

Chapter 2

Hopping Mechanism

Abstract In the limit of strong electron–phonon coupling and weak intermolecular electronic coupling, a charged molecule undergoes a large geometry relaxation, which eventually traps the charge. In this case, the charge transport can be viewed as an intermolecular hopping process. With the known electron transfer rates between neighboring molecules, the charge carrier mobility can be evaluated through the Einstein relation from random walk simulations. In general, the classical Marcus electron transfer theory, which works well in the high-temperature limit. For a better understanding, we incorporate the nuclear tunneling effect arising from the intramolecular high-frequency vibrations to characterize the transport behavior at room temperature. Dynamic disorder effect arising from the intermolecular low-frequency vibrations is found to be very much materials structure or space-dimension dependent, which may give rise to the phonon-assisted current.

Keywords Hopping mechanism • Marcus electron transfer rate • Random walk simulation • Temperature dependence of mobility • Nuclear tunneling • Dynamic disorder

In [Sect. 2.1](#), we describe the general methodology to simulate the hopping mobility using the electron transfer rate formalism. This approach is applied to different organic materials and discussed in [Sects. 2.2, 2.3, 2.4](#). [Section 2.5](#) investigates the nuclear tunneling effect of the intramolecular vibrations, and finally [Sect. 2.7](#) is about the dynamic disorder effect of the intermolecular modes. For each of these improvements, application examples are presented in [Sects. 2.6](#) and [2.8](#), respectively.

2.1 General Methodology

This chapter deals with strong electron–phonon interaction limit that the charge is regarded as localized in a single molecule. The charge transport consists of successive hopping from molecule to molecule, overcoming the trap caused electron scatterings with intramolecular vibrations. In the hopping picture to evaluate the charge mobility, there are two important rate processes at different spatial scales, namely, the electron transfer within molecular dimers and the electron diffusion in organic solids. The previous process can be characterized by the intermolecular electron transfer rate at the atomistic level, while the latter can be simulated at the molecular level by the random walk technique, regarding each molecule as a lattice site. When the intermolecular electronic coupling, also called electron transfer integral, V , is much smaller than the reorganization energy of the electron transfer process between a molecular dimer, λ , the electron transfer rate at high temperature, T , falls well into the hopping regime. For organic materials, the intermolecular interaction is of van der Waals type. In general, V is smaller than λ , and thus the Marcus rate is usually adopted to evaluate the room-temperature mobilities.

2.1.1 Marcus Electron Transfer Rate

The Marcus formula for electron transfer rate reads [1]

$$k = \frac{V^2}{\hbar} \sqrt{\frac{\pi}{\lambda k_B T}} \exp \left\{ -\frac{(\Delta G^0 + \lambda)^2}{4\lambda k_B T} \right\} \quad (2.1)$$

Here, $\hbar$ is the reduced Planck constant, k_B is the Boltzmann constant, and ΔG^0 is the free energy difference between the initial and final molecular sites. For molecular crystals with only one type of molecules, ΔG^0 is generally zero since all molecules in the crystal are equivalent. In Eq. 2.1, V and λ are the two most important parameters, both of which are related to the material itself. Various approaches have been proposed to calculate these two parameters in the literature, as presented below.

2.1.2 Transfer Integral

The intermolecular transfer integrals can be calculated through various numerical methods. Three of them, including the direct method [2], the site-energy correction method [3], and the band-fitting method [4], have been widely used in the literature, and thus will be detailedly discussed below.

2.1.2.1 Direct Method

The direct scheme to obtain the intermolecular transfer integral was proposed by Fujita et al. in modeling scanning tunneling microscopy [2] and later adopted by Troisi and Orlandi to study the charge transport in DNA and pentacene crystal [5]. At the Hartree-Fock (HF) level, the transfer integral reads:

$$\begin{aligned}
 V_{e/h} &= \left\langle \phi_{\text{LUMO/HOMO}}^{0,\text{site1}} \left| F^0 \right| \phi_{\text{LUMO/HOMO}}^{0,\text{site2}} \right\rangle \\
 &= \left\langle \phi_{\text{LUMO/HOMO}}^{0,\text{site1}} \left| h_{\text{core}} \right| \phi_{\text{LUMO/HOMO}}^{0,\text{site2}} \right\rangle \\
 &\quad + \sum_{l(\text{occ.})} \left(\left\langle \phi_{\text{LUMO/HOMO}}^{0,\text{site1}} \phi_l^0 \left| \phi_{\text{LUMO/HOMO}}^{0,\text{site2}} \phi_l^0 \right\rangle \right. \\
 &\quad \left. - \left\langle \phi_{\text{LUMO/HOMO}}^{0,\text{site1}} \phi_{\text{LUMO/HOMO}}^{0,\text{site2}} \left| \phi_l^0 \phi_l^0 \right\rangle \right) \right) \quad (2.2)
 \end{aligned}$$

Here, $\phi_{\text{LUMO/HOMO}}^{0,\text{site1}}$ and $\phi_{\text{LUMO/HOMO}}^{0,\text{site2}}$ represent the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbitals (LUMO) of the two adjacent molecules when no intermolecular interaction is present. F^0 is the Fock operator for the dimer, which is calculated with the unperturbed molecular orbitals.

It has been shown that the HF bandwidth for a polymer is always about 20–30% larger than the experimental results [6]. Moreover the coupling calculated from density functional theory (DFT) is usually about 20% less than that from HF [7]. Therefore, in Eq. 2.2, it is better to adopt the Kohn-Sham–Fock operator instead of the Fock operator:

$$F^0 = S C \varepsilon C^{-1} \quad (2.3)$$

Here, S is the intermolecular overlap matrix, and C and ε are the Kohn-Sham molecular orbital coefficients and eigenenergies of the non-interacting dimer, respectively. In practice, the molecular orbitals of the two individual molecules are calculated separately by the standard self-consistent field procedure. These non-interacting orbitals are then used to construct the Kohn–Fock matrix. After one-step diagonalization without iteration, the orbital coefficients and eigenenergies, and thus the Fock operator for the non-interacting dimer can be calculated.

2.1.2.2 Site-Energy Correction Method

When the self-consistent field is performed to construct the Kohn-Sham–Fock operator in Eq. 2.3, Valeev and coauthors noticed that the site-energy difference should be taken into account when the dimer is not cofacially stacked [3]. For example, assuming that HOMO and HOMO-1 of the dimer result only from the interaction of the monomer HOMOs, $\{\Psi_i\}$, the dimer molecular orbitals and the corresponding orbital energies follow the secular equation:

$$\mathbf{HC} - E\mathbf{SC} = 0 \quad (2.4)$$

Here, $\mathbf{H}$ and $\mathbf{S}$ are the Hamiltonian and overlap matrices of the system:

$$\mathbf{H} = \begin{pmatrix} e_1 & J_{12} \\ J_{12} & e_2 \end{pmatrix} \quad (2.5)$$

$$\mathbf{S} = \begin{pmatrix} 1 & S_{12} \\ S_{12} & 1 \end{pmatrix} \quad (2.6)$$

The matrix elements above are

$$e_i = \langle \Psi_i | \hat{H} | \Psi_i \rangle \quad (2.7)$$

$$J_{ij} = \langle \Psi_i | \hat{H} | \Psi_j \rangle \quad (2.8)$$

$$S_{ij} = \langle \Psi_i | \Psi_j \rangle \quad (2.9)$$

Since the basis sets, namely the HOMOs of the adjacent individual molecules, are not orthogonal with each other, a Lowdin's symmetric transformation can be applied to get an orthonormal basis set, which also maintains as much as possible the initial local character of the monomer orbitals. With such a symmetrically orthonormalized basis, we have the effective Hamiltonian:

$$\mathbf{H}^{\text{eff}} = \begin{pmatrix} e_1^{\text{eff}} & J_{12}^{\text{eff}} \\ J_{12}^{\text{eff}} & e_2^{\text{eff}} \end{pmatrix} \quad (2.10)$$

Here, the off-diagonal term is the effective transfer integral which has considered the site-energy correction: [3]

$$J_{12}^{\text{eff}} = \frac{J_{12} - \frac{1}{2}(e_1 + e_2)S_{12}}{1 - S_{12}^2}. \quad (2.11)$$

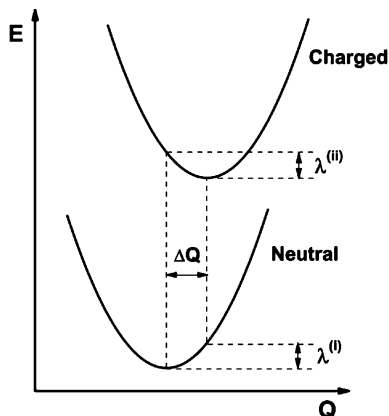
2.1.2.3 Band-Fitting Method

Within the tight binding model, if the site energies of all molecules are equivalent, the energy band can be expressed as:

$$\varepsilon(\mathbf{k}) = \varepsilon_0 + \sum \varepsilon_{ij} e^{-i\mathbf{k} \cdot \mathbf{R}_{ij}} \quad (2.12)$$

Here, i is any molecule in the unit cell which has been chosen as a reference, j runs over all the chosen neighbors of molecule i , $\mathbf{k}$ is the wavevector, and $\mathbf{R}_{ij}$ is the spatial vector between molecules j and i . A first-principles density functional theory band structure can be projected to Eq. 2.12 through fitting all the transfer integrals for the corresponding molecular dimers [4].

