $n$  labels the  $n$ -th molecule,  $\mathbf{r}_n$  denotes the position vector to the center of molecule  $n$  and  $\phi_c(\mathbf{r} - \mathbf{r}_n)$  is a molecular orbital centered at  $\mathbf{r}_n$ . All  $\phi$ 's are identical except for the location and orientation in space. The subscript  $c$  refers to the molecular orbital appropriate to an excess carrier (hole or electron). Thaxton *et al* [53] used a similar approach to calculate the band structure of naphthalene, tetracene and pentacene crystals. The calculated bands are very narrow. Katz *et al* [54] improved the calculations by introducing self consistent field (SCF) atomic orbitals (AO's) instead of Slater orbitals used by earlier workers. Silbey *et al* [55] further improved these calculations by including the effect of intermolecular electron exchange and vibronic coupling in the weak coupling scheme. Later, Mathur and coworkers [56-61] reported much more sophisticated band structure calculations on a number of organic molecular crystals. All band structure calculations involve the calculation of intermolecular resonance integrals, (IRI: some authors refer them as Transfer Integral T I's). The degree of sophistication in evaluating IRI's is reflected in the accuracy and correctness of band structure calculations. Yadav *et al* [62-66] explained their results on transport properties for three new series of organic materials (Anthraquinone derivatives, Merocyanines and Cyanines) by using band theory in the low field region only. The possibility of using band model for explaining the results on organic dyes in the low field region was also indicated by Mathur *et al* [67,68].

For most organic crystals, the carrier mobilities are very low and the difficulties in the use of band theory are expected. From Uncertainty Principle, Ioffe [69,70], Fröhlich and Sewell [71] and Bosman and Van Daal [72] have derived two conditions for the applicability of band model. They are :

- (i) Carrier mean free-path must be larger than lattice constant and
- (ii) Carrier mobility must be larger than  $(3\omega/kT)$ ,  $\omega$  being the band width.

Another requirement for the applicability of band model [73] is that the band width must be larger than lattice vibration energy, *i. e.*  $\omega > \hbar\omega_0$ , where  $\omega_0$  is the Debye frequency for acoustic waves, and hence

$$\mu > (qa^2/\hbar^2) \left( \frac{\hbar\omega_0}{kT} \right). \quad (4)$$

Calculations based on band model often seem to fail in satisfying these conditions or fall in a border line region. The estimated mean free path,  $\lambda$  of charge carriers in anthracene comes out to be 3-4 Å. This is less than lattice constant, suggesting that carriers are scattered on every molecule of the lattice *i.e.* they are localized on each molecule. This is self contradictory for band model. Brushtein and Williams [43-47] have critically examined the applicability of band model to organic molecular crystals using the band structure calculations of Mathur and Kumar [56] and Singh and Mathur [57]. They concluded that the band model is not applicable to these solids. It may be pointed out that the calculation of relaxation time and free path is based on drift mobility values for real crystals while the theoretical calculations used are for ideal trap free solids.

#### 4.3. Hopping models :

There exists various hopping transport models [9,11,28]. The first one is simple model of quantum mechanical tunnelling [49] through intermolecular barriers, which has already been discussed. This does not require activation energy and therefore, should be temperature independent. In real molecular crystals, we observe generally a pronounced temperature dependence of mobilities, revealing the possibility of this model. The second one is simple hopping model, according to which the charge carrier is trapped at each molecular site and moves over the intermolecular barrier *via* a thermally activated process. However, such phonon activated hopping mechanism could not succeed in explaining the temperature dependence of drift mobilities ( $\mu \propto T^{-n}$ ) in anthracene type crystals. Another model is resonance transfer model (RTM) proposed by Glasser and Berry [73] which is an intermediate between the two models mentioned above. According to this model, the primary mechanism is tunneling of excess charge carriers between the neighbouring molecules, the probability of which is considered as a sensitive function of the vibrational states of the lattice. In an excited vibrational state, two molecules approach each other more closely than they do in a vibrational ground state and tunneling takes place. This type of phonon assisted tunneling is called 'Resonance Transfer', which was simplified to a simple random hopping (non correlated) of the charge carriers from one localized site to the other. That means, each jump is actually independent of the preceding one. The hopping times are inversely proportional to the transfer integrals. The calculated mean hopping times ( $\nu_n$ ) by them for the holes and electrons in anthracene were in good agreement with those evaluated experimentally. They have used a discrete probability distribution based on transfer integral calculated for an equilibrium configuration of the crystal. However, the probability function depends not only on the distribution of the neighbouring sites of localized carrier but also on



the intermolecular vibrational quantum numbers. This requires the knowledge of a detailed phonon spectrum and how it affects the transfer integrals.