Fig. 2.1 Schematic representation of the potential energy surfaces of the neutral and charged molecules. Q is the reaction coordinate, and the sum of the two relaxation energies $\lambda^{(i)}$ and $\lambda^{(ii)}$ is the internal reorganization energy. Reproduced from Ref. [14] by permission of The Royal Society of Chemistry



2.1.3 Reorganization Energy

The reorganization energy is composed of two parts, the internal reorganization (λ_i) and the external polarization (λ_e) [8]. The former term λ_i reflects the change in molecular geometry associated with going from the neutral state to the ionized state, and vice versa. And the latter term λ_e describes the change in electronic polarization of the surrounding molecules. The external contribution is difficult to evaluate theoretically, and thus is normally neglected during discussion. In some cases, a magnitude of 0.2–0.6 eV is assumed for λ_e as will be seen in Sect. 2.2 for general understanding of the role of λ_e . In the following, we will only discuss the calculation of the internal reorganization energy at the first principle level.

2.1.3.1 Diabatic Potential Surface

If we obtain the diabatic potential surfaces of the neutral and charged molecules, as shown in Fig. 2.1, we can easily calculate the reorganization energy of the charge transfer reaction between a molecular dimer, which is a sum of two relaxation energy terms: (i) the difference between the energy of the neutral molecule in its equilibrium geometry and in the relaxed geometry characteristic of the ion and (ii) the difference between the energy of ion in its equilibrium geometry and in the neutral relaxed geometry.

2.1.3.2 Normal Mode Analysis

The normal mode analysis provides an approach to obtain the total relaxation energy from the contributions of each vibrational mode: [9]

$$\lambda_i = \frac{k_i}{2} \Delta Q_i^2 = \hbar \omega_i S_i \quad (2.13)$$

$$\lambda = \sum_i \lambda_i \quad (2.14)$$

Here, i runs over all the vibrational normal modes (NM), k_i and ω_i are the corresponding force constant and frequency, ΔQ_i represents the displacement between the equilibrium geometries of the neutral and charged molecules, and S_i denotes the Huang-Rhys factor measuring the electron-phonon coupling strength for the i th normal mode.

2.1.4 Mobility Evaluation

With the knowledge of the charge transfer rates between neighboring molecules, one can evaluate the charge mobility simply from the information of one single hopping step, or more accurately through random walk simulation for the charge diffusion trajectories.

2.1.4.1 Single-Step Approximation with Electric Field

In principle, the charge carrier mobility (μ) can be obtained from its definition as the ratio between the charge drift velocity (v) and the driving electric field (F): [7]

$$\mu = \frac{v}{F} \quad (2.15)$$

Assuming that the charge transport is a Boltzmann hopping process and one pathway with only one single hopping step can characterize the whole diffusion properties, v can be approximately calculated from the nearest inter-site distance (a) and the hopping time (τ), which is actually the reciprocal of the charge transfer rate (k):

$$v \approx a/\tau = ak \quad (2.16)$$

Note that within this approach, an additional contribution from the electric field should be added to the free energy part of Eq. 2.1:

$$k = \frac{V^2}{\hbar} \sqrt{\frac{\pi}{\lambda k_B T}} \exp \left\{ -\frac{(\Delta G^0 + eFa + \lambda)^2}{4\lambda k_B T} \right\} \quad (2.17)$$

2.1.4.2 Single-Step Approximation with Einstein Relation

The Einstein relation sets up the relationship between the mobility and the diffusion constant (D): [10, 11]

$$\mu = \frac{e}{k_B T} D \quad (2.18)$$

$$D = \frac{1}{2d} \frac{\langle l(t)^2 \rangle}{t} \quad (2.19)$$

Here, $l(t)$ is the distance between the charge position at time t and its starting point at time zero. Earlier treatment for the hopping mobility was obtained as [12]

$$D = a^2 k \quad (2.20)$$

where a is the intermolecular spacing and k is the charge transfer rate, namely, the inverse of hopping time. Such an approach requires only a molecular dimer to estimate the bulk mobility. Later, this model has been extended to average over all the neighbors: [13]

$$D \approx \frac{1}{2d} \sum_i P_i \cdot r_i^2 k_i \quad (2.21)$$

Here, d is the space dimension, namely, $d = 1, 2, 3$ for 1D, 2D and 3D systems, respectively. The index i covers all the hopping pathways out of a chosen reference molecule with r_i being the corresponding hopping distance, which is usually expressed as the intermolecular center to center distance, and k_i being the charge transfer rate. P_i is the relative probability to choose the i th pathway:

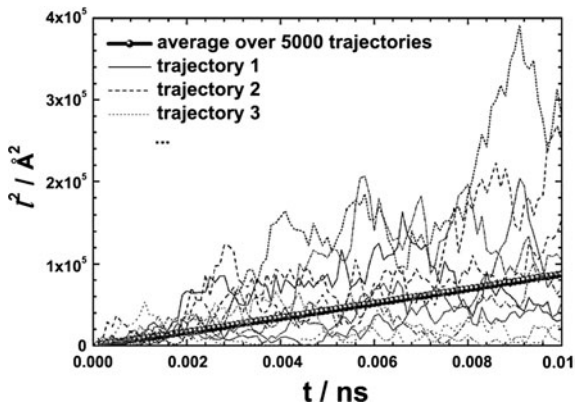
$$P_i = k_i / \sum_j k_j \quad (2.22)$$

2.1.4.3 Random Walk Monte Carlo Simulation

The mobility is a bulk parameter, therefore it should be strongly related to the long range molecular packing, which may provide entirely different transport networks and give different results compared with the simple estimations in previous two sections considering only one single hopping step, especially for inhomogeneous system [14]. To solve this problem, we should model the Brownian motion of charge transport explicitly. Thereby, we propose a random walk scheme to simulate the charge diffusion using the Monte Carlo technique. First, we take the experimental measured crystal structure exactly for simulation and choose an arbitrary molecule within the bulk as the starting point for the charge. The charge is only allowed to hop to its nearest neighbor molecules. To decide which the next site is for the charge to land in, a random number r uniformly distributed between 0 and 1 is generated. Then the charge is allowed to go along the i th specified direction when $\sum_{j=1}^{i-1} P_j < r \leq \sum_{j=1}^i P_j$, where P_j is the relative hopping probability given by Eq. 2.22. The hopping distance is taken to be the intermolecular center distance of the corresponding pathway and the hopping time is set to $1/\sum_j k_j$. Such Monte Carlo simulation keeps going until the diffusion distance exceeds at least 10^2 – 10^3 times the lattice constant. Following the same process, thousands of simulations should be performed to get a linear relationship between the mean-square displacement and the simulation time to get the diffusion

Fig. 2.2 A typical time-dependent squared displacement from random walk simulations.

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coefficient according to Eq. 2.19 (see Fig. 2.2). The mobility is finally calculated through the Einstein relation in Eq. 2.18. It has been shown that two thousand simulations are enough to get converged results of mobility [9]. Note that organic crystals generally have layer-by-layer ordered structures with weak electronic couplings between layers and much larger electronic coupling within each layer, thus the isotropic diffusion assumed in Sect. 2.1.4.2 is generally not valid, but the Monte Carlo procedure can be used to simulate the anisotropic mobilities when the charge trajectories are projected to a specified lattice direction.

2.2 Application I: Siloles

The silicon containing cyclic π -conjugated system silole (silacyclopentadiene) is a promising emissive material because of its notable aggregation-enhanced emission [15, 16] and high PL efficiency [17, 18] in thin solid films. Siloles are also believed to be excellent electron transport materials because the presence of the silicon atom lowers the LUMO energy level relative to that of pure hydrocarbon molecules and this facilitates electron injection. The lowering of the LUMO has been ascribed to the interaction between the σ^* orbital of two exocyclic σ -bonds on the silole ring and the π^* orbital of the butadiene moiety [19, 20]. Here, we apply the methods described in Sect. 2.1 to investigate the charge transport properties in two silole-based compounds, i.e., 1,1,2,3,4,5-hexaphenylsilole (HPS) and 1-methyl-1,2,3,4,5-pentaphenyl-silole (MPPS), as shown in Fig. 2.3.

2.2.1 Computational Details

We adopt the single crystal structures of HPS [21] and MPPS [22] from experiment and generate a variety of possible intermolecular hopping pathways. The unit cells of both HPS and MPPS contain two inequivalent molecules, namely, type A and B. As a result, there are two kinds of pathways, i.e., A–A, and A–B, if we take

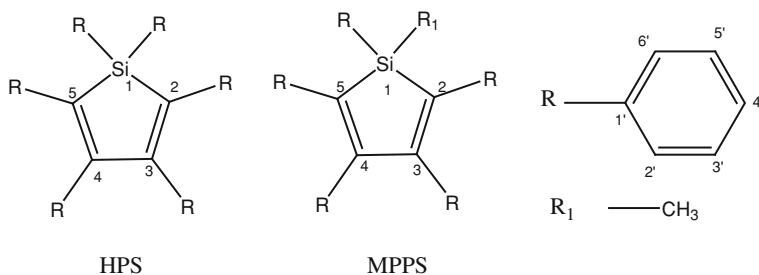


Fig. 2.3 Chemical structure of HPS (*left*) and MPPS (*right*). Reprinted with permission from Ref. [7]. Copyright 2006 American Chemical Society

molecule A as the reference. The first occurs only between cells, while the latter can occur both within and between cells. Using the primitive cell (0, 0, 0) as a reference, all the pathways can be defined with their cell indexes (h, k, l) and molecule types. The intermolecular transfer integrals are calculated based on the direct method according to Eq. 2.2. The internal reorganization energies are calculated with the diabatic energy surface approach as shown in Sect. 2.1.3.1. All these calculations are performed with the Gaussian 03 package [23]. The external reorganization energies are set to be 0.2–0.6 eV. The mobilities are calculated with the simple model introduced in Sect. 2.1.4.1.

2.2.2 Results and Discussion

2.2.2.1 Transfer Integral

The calculated transfer integrals for HPS and MPPS crystals are listed in Tables 2.1 and 2.2, respectively. For HPS, the largest transfer integral for electron and hole are found to be 17.69 meV and 14.10 meV, respectively which are quite close with each other. For MPPS, the situation is quite similar (33.47 vs. 43.97 meV), but the transfer integrals are generally much larger than HPS. This can be easily understood by their difference in intermolecular distances (see Table 2.3). For the most important pathways, the inter-carbon distances in MPPS are around 6.71–6.86 Å, which are much smaller than those of HPS within the range of 9.16–11.74 Å. This is due to the fact that the phenyl group presents larger hindrance than the methyl group and thus MPPS has greater π – π overlap. Besides, we can find that there exist channels where electron transfer is much larger than that for the hole, e.g., channels I, VI, and X for HPS and channels I, VIII, and IX for MPPS, while there are just few channels that hole transfer integral is larger than electron. This can be explained by the charge distributions of the frontier orbitals. Taking HPS as an example, the LUMO wave function is mainly localized on the silole ring, especially on the 2-, 1-, and 5-positions (see Fig. 2.4), and there is also considerable electron density on the 1'-position of the silicon exocyclic aryl ring, which is due to the interaction between the σ^* orbitals of the two exocyclic σ

Table 2.1 Charge transfer integrals (t_h for hole and t_e for electron) between molecule A in HPS (0, 0, 0) unit cell and the other most possible adjacent molecules

Pathway	A-B										
	A-A										
Channel	I	II	III	IV	V	VI	VII	VIII	IX	X	XI
Partner	($\pm 1, 0, 0$)	(0, $\pm 1, 0$)	(0, 0, ± 1)	(0, 0, 0)	(-1, 0, 0)	(0, -1, 0)	(0, 0, -1)	(-1, -1, 0)	(-1, 0, -1)	(0, -1, -1)	(-1, -1, -1)
Si-Si distance (Å)	9.53	10.04	16.31	7.20	8.70	8.78	9.99	12.40	13.18	13.85	18.03
t_h (meV)	0.79	0.46	0.03	17.69	0.08	2.39	2.26	0.05	4.87	2.39	0.03
t_e (meV)	6.61	1.17	0.03	12.82	1.25	14.10	1.85	0.14	4.41	12.05	0.19

Table 2.2 Charge transfer integrals (t_h for hole and t_e for electron) between molecule A in MPPS (0, 0, 0) unit cell and the other most possible adjacent molecules

Pathway	II (A-B)										
	I (A-A)										
Channel	I	II	III	IV	V	VI	VII	VIII	IX	X	XI
Partner	($\pm 1, 0, 0$)	($0, \pm 1, 0$)	($0, 0, \pm 1$)	($0, 0, 0$)	($-1, 0, 0$)	($0, -1, 0$)	($0, 0, -1$)	($-1, -1, 0$)	($-1, 0, -1$)	($0, -1, -1$)	($-1, -1, -1$)
Si-Si distance (Å)	10.19	11.27	11.98	13.72	7.48	15.33	10.66	10.42	6.10	12.88	9.76
t_h (meV)	7.70	1.09	4.54	0.03	33.47	5.82	0.54	4.38	2.10	0.98	3.10
t_e (meV)	15.08	0.54	1.39	0.08	43.97	4.08	0.49	7.95	18.04	1.74	1.80

Table 2.3 Interatomic distances (in Å) in the molecular dimers for HPS and MPPS

Channel	Si1–Si1	C2–C2	C5–C5	C3–C3	C4–C4
HPS-IV	7.61	9.63	9.63	11.74	11.74
HPS-VI	8.78	9.16	9.16	10.26	10.26
MPPS-V	7.48	6.71	6.71	6.86	6.86
MPPS-IX	6.10	8.48	8.48	10.82	10.82

Fig. 2.4 HOMO and LUMO of HPS molecule. Reprinted with permission from Ref. [7]. Copyright 2006 American Chemical Society

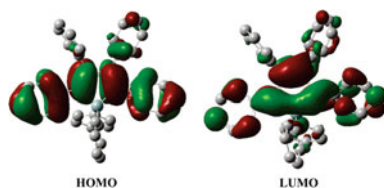


Fig. 2.5 HPS dimer structures, including frontier molecular orbitals of (0, 0, 0) A (down) and (0, −1, 0) B (up) molecules. The *left panel* shows the HOMOs and the *right panel* shows in LUMOs. Reprinted with permission from Ref. [7]. Copyright 2006 American Chemical Society

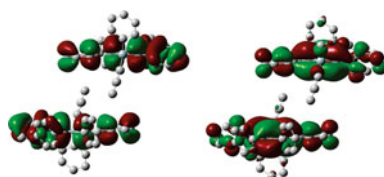


Table 2.4 Calculated internal reorganization energies (in eV) for MPPS and HPS

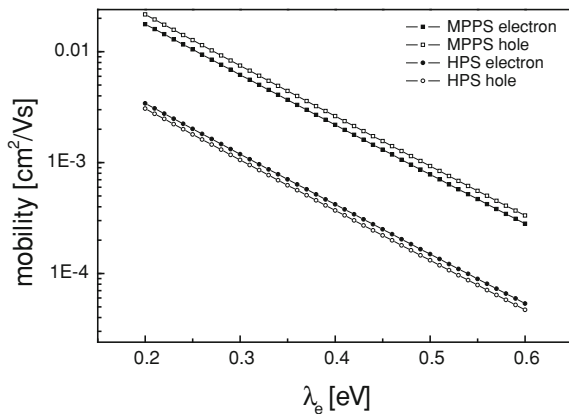
		Neutral to ion	Anion to ion	Total
MPPS	Electron	0.18	0.16	0.34
	Hole	0.14	0.13	0.27
HPPS	Electron	–	–	0.32
	Hole	–	–	0.27

orbital on the ring silicon and the π^* orbital of the butadiene moiety [24]. On the other hand, the HOMO (hole) is primarily located on the C2=C3 and C4=C5 double bonds in the silole ring as well as on the 2- and 5-positions in the aryl rings. The different contribution of the LUMO and HOMO orbitals may induce different relative strength of overlap between molecules for different pathways. For example, in the configuration of channel VI (see Fig. 2.5), the distances between silole rings at the 1-, 2-, and 5-positions of the (0, 0, 0) A molecule and the (0, −1, 0) B molecule are smaller than those at the 3- and 4-positions, which eventually make the intermolecular overlap for LUMOs larger than that for HOMOs.

2.2.2.2 Reorganization Energy

The calculated internal reorganization energies are given in Table 2.4. We can find that the total reorganization energies for MPS and HPS are similar, and the

Fig. 2.6 Theoretical estimation of the room-temperature carrier mobilities for MPPS and HPS for the most favored transport channel, with an applied electric field of $F = 10^6$ V/cm. Reprinted with permission from Ref. [7]. Copyright 2006 American Chemical Society



reorganization energy for the hole is slightly smaller than that for the electron in both MPPS and HPS.

2.2.2.3 Room-Temperature Mobility

The largest transfer rates (channel IV for both HPS and MPPS) are used to calculate the mobilities. In Fig. 2.6, we show the room-temperature mobility as a function of the external reorganization energy for an electric field of $F = 10^6$ V/cm, which is a typical value for organic light emitting diode devices. An interesting discovery is that, although in most cases, electron mobility is observed to be much smaller than hole mobility in organic materials, the calculated mobilities of electron and hole are about the same in HPS and MPPS. This can be explained by the fact that the reorganization energy of hole is smaller than electron and more transport channels exist for electron than hole. Such balanced electron and hole mobilities in siloles should be one of the reasons for the high electroluminescence efficiency. Besides, the mobility of MPPS is generally one magnitude larger than that of HPS because the transfer integral of MPPS is larger than HPS and their reorganization energies are quite close.

2.3 Application II: Triphenylamine Dimers

Triphenylamine (TPA) derivatives have been widely employed as hole transport materials in molecular electronics applications [25, 26]. However, their performances have been found to be unsatisfactory due to their amorphous nature in the solid state [27–29]. In order to improve the mobility of TPA, a design strategy of making dimers of TPA, either in the form of a macrocycle or a linear chain (see Fig. 2.7), has been performed [30, 31]. This part tends to understand the origin of their mobility-structure relationship from bottom up.

Fig. 2.7 Chemical structure of the cyclic triphenylamine (denoted as compound 1, *upper panel*), and a linear analog (denoted as compound 2, *lower panel*). Reproduced from Ref. [31] by permission of the AAS

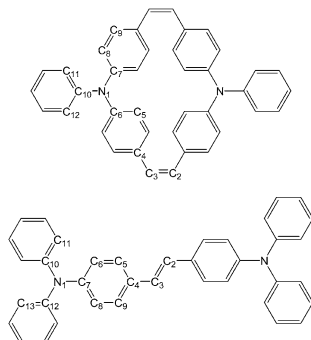
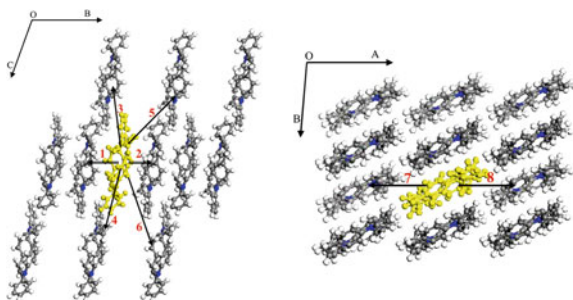


Fig. 2.8 Hopping pathways for compound 1. Reprinted with permission from Ref. [30]. Copyright 2006 American Chemical Society



2.3.1 Computational Details

The crystal structures are taken from experimental X-ray analyzed crystallographic data [30]. The transfer integrals are evaluated within direct scheme of Kohn-Sham-Fock operator as described in Sect. 2.1.2.1. The reorganization energy is obtained with the diabatic potential surfaces. And the mobility is calculated from single-step approach with Einstein relation introduced in Sect. 2.1.4.2. All quantum chemistry calculations are performed within Gaussian03 package [23].