As already mentioned, electron interaction with the lattice and the surrounding electrons play an important role. The charge carrier transport takes place coherently according to band model or by random jumps according to hopping model, depends on : whether the electron coupling is strong with intermolecular vibrations (lattice or acoustic phonons) or with intramolecular vibrations (optical mode phonons), whether the electron lattice interaction is strong when compared to intermolecular electron exchange interaction and also on whether the electron coupling with lattice is linear or quadratic in phonon coordinates. Glarum [74] has considered electron interaction with intermolecular vibration and concluded that carrier transport in anthracene might be intermediate between band and hopping limits. By considering the interaction of charge carriers with molecular vibrations, Siebrand [75] has also arrived at the same conclusion. The electron phonon interactions have also been treated by Gosar and Choi [76] for hopping transport based on linear interactions with acoustic phonons. They assumed that the electron motion is incoherent in all directions due to strong electron-phonon interactions and obtained that the phonon-induced electron hopping (PIEH) gives a mobility component proportional to  $T^{1/2}$  which cannot explain the experiments. Madhukar and Post [77] remarked that the mobility component given by the PIEH is independent of temperature in the Haken and Reineker's model [78] which regards the transfer integral of electron as fluctuating very rapidly due to lattice vibrations. This model can be justified only when the energy dispersion of lattice vibrations is much larger than the total conduction-band width [79]. Using the small polaron model [80], Munn and Siebrand [81] tried to explain the charge carrier transport in anthracene. They considered that the electron-phonon interaction is quadratic in phonon coordinates.

#### 4.4. Holstein's small polaron hopping theory :

When the electron interaction with intramolecular vibrations is too strong, during the time, the electron remains on a particular site, it polarizes the surrounding lattice and then gets trapped in a self induced potential well. The polarization tends to follow the electron. The combination of electron and the polarization field is considered as a quasi-particle, which is named as 'Polaron'. In organic molecular crystals, the electron-phonon interaction is strong but of short range unlike in ionic crystals. The polarization extends only to small region and hence the polaron is referred to as a small polaron.

The polaron can move either as a result of tunnelling between equivalent localized states centered on different sites or by hopping between two non-equivalent localized sites involving emission and absorption of phonons. The tunnelling is analogous to wave like motion (band conduction) whereas the hopping is a phonon activated process which is predominant at high temperatures. The basic expression for mobility is given by

$$\mu = \frac{ea^2}{kT} P, \quad (5)$$

where  $a$  is the lattice periodicity and  $P$  is the probability of hopping. For the value of  $P$ , there exists two distinct cases.

(i) *Adiabatic case* :

When the electronic transfer integral,  $J > \hbar\omega_0$  (where  $\omega_0$  is predominant phonon frequency), the carrier adjusts rapidly to the motion of the lattice and is very likely to hop to the neighbouring site. The hopping probability is given by

$$P = \frac{\omega_0}{2\pi} \exp\left(\frac{-W_p}{2k_B T}\right), \quad (6)$$

where  $W_p$  is the small polaron binding energy.

(ii) *Non adiabatic case* :

When  $J > \hbar\omega_0$ , carrier adjusts itself too slowly to the motion of the lattice and misses many coincidence events before making a hop. The hopping probability is then given by

$$P = \frac{1}{\hbar} \left( \frac{\pi}{2W_p kT} \right)^{1/2} J^2 \exp(-W_p / 2kT). \quad (7)$$

This limit seems to be applicable to majority of molecular solids. Important point to be noticed is the presence of the term  $J^2$ , indicating that the anisotropy of the transfer integral is a prominent factor in the observed mobility anisotropy values.