2.3.2 Results and Discussion

2.3.2.1 Transfer Integral

The chosen pathways are shown in Figs. 2.8 and 2.9 for compound 1 and 2, respectively. And the corresponding transfer integrals are given in Tables 2.5 and 2.6. Since there are two molecules in the unit cell of compound 2, two sets of data are given corresponding to choosing either of them as the reference molecule. It is found that the calculated two sets of transfer integrals do not differ much, e.g., the largest transfer integral is 8.65×10^{-3} and 6.26×10^{-3} eV, respectively. Besides, the magnitude of the transfer integrals for both compounds is also quite close.

Fig. 2.9 Hopping pathways for compound 2. Reprinted with permission from Ref. [30]. Copyright 2006 American Chemical Society

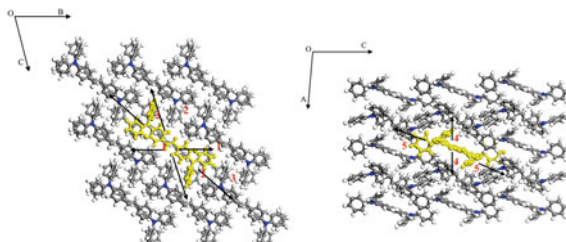


Table 2.5 Calculated transfer integrals for eight pathways in compound 1

Pathway	Distance (Å)	V (eV)
1	5.133	4.86E-3
2	5.328	8.65E-3
3	13.502	2.50E-3
4	13.974	7.43E-3
5	15.927	1.36E-7
6	15.406	1.21E-8
7	10.642	4.09E-3
8	10.642	4.09E-3

Table 2.6 Calculated two sets of transfer integrals for compound 2

Set	Pathway	Distance (Å)	V (eV)
1	1	11.334	4.35E-3
	2	12.491	9.97E-5
	3	19.102	2.19E-4
	4	5.312	5.64E-3
	5	13.575	3.03E-3
2	1	11.334	6.26E-3
	2	12.491	1.68E-3
	3	19.102	3.08E-3
	4	5.312	5.67E-3
	5	13.575	3.03E-7

2.3.2.2 Reorganization Energy

For compound 1, the reorganization energy is calculated to be 0.173 eV, which is much smaller than that of compound 2, 0.317 eV. This difference in internal reorganization energy can be explained through the structure difference between optimized neutral molecule and cation (see Table 2.7). From the difference in bond lengths, bond angles, and the torsions, we can find that the change in geometry from neutral molecule to cation is smaller in compound 1 than compound 2, since

Table 2.7 The optimized geometrical parameters for the neutral and cation structures of compounds 1 and 2, including bond lengths, bond angles, and dihedral angles values

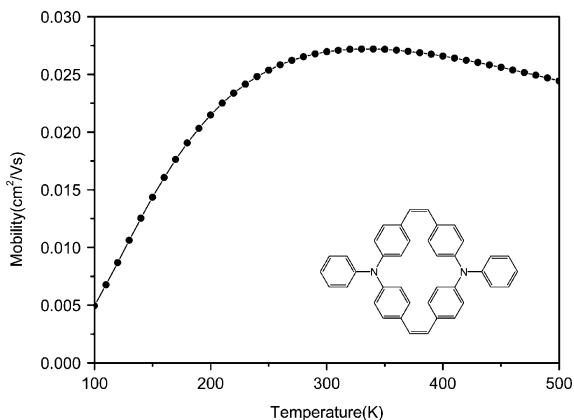
		Neutral	Cation	Δ
Compound 1	C ₂ C ₃	1.35 Å	1.36 Å	0.01 Å
	C ₃ C ₄	1.48 Å	1.46 Å	−0.02 Å
	N ₁ C ₆ , N ₁ C ₇	1.42 Å	1.41 Å	−0.01 Å
	C ₇ C ₈	1.40 Å	1.41 Å	0.01 Å
	C ₈ C ₉	1.40 Å	1.39 Å	−0.01 Å
	C ₁₀ C ₁₁ , C ₁₀ C ₁₂	1.41 Å	1.40 Å	−0.01 Å
	C ₁₀ N ₁ C ₇ , C ₁₀ N ₁ C ₆	121.3°	121.1°	−0.2°
	C ₆ N ₁ C ₇	117.4°	117.9°	0.5°
	C ₁₁ C ₁₀ N ₁ C ₇	35.1°	40.7°	5.6°
	C ₅ C ₆ N ₁ C ₇	44.0°	40.2°	−3.8°
	C ₈ C ₇ N ₁ C ₁₀	46.1°	41.3°	−4.8°
Compound 2	C ₂ C ₃	1.35 Å	1.37 Å	0.02 Å
	C ₃ C ₄	1.46 Å	1.43 Å	−0.03 Å
	C ₄ C ₅ , C ₄ C ₉	1.41 Å	1.42 Å	0.01 Å
	C ₅ C ₆ , C ₈ C ₉	1.39 Å	1.38 Å	−0.01 Å
	C ₆ C ₇	1.41 Å	1.42 Å	0.01 Å
	C ₇ C ₈	1.40 Å	1.42 Å	0.02 Å
	N ₁ C ₇	1.42 Å	1.38 Å	−0.04 Å
	N ₁ C ₁₀ , N ₁ C ₁₂	1.42 Å	1.43 Å	0.01 Å
	C ₄ N ₁ C ₃	120.1°	121.3°	0.2°
	C ₄ N ₁ C ₂	119.7°	117.5°	−2.2°
	C ₂ N ₁ C ₃	120.2°	121.2°	1.0°
	C ₁₁ C ₁₀ N ₁ C ₇	42.2°	51.2°	10.0°
	C ₁₃ C ₁₂ N ₁ C ₁₀	42.5°	51.2°	8.7°
	C ₆ C ₇ N ₁ C ₁₀	39.6°	24.0°	−15.6°

the closed ring structure restricts the rotation of the phenyl groups. As a result, lower reorganization energy is obtained.

2.3.2.3 Room-Temperature Mobility

The average room-temperature hole mobilities are calculated to be $2.7 \times 10^{-2} \text{ cm}^2/\text{Vs}$ for compound 1 and $1.9 \times 10^{-3} \text{ cm}^2/\text{Vs}$ for compound 2. These values compare quite well with the experimental results of $0.5\text{--}1.5 \times 10^{-2} \text{ cm}^2/\text{Vs}$ for 1 and $2 \times 10^{-4} \text{ cm}^2/\text{Vs}$ for 2, respectively, except that the theoretical value for 2 is about one order of magnitude larger than the experimental value. It seems that the experimental mobility for 2 can still be improved by subsequent processing and optimization of the material. Since the two compounds are similar in transfer integrals, the difference in mobility can be attributed to their difference in reorganization energy. Therefore, material with macro-cyclic structure is more favorable for charge transport than linear structure due to smaller reorganization energy during charge transport processes.

Fig. 2.10 The predicted temperature dependence of the drift mobility for compound 1. Reproduced from Ref. [31] by permission of the AAS



2.3.2.4 Temperature Dependence of Mobility

The temperature dependence of mobility is an important topic to understand the charge transport mechanism in organic materials. Here, we show how Marcus theory describes this temperature dependence, using compound 1 and 2 as examples. We assume that both the transfer integrals and the reorganization energy do not change with temperature, but we note that the impact of such change will be detailedly investigated for another organic material in Chap. 3. Combining Eqs. 2.1, 2.18, and 2.20, it is easy to see that the mobility should have a temperature dependence of $T^{-3/2} \exp(-\lambda/4k_B T)$. The exponential law, $\exp(-\lambda/4k_B T)$, dominates at low temperatures and the power law, $T^{-3/2}$, dominates at high temperature after the barrier is fully overcome, namely, the mobility increases with the increase of temperature at low T and decreases with temperature at high T (see Fig. 2.10). The maximum of mobility is directly related to the barrier height of $\lambda/4$. It should be noted that Marcus theory can only be applied at high temperature since the quantum tunneling effect of the nuclear motions, which is very important at low temperatures, has been neglected. The improvement of adding quantum effects inside the hopping picture will be discussed in Sect. 2.4. In Chaps. 3 and 4, the temperature dependence of mobility will also be discussed in-depth using other theoretical models.

2.4 Application III: Oligothiophenes

Oligothiophene (nT) is one of the earliest organic materials for organic thin film field-effect transistors (FETs) [32, 33]. Thiophene-based materials exhibit a variety of intra- and intermolecular interactions originating from the high polarizability of sulfur electrons in the thiophene rings [34]. Therefore, thiophene oligomers can be regarded as a versatile building block for organized structures. The crystals of oligothiophenes exhibit a herringbone structure with different number of molecules in the unit cell (Z), depending on the sublimation temperatures (see

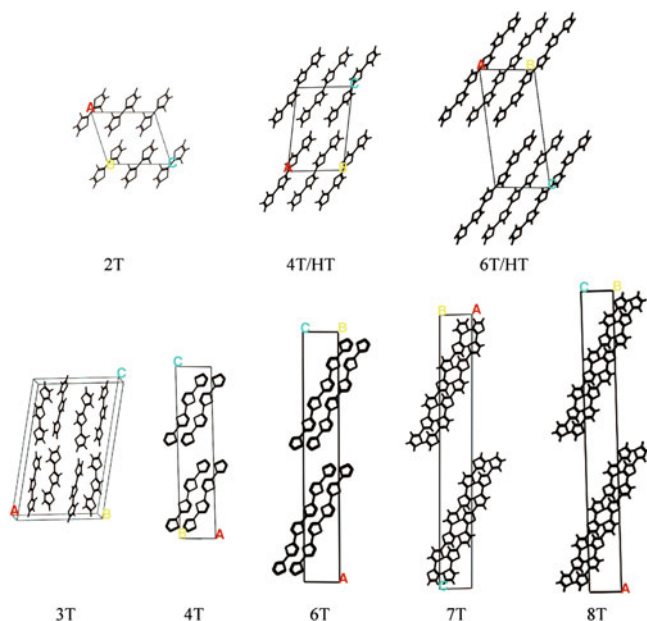


Fig. 2.11 Crystal structures of α - n Ts. Reprinted with permission from Ref. [9]. Copyright 2008 American Chemical Society

Fig. 2.11). For the high-temperature (HT) phase, $Z = 2$ for 2, 4, and 6T, while for low temperature (LT) phase, $Z = 4$ for 4, 6, 7, and 8T. In addition, for 3T, $Z = 8$. Using n T as a series of model systems, hereby, we discuss the influence of crystal structure and molecular size on mobility.

2.4.1 Computational Details

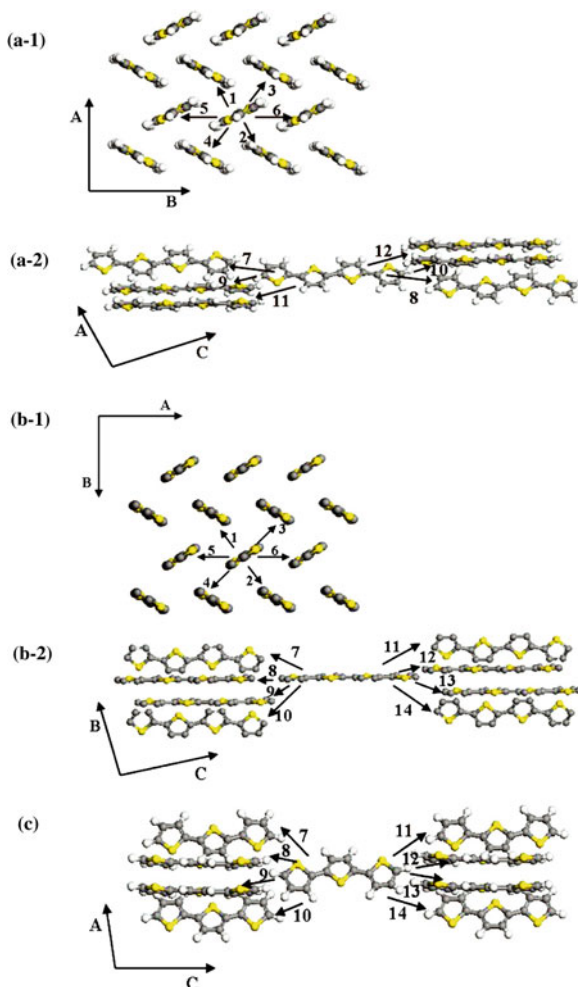
The transfer integrals are calculated within the direct scheme and the reorganization energies are obtained through the NM analysis. The Huang–Rhys factors are evaluated through the DUSHIN program [35]. After obtaining the Marcus transfer rates, the mobility is calculated with a random walk simulation, which is introduced in Sect. 2.1.4.3.

2.4.2 Results and Discussion

2.4.2.1 Transfer Integral

The oligothiophenes with the same Z has very similar crystal structures. Thus we only show the chosen hopping pathways for 4T/HT ($Z = 2$), 4T/LT ($Z = 4$), and

Fig. 2.12 Charge hopping pathways schemes for 4T/HT (a), 4T/LT (b), and 3T (c). **a-1** and **b-1** display the hopping routes in the same molecular layer, and **(a-2)** and **(b-2)** are between different molecular layers. Reprinted with permission from Ref. [9]. Copyright 2008 American Chemical Society



3T ($Z = 8$) in Fig. 2.12. The calculated transfer integrals are given in Tables 2.8 and 2.9. There, we can find that the transfer integrals are not influenced by the oligomer length within the same group of packing. Besides, the largest transfer integral for $Z = 2$ crystals is about 34–40 meV, which is about twice as much as that for the $Z = 4$ phase, which is only about 18 meV. To understand this phenomenon, we illustrate explicitly the packing structures for the dimer along the principal pathway for the HT and LT phases of 4T and 6T, as well as their HOMO coefficients (see Fig. 2.13). As is known, the transfer integral is increased if both are bonding or antibonding interactions between the π -atomic orbitals and decreased when there occurs a cancelation between bonding and antibonding overlap. It is noted that for the LT phase, there exists a displacement of about half a thiophene ring width, while for the HT phase, the displacement is about one

Table 2.8 Calculated transfer integrals (V , in meV) and intermolecular distances (d , in Å) for all pathways for 4T/LT, 4T/HT, and 6T/HT at the DFT/PW91PW91/6-31G* level

Pathway	2T		4T/HT		6T/HT	
	V	d	V	d	V	d
1	34	5.34	40	5.31	36	5.38
5	6	5.90	4	5.75	3	5.68
7	1	10.00	0.7	17.82	0.4	25.68
9	12	8.31	2	15.81	0.7	23.38

Table 2.9 Calculated transfer integrals (V , in meV) and intermolecular distances (d , in Å) for all pathways of other than $Z = 2$ crystal phases for 3, 4, 6, 7, and 8T at the DFT/PW91PW91/6-31G* level

Pathway	3T		4T		6T		7T		8T	
	V	d	V	d	V	d	V	d	V	d
1	7	4.67	12	4.93	18	4.98	18	4.81	17	4.92
2	13	5.06	17	5.01	16	4.92	14	4.97	17	4.96
3	13	4.72	17	5.01	16	4.92	17	4.82	17	4.96
4	13	5.06	12	4.93	18	4.98	18	4.97	17	4.92
5	0.4	5.64	18	6.08	10	6.03	13	5.95	9	6.00
6	0.4	5.64	18	6.08	10	6.03	13	5.95	9	6.00
7	2	12.16	5	16.49	2	24.18	0.4	28.82	1	31.88
8	4	13.25	3	17.63	2	25.34	0.4	29.67	0	30.73
9	4	13.20	4	15.55	3	23.16	1	27.68	0.5	32.95
10	19	12.29	0.0	16.96	0.0	24.51	0.3	28.84	0	32.13
11	0	14.87	5	16.49	2	24.18	1	29.17	1	31.88
12	4	13.20	0.2	15.41	0.1	23.04	2	27.05	1	33.05
13	4	13.25	2	17.46	1	25.22	0	28.37	1	30.82
14	0.3	14.53	0	16.96	0	24.51	2	28.07	0	32.13

thiophene ring. Combined with the HOMO orbital charge distributions, one can easily rationalize that the molecular packing in the HT phase favors hole transfer better than the LT phase. And their transfer integral can differ about 2–3 times even though the intermolecular distances are almost the same.

2.4.2.2 Reorganization Energy

From Table 2.10, it is easy to find that the calculated reorganization energies from the adiabatic potential surface method are very similar with those from the normal mode analysis. This indicates that the molecular reorganizing process can be well-described by the harmonic oscillator model as assumed in Marcus theory. It is also seen that the reorganization energy decreases as the chain is elongated. To understand the reason, we display the partition of the relaxation energies of 4T and 8T into the contributions of each normal mode, which is shown in Fig. 2.14. We can see that the contributions from the high-frequency parts (1,200–1,600 cm^{-1})

Fig. 2.13 Intermolecular displacements taken from crystal packing along the long axis of thiophene for the dominant pathway. HOMOs of 4T and 6T also are shown. Reprinted with permission from Ref. [9]. Copyright 2008 American Chemical Society

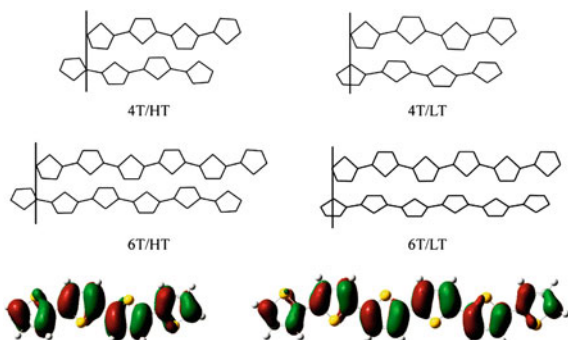


Table 2.10 Calculated reorganization energies by adiabatic potential surfaces of the neutral and cation species and by NM analysis at the DFT-B3LYP/6-31G* level

Molecules	Reorganization energy	
	Adiabatic potential	Normal mode
2T	361	364
3T	316	323
4T	286	288
5T	265	274
6T	244	255
7T	224	238
8T	203	212

decrease remarkably when going from 4T to 8T, which means that the C–C single and double stretching modes are influenced by the conjugation length [36].

2.4.2.3 Mobility

The calculated mobilities are shown in Fig. 2.15. Within the group of nT crystals with the same Z , the mobility increases with the number of thiophene rings, n , since they have close transfer integrals, but the reorganization energy decreases with the chain length. Besides, the HT phase ($Z = 2$) leads to a larger drift mobility than the LT phase ($Z = 4$). This is because the former has larger transfer integral than the latter, while the reorganization energy is the same.