#### 4.5. Munn and Siebrand model :

As mentioned earlier, using a quadratic electron-phonon (optical) coupling in molecular out-of-plane vibrational coordinates, Munn and Siebrand [81] have proposed a model for charge carrier transport in aromatic hydrocarbon crystals. This theory is based on a linear chain model. It assumes a linear chain of diatomic molecules fixed at a distance apart. A one-electron treatment is used and the carrier wave function is given under tight binding approximation as a linear combination of localized molecular ion electronic wave functions.

$$\psi [R, (X_r)] = \sum_n a_n (X_r) \psi (R - nd, X_n), \quad (8)$$

where  $R$  is coordinate of carrier,  $(x_r)$  depends on set of intermolecular coordinates of all oscillators.  $n$  labels the site of molecular ion,  $a_n(x_r)$  is a complicated model coefficient. A single excess electron is assumed to interact only with intramolecular vibrations, after suppressing the intermolecular vibrations by fixing centers of mass of oscillators at site  $(na)$ . There are three main interactions :

- (1) Mechanical coupling  $W$  between adjacent oscillators (vibrational coupling),
- (2) Electronic coupling  $J$  between adjacent molecules,
- (3) Electron-phonon quadratic interaction  $W_L$ .

In plane stretching, molecular modes have relatively small effect on carrier transport, whereas the out-of-plane vibrations are very efficient in obstructing charge carrier transport. According to Munn and Siebrand, the mobility is given by

$$\mu = \left( \frac{ea^2}{kT} \right) \sum_{n=1}^{n-1} E_r^2 \cdot r_n, \quad (9)$$

where  $E_r$  is a transfer integral and  $r_n$  is a complicated function of model parameter. This expression is independent of the model of transport, and applicable to band and hopping transport. Munn and Siebrand have realized three limiting cases.

(i) *Hopping in slow-electron limit :*

When the electron exchange energies are small compared to phonon dispersion energies and the transfer of electron between adjacent molecules is the rate determining step, the condition for this limit is

$$\hbar \omega_2^4 / \omega_o^3 \gg \hbar \omega_1^2 / \omega_o \gg 4J. \quad (10)$$

(ii) *Hopping in slow-phonon limit :*

In this case, the electron exchange energies are large compared with the phonon dispersion energies and the transfer of electron between the adjacent molecules is limited by the rate of phonon transfer. The condition for this limit is

$$\hbar \omega_2^4 / \omega_o^3 \gg 4J \gg \hbar \omega_1^2 / \omega_o. \quad (11)$$

From the expression for mobility derived by Munn and Siebrand, transport in both these limits should give rise to slight temperature activated mobilities.

(iii) *Quasi-free electron coherent transport in slow-phonon limit :*

Carrier transport takes place in this limit when the electron coupling is much stronger than both the vibrational coupling and the electron phonon coupling. In this limit, mobility decreases with temperature similar as in traditional band theory.

Munn and Siebrand's theory could successfully explain the charge carrier transport in anthracene [81] and naphthalene [82]. However, it is difficult to apply this theory to experimental results on other crystals because of the lack of knowledge of the values of  $\omega_o$ ,  $\omega_1$ ,  $\omega_2$ , and  $J$ .

4.5.1. *A critique of Munn and Seibrand theory :*

In Munn and Seibrand theory, the electron-phonon interaction quadratic with respect to normal coordinates of intramolecular vibrations is regarded as dominant. As mentioned by Druger [25] in his review article, the theory has extensively been used to analyze experimental data by many experimentalist. Munn and Seibrand have concluded that the electron motion in  $c'$  direction of anthracene is diffusive while that along the  $(a,b)$  plane has a considerable amount of coherence. Druger [25] pointed out that the calculation procedure of

their theory contains some neuristic steps which are not justified from any general basis. Sumi [83] points out that in their theory, the motion is calculated with the use of one dimensional model for each direction of electron motion. If electron motion was diffusive in all directions, their model would not be qualitatively inconsistent. But when electron motion is diffusive only in one ( $c'$ ) direction and it is coherent in two other ( $a$  and  $b$ ) directions, this model is quite inadequate.

Munn and Siebrand considered the quadratic interaction as dominant. But the quadratic interaction is not strong enough to explain the width of the exciton absorption peak in organic molecular crystals at room temperature [79].