2.5 Incorporate Nuclear Tunneling Effect in the Hopping Picture

The Marcus charge transfer rate works for extreme high-temperature regimes. At room temperature, $k_B T$ is about 200 cm^{-1} , which is much smaller than some of the high-frequency vibrations, e.g., the single and double bond stretching modes with frequency $1,200\text{--}1,600 \text{ cm}^{-1}$ (as shown in Fig. 2.14). Therefore the nuclear

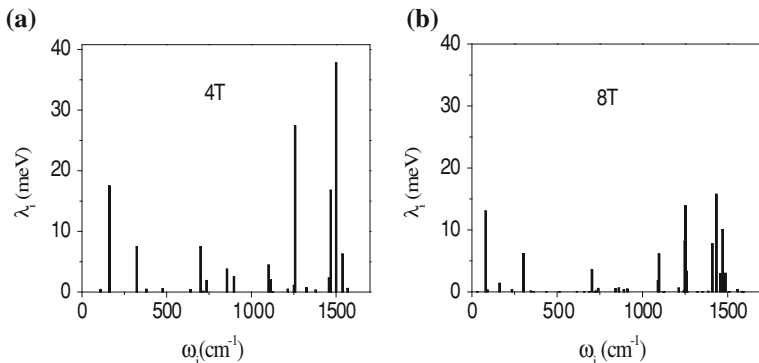
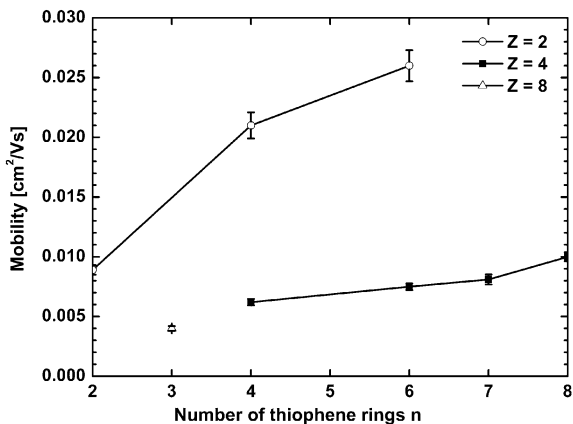


Fig. 2.14 Contribution of the vibrational modes to the cationic relaxation energy for 4T (a) and 8T (b). Reprinted with permission from Ref. [9]. Copyright 2008 American Chemical Society

Fig. 2.15 Drift mobility versus the number of thiophene rings. Reprinted with permission from Ref. [9]. Copyright 2008 American Chemical Society



tunneling effect of these modes needs to be taken into account in calculating the charge transfer rate. In following, we will use the Fermi's Golden rule to obtain the charge transfer rate, and show the role of nuclear tunneling on charge carrier mobility.

2.5.1 Fermi's Gold Rule

The charge transfer rate formula considering the quantum effects was derived by Jortner [37] and Lin et al. [38] It starts from the general Fermi's Golden rule for the transfer rate from the initial state, $|i\rangle$, to the final state, $|f\rangle$:

$$k = \frac{2\pi}{\hbar^2} V_{fi}^2 \delta(\hbar\omega_{fi}) \quad (2.23)$$

Here, V_{fi} and $\hbar\omega_{fi}$ are the coupling and energy difference between the final and initial state. If we write the contributions of the electronic state and the nuclear vibrational state separately, we get

$$k = \frac{2\pi}{\hbar^2} V^2 \sum_{v,v'} P_{iv} |\langle \Theta_{fv'} | \Theta_{iv} \rangle|^2 \delta(\hbar\omega_{fv',iv}) \quad (2.24)$$

Now V is the transfer integral described previously in Sect. 2.1, i.e., the coupling between the final and initial electronic states, v (v') is the quanta of the nuclear vibration in the initial (final) state, P_{iv} is the distribution function of v th vibrational quanta in the initial state, $\Theta_{iv(fv')}$ is the wave function of the initial (final) nuclear vibration, and $\hbar\omega_{fv',iv}$ is the energy different between the final and initial vibronic states. If the nuclear vibration consists of a collection of independent harmonic oscillators, we have

$$\Theta_{iv} = \prod_j \chi_{iv_j}(Q_j) \quad (2.25)$$

$$\Theta_{fv'} = \prod_j \chi_{fv'_j}(Q'_j) \quad (2.26)$$

$$P_{iv} = \prod_j P_{iv_j} \quad (2.27)$$

$$\omega_{fv',iv} = \omega_{fi} + \sum_{v_j} \sum_{v'_j} \left[\left(v'_j + \frac{1}{2} \right) \omega'_j - \left(v_j + \frac{1}{2} \right) \omega_j \right] \quad (2.28)$$

where

$$\chi_{v_j}(Q_j) = (\beta_j / \sqrt{\pi} 2^{v_j} v_j!)^{1/2} H_{v_j}(\beta_j Q_j) \exp(-\beta_j^2 Q_j^2 / 2) \quad (2.29)$$

$$\begin{aligned} P_{iv} &= \left[\sum_v \exp\left(\frac{-E_{iv}}{k_B T}\right) \right]^{-1} \exp\left(\frac{-E_{iv}}{k_B T}\right) \\ &= \prod_j^N 2 \sinh \frac{\hbar\omega_j}{2k_B T} \exp\left(-\hbar\omega_j \left(v_j + \frac{1}{2}\right) / k_B T\right) \end{aligned} \quad (2.30)$$

with $\beta_j = (\omega_j/\hbar)^{1/2}$ and H_{v_j} are the Hermite polynomials. Expressing the δ function as a Fourier integral in time, Eq. 2.24 becomes

$$k = \frac{V^2}{\hbar^2} \int_{-\infty}^{\infty} dt e^{it\omega_{fi}} \prod_j G_j(t) \quad (2.31)$$

$$G_j(t) = \sum_{v_j} \sum_{v'_j} P_{iv_j} \left| \langle \chi_{fv'_j} | \chi_{iv_j} \rangle \right|^2 \exp \left(it \left\{ \left(v'_j + \frac{1}{2} \right) \omega'_j - \left(v_j + \frac{1}{2} \right) \omega_j \right\} \right) \quad (2.32)$$

After employing the Slater sum and the displaced harmonic oscillator approximation [39], Eq. 2.32 can be evaluated as:

$$G_j(t) = \exp \left[-S_j \left\{ (2n_j + 1) - n_j e^{-it\omega_j} \omega_j - (n_j + 1) e^{it\omega_j} \right\} \right]. \quad (2.33)$$

where $n_j = 1/(\exp(\hbar\omega_j/k_B T) - 1)$ and $S_j = \lambda_j/\hbar\omega_j$ are the population and the Huang–Rhys factor of the j th normal mode. Substituting Eq. 2.33 into Eq. 2.31 yields the quantum charge transfer rate expression:

$$k = \frac{V^2}{\hbar^2} \int_{-\infty}^{\infty} dt \exp \left\{ it\omega_{fi} - \sum_j S_j \left[(2n_j + 1) - n_j e^{-it\omega_j} - (n_j + 1) e^{it\omega_j} \right] \right\} \quad (2.34)$$

Finally, we take the real part of the integration of Eq. 2.34 and get:

$$k = \frac{V^2}{\hbar^2} \int_0^{\infty} dt \exp \left\{ - \sum_j S_j (2n_j + 1) (1 - \cos \omega_j t) \right\} \cos \left(\sum_j S_j \sin \omega_j t \right) \quad (2.35)$$

2.5.2 Short-Time Integration in Fermi's Golden Rule

We notice that the integral function in Eq. 2.35 is actually a periodic function, and thus it does not make any sense to calculate this integration up to infinite time range. However, in real materials, there always exist various external scattering mechanisms like defects and additional interaction with the environment, both of which have not been considered in the dimer model for the charge transfer rate here. Therefore the time range for integration in Eq. 2.35 is always limited. In practice, when the electron–phonon coupling is large and/or the temperature is high enough, the integral function in Eq. 2.35 can decay very quickly and remain negligible for a long time which is comparable with the period of the function. Therefore it is quite reasonable to calculate the integration just within the first period. If it is not the case, namely, the integral function oscillates with time and does not really decay to very small values, one needs to make a kind of cutoff to the integral time. One advisable approach is to choose the most important mode for the charge transfer process, i.e., the mode with the most significant Huang–Rhys factor, and apply the short-time approximation $\exp(it\omega_j) \approx 1 + it\omega_j + (it\omega_j)^2/2$, where the last term provides an overall decay factor in the integrand and guarantees the convergence for Eq. 2.35.

2.5.3 From Fermi's Golden Rule to Marcus Rate

In the strong coupling limit (i.e., $\sum_j S_j \gg 1$) and/or the high-temperature limit ($k_B T \gg \hbar \omega_j$), we can use the short-time approximation automatically for all the vibrational modes, namely, keeping only the three leading terms in the infinite expansion $\exp(it\omega_j) = 1 + it\omega_j + (it\omega_j)^2/2 + \dots$, and then Eq. 2.34 becomes

$$k = \frac{V^2}{\hbar^2} \int_{-\infty}^{\infty} dt \exp \left[it \left(\omega_{fi} + \sum_j S_j \omega_j \right) - \frac{t^2}{2} \sum_j S_j \omega_j^2 (2n_j + 1) \right] \quad (2.36)$$

or

$$k = \frac{V^2}{\hbar^2} \sqrt{\frac{2\pi}{\sum_j S_j \omega_j^2 (2n_j + 1)}} \exp \left[-\frac{(\omega_{fi} + \sum_j S_j \omega_j)^2}{2 \sum_j S_j \omega_j^2 (2n_j + 1)} \right] \quad (2.37)$$

In the high-temperature regime, we have $n_j = k_B T / \hbar \omega_j \gg 1$, and Eq. 2.37 reduces to the Marcus formula, Eq. 2.1, with $\Delta G^0 = \hbar \omega_{fi}$ and $\lambda = \sum_j S_j \hbar \omega_j$.

2.6 Application: Oligoacenes

Oligoacenes such as tetracene, rubrene, and pentacene (see Fig. 2.16) are among the most promising classes of organic semiconductors for (opto)electronic applications [40]. The planarity and rigidity of tetracene and pentacene molecules facilitate good intermolecular ordering, and their extended π -conjugation over the whole molecule enables large intermolecular electron overlap. Rubrene is a star derivative of tetracene with additional four phenyl side groups, which further enhance tight crystal packing. Here, we use tetracene and rubrene as model systems to investigate the role of nuclear tunneling effect on charge transport properties.

2.6.1 Computational Details

Transfer integrals are obtained with the direct scheme with Kohn-Sham–Fock operator described in Sect. 2.1.2.1. Normal mode analysis is performed to get all the intramolecular vibrational frequencies and the corresponding Huang–Rhys factors. The mobility is obtained through random walk simulation with the quantum charge transfer rate in Eq. 2.35. Tetracene and Rubrene form layer-by-layer crystals. The chosen hopping pathways within the layer are shown in Fig. 2.17.

Fig. 2.16 Chemical structures of tetracene, rubrene, and pentacene

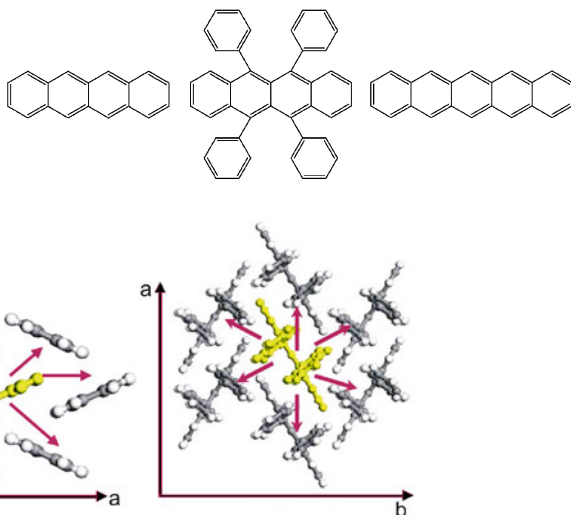


Fig. 2.17 Chosen intra-layer pathways for tetracene crystal (*left*) and rubrene crystal (*right*). Reprinted from Ref. [39] by permission of APS

2.6.2 Results and Discussion

2.6.2.1 Transfer Integral

The largest transfer integral calculated for rubrene comes from the *a* direction (see Fig. 2.17), 102.4 meV, which is much larger than that for tetracene which is about 40 meV. This can be understood from their molecular packings. Both rubrene and tetracene have a herringbone motif in the *ab* plane where the most significant electronic couplings are found. However, due to the phenyl side groups, the long molecule axes lie in the *ab* plane in rubrene, while in tetracene, they come out of that plane. This modulation leads to no short-axis displacement along the *a* direction and cofacial π -stack with some long-axis displacement.

2.6.2.2 Normal Mode Analysis

The contribution of individual vibrational modes to the total reorganization energy is shown in Fig. 2.18. For tetracene, it is found that high-frequency C–C bond stretching modes present dominant electron–phonon couplings. And rubrene differs strongly with tetracene in the low-frequency region due to the twisting motions of the four phenyl groups being strongly coupled with the charge transfer process, similar with the results for oligothiophenes shown in Fig. 2.14. As a result, the reorganization energy of rubrene (150 meV) is much larger than that of tetracene (105 meV).

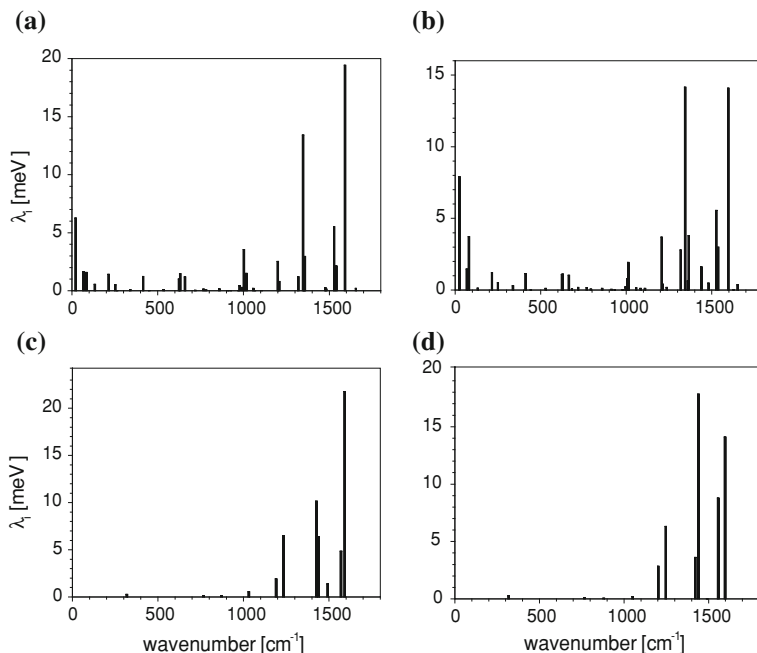


Fig. 2.18 Contribution of the individual vibrational modes to the relaxation energies for neutral and cationic molecules, (a) neutral rubrene, (b) cationic rubrene, (c) neutral tetracene, and (d) cationic tetracene. Reprinted from Ref. [39] by permission of APS

2.6.2.3 Temperature Dependence of Mobility

We calculate the temperature-dependent charge transfer rate with both the Marcus theory and the Fermi's golden rule (see Fig. 2.19a). It is found that the quantum transfer rate is nonzero and almost constant below 10 K due to the quantum tunneling nature of the nuclear vibrations at low temperatures. It then increases with temperature and reaches a maximum at about 130 K and finally decreases gradually. This behavior is significantly different with the classical Marcus rate. For the transition point of the charge transfer rate at higher temperatures, which corresponds to the thermal activation over a barrier, the classical Marcus theory gives $\lambda/4 = 37.5 \text{ meV} \sim 435 \text{ K}$, while the nuclear tunneling reduces this height to only 130 K. The corresponding temperature dependence of mobility for rubrene is shown in Fig. 2.19b. The mobility decreases rapidly from 1 to 10 K, then increases slowly until 30 K, and decreases slowly again at higher temperatures. These can be fully explained by the general $k(T)/T$ behavior within the hopping picture. For tetracene, the charge transfer rate remains constant up to room temperature (see Fig. 2.20) since the contributed vibrations are all high-frequency modes and the nuclear tunneling effect is extremely strong. Accordingly, the mobility decreases with temperature throughout the whole temperature range, showing a band-like behavior.

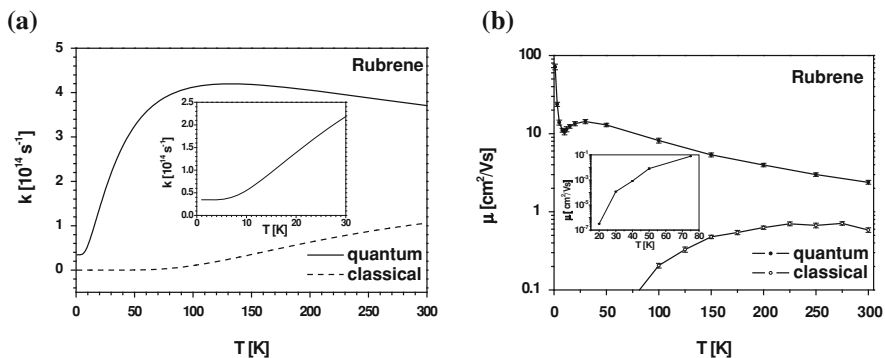
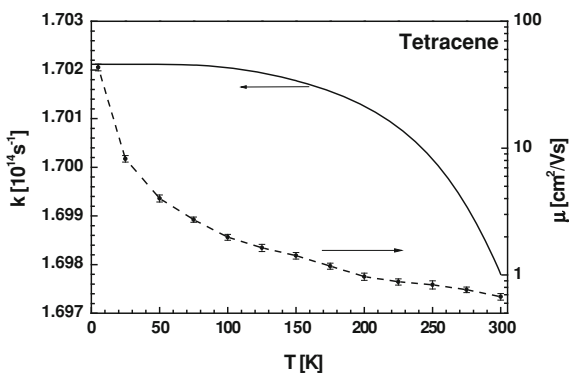


Fig. 2.19 **a** Hole transfer rate as a function of temperature for the rubrene dimer with the largest transfer rate. The inset shows quantum CT rate below 5 K; **b** 3D averaged hole mobilities as a function of temperature. The inset shows the mobility from Marcus theory in low temperature. Reprinted from Ref. [39] by permission of APS

Fig. 2.20 Hole transfer rate and 3D averaged hole mobility in tetracene as a function of temperature obtained from the present quantum theory. Reprinted from Ref. [39] by permission of APS



2.6.2.4 Anisotropy of Mobility

Notice that the results shown above are averaged over all directions in 3D and thus are isotropic mobilities. Considering that the real molecular crystals are highly anisotropic, the comparison between the calculated data here and the experiment along each direction is not reasonable. To investigate the strength of anisotropy, one can also perform the 2D-averaged simulations within the layer plane of the crystals. It is found that the mobility is reduced by a factor of 2.5–2.8 for tetracene and rubrene from 2D to 3D structures due to the weaker interlayer couplings.