Small polaron approach of Gosar and Choi [76] has been extended by Vilfan [84] and by Efrima and Metiu [85]. Vilfan has tried to explain the temperature independent mobility by considering a proper mixing of two phonon induced mobility components. One component corresponds to usual electron-phonon interaction which is linear in normal coordinates of the lattice vibrations while the other component corresponds to a quadratic interaction. The two terms contain  $T^{-1/2}$  and  $T^{+1/2}$  in pre-exponential factors and Vilfan insists that the temperature-independent mobility is a result of proper mixing of the two components. Efrima and Metiu took into account inharmonic effects of lattice vibrations which induce the transfer integral. Their theory gives temperature independent mobility if thermal energy is much larger than electron phonon coupling energy ( $k_B T \gg 1/2 S$ ). This forced them to assume that  $S/k_B$  is much smaller than  $T$ . If we accept that electron band width,  $\Delta$  is of the order of 0.1 eV than the stability condition for small-polarons ( $S > 1/2 \Delta$ ) and the condition for small-polaron conduction ( $S > \Delta$ ) are violated and their theories loose internal consistency.

#### 4.6. Other theories :

Recent observation of ATIM prompted Sumi to consider the electrical conduction in organic molecular crystals in a series of papers [83,86-88]. He started by considering the electron mobility in anthracene. He assumed that the electron motion is incoherent only in one direction with a narrow band width and that lattice vibration energies are much smaller than the total conduction band width. He used a simple formulation based on Fermi's golden rule to explain the temperature-independent mobility in the  $c'$  direction. He extended this work by using a unified treatment based on the linear response theory of Kubo [89]. He further assumed that the electron motion in the  $c'$  direction is diffusive and the electron hops through the phonon induced electron transfer under the condition that the electron motion along the ( $a, b$ ) plane is coherent in the two dimensional Bloch-band state, and that phonon energies are much smaller than the total band width of the conduction band of electron. His model results from band structure calculations which shows that the conduction band is highly anisotropic, being very narrow only in one ( $c'$ ) direction. It is in this narrow band direction that ATIM was observed. The hopping electron motion considered by Sumi is different from that of the usual hopping conduction model for localized electrons, in which electron motion is assumed to be diffusive in all the directions, because of strong electron-phonon interaction through two channels : one cause by the transfer integral of electron of the rigid lattice and another by the

change of the transfer integral in the course of rotational vibration of the molecules. The second channel is dominant at high temperatures, giving rise to ATIM. On the other hand, mobility through the first channel increases as the electron-phonon scattering within the (*a*, *b*) plane becomes less frequent below the Debye temperature, while mobility through the second channel is suppressed in this temperature region.

Besides Sumi's librational phonon theory [87], Reineker *et al* [90] presented the Liouville-equation approach for understanding the electron mobilities in naphthalene. Both these analyses predict the appropriate qualitative behaviour but require a phonon frequency which is smaller than the lowest known libration in naphthalene. Anderson *et al* [91], used a Boltzman equation treatment which provided good fits with the data below 100 K in all crystallographic directions of naphthalene. But yield mean free paths data less than a lattice constant for most of the data for the *c*'direction and thus, it is to be internally consistent. Silbey and Munn [92] have considered a polaronic approach. Their theory results in perturbation parameter which are not consistent with the analysis of low temperature mobilities ( $T \ll 100$  K). For the high temperature mobilities, it is consistent with data but requires phonon frequencies that are higher than that of the highest librational mode and lower than that of the lowest totally symmetric internal mode in naphthalene [93].

Recently Kenkre *et al* [94] have presented a unified quantitative explanation of the photo-injected electrons in naphthalene for all directions and temperatures. The theory proposed is based on a polaronic description of the charge carriers and the calculation-scheme employs a perturbation from the site-local states. The calculation scheme includes a perturbation from localized states [95,96] and treats static disorder simply but explicitly through the parameter *a*.

An important conclusion of their calculations is that photo-injected charges move as polaron in all the directions.

### Acknowledgments

Authors wish to thank Professor D C Dube, Physics Department of Indian Institute of Technology, Delhi for his several stimulating discussions. One of the authors (HOY) also acknowledges the financial support from DST, New Delhi, India.

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