2.7 Incorporate Dynamic Disorder Effect in the Hopping Picture

2.7.1 Two-Step Approach

In both the general hopping description described in [Sect. 2.1](#) and the improved approach with nuclear tunneling effect introduced in [Sect. 2.5](#), only the local electron–phonon couplings are considered, namely the site energies are modulated by nuclear vibrations while the intermolecular electronic couplings are kept fixed. However, at room temperature, it is obvious that the relative orientation of molecules fluctuates all the time since the intermolecular interaction is van der Waals-type weak, and thus the transfer integrals are also strongly modulated by nuclear motions. We notice that the nonlocal electron–phonon couplings are dominated by low-frequency intermolecular modes [\[41\]](#) with period (about 600 fs) much larger than the time of a single charge transfer process (a few to tens of femtoseconds) for good organic semiconductors [\[42\]](#). Therefore one can perform a two-step approach to include the nonlocal electron–phonon couplings inside the hopping picture, namely, the transfer integrals are kept constant during the charge transfer processes and they are updated after each hopping step.

2.7.2 Multi-Scale Simulation

It is mentioned above that the nuclear vibrations which are important for modulating the transfer integrals are low-frequency modes, thus it is quite straightforward to introduce molecular dynamics (MD) to describe their classical manner. One can build a supercell containing enough number of investigated molecules, and perform MD simulations to get the trajectory of the nuclear dynamics. At each snapshot, the intermolecular transfer integrals can be calculated with the dimer methods quantum chemically described in [Sect. 2.1.2](#). To get real time evolution of the transfer integrals, a discrete Fourier transformation is performed to these discrete data points:

$$V_{mn}(t) = \langle V_{mn} \rangle + \sum_{k=0}^{N/2} \text{Re}V_k \cos(\omega_k t + \phi_0) + \sum_{k=0}^{N/2} \text{Im}V_k \sin(\omega_k t + \phi_0) \quad (2.38)$$

Here, N is the total number of MD snapshots, $\text{Re}V$ and $\text{Im}V$ are the amplitudes of cosine and sine basis functions, on the basis of which the contributions of different phonons to the transfer integral fluctuation can be achieved. The same type of molecular dimers in the crystal should have the same Fourier coefficients with

different phase factors ϕ_0 . The phase factors can be chosen randomly because there's hardly any fluctuation correlation between transfer integrals of different pairs [42]. Therefore, one can deal with several typical dimers to get the Fourier coefficients, and the time-dependent transfer integrals between all molecular dimers can be realized according to Eq. 2.38 with different phase factors. Random walk Monte Carlo simulation technique can be carried out to investigate the charge carrier mobility after slight modifications. For example, initially for each molecular dimer, a phase factor ϕ_0 is chosen randomly as $r\omega_k t_{\text{simu}}$, where r is uniformly distributed in $[0, 1]$ and t_{simu} is the total MD simulation time. And the transfer integrals are updated using Eq. 2.38 for the new time after each hopping step.

2.8 Application: Pentacene

The chemical structure of pentacene is already shown previously in Fig. 2.16. The thin-film phase of pentacene is a substrate-induced polymorph, commonly existing in pentacene thin-film transistors with hole mobility exceeding $5.0 \text{ cm}^2/\text{Vs}$ [43], and has thus received a lot of attention. Here, we perform a multi-scale approach proposed above, namely, MD simulations to achieve the time evolution of molecule geometries, quantum chemical calculations for the transfer integrals at each MD snapshot, and Monte Carlo method to simulate charge carrier diffusion, to study the charge transport mechanism in the thin-film phase of pentacene crystal.

2.8.1 Computational Details

We choose a $3 \times 3 \times 3$ supercell for molecular dynamics based on the experimental crystal structure (see Fig. 2.21) [44]. The MD simulation with fixed lattice constants is carried out at five constant temperatures, i.e., 100, 150, 200, 250, and 300 K with COMPASS force field within the Materials Studio package [45]. The simulation time is set to be 100 ps with a time step of 2 fs, and the dynamic trajectories are extracted every 30 fs after thermal equilibration of 40 ps with a total number of 2,000 snapshots. Within one layer, each molecule has six nearest neighbors. From the symmetry, we only calculate the transfer integrals for typical molecular dimers A, B, and C (see Fig. 2.21). The transfer integrals at each snapshot are calculated with site-energy correction method in Sect. 2.1.2.2 at the PW91PW91/6-31G* level within Gaussian 03 package [23]. The simulation time for a single Monte Carlo is 10 ps and 5,000 simulations are performed to get the carrier mobility.

Fig. 2.21 (Left) A $3 \times 3 \times 3$ supercell structure of pentacene crystal of thin film phase; (right) an ab plane extracted from the supercell. The three arrows indicate three typical dimers A, B, and C. Reproduced from Ref. [42] by permission of the PCCP Owner Societies

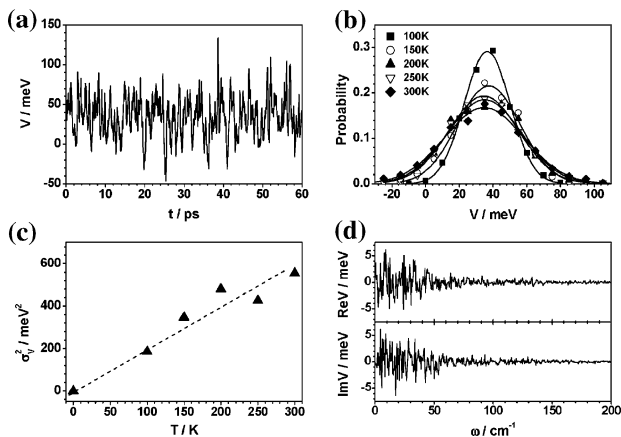
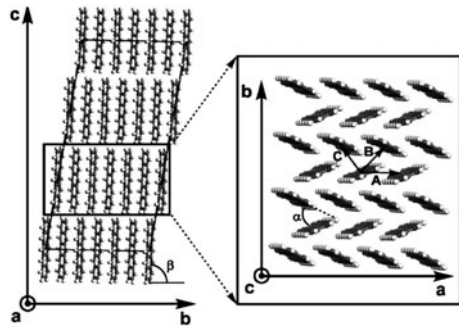


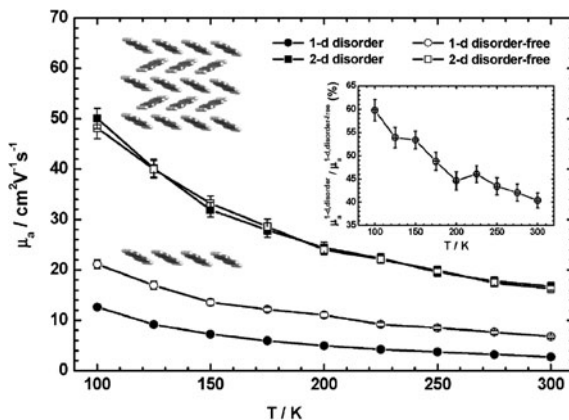
Fig. 2.22 **a** Thermal fluctuation of the transfer integral (dimer A) at 300 K; **(b)** distribution of the transfer integrals at different temperatures; **c** square of the standard deviation of transfer integral versus temperature, where σ_V is set to zero at zero temperature in classical limit; **d** Fourier transformation of thermal deviation amplitude at 300 K. Reproduced from Ref. [42] by permission of the PCCP Owner Societies

2.8.2 Results and Discussion

2.8.2.1 Transfer Integral Fluctuation

A typical calculated time evolution of the transfer integral is shown in Fig. 2.22a. The thermal fluctuation is of the same order of magnitude as the average value, which agrees with observation in other polymorph of pentacene crystals [41]. They follow the Gaussian distributions with almost temperature independent mean

Fig. 2.23 Temperature-dependent hole mobility along the a axis with and without dynamic disorder in 1D (circles) and 2D (squares). Ratio between the mobility with and without dynamic disorder in 1D is shown in the inset. Reproduced from Ref. [42] by permission of the PCCP Owner Societies

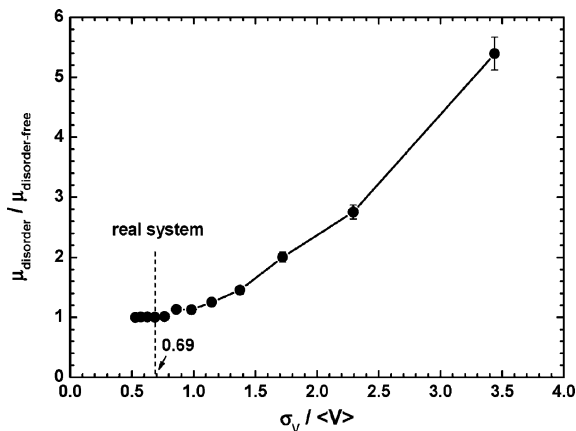


values (see Fig. 2.22b), and the square of the standard deviation σ_V is a linear function of temperature (see Fig. 2.22c). This can be understood by the combined effects of Boltzmann distribution of intermolecular distances and the widely assumed linear electron–phonon coupling. Accordingly, the Fourier coefficients, ReV and ImV, should also follow the $T^{0.5}$ law. From Fig. 2.22d, we reproduce that the major contribution to the transfer integral fluctuation comes from low-frequency modes ($<50 \text{ cm}^{-1}$), belonging to intermolecular vibrations.

2.8.2.2 Mobility in 1D and 2D Cases

We investigate the 1D (i.e., a molecular chain along a direction of the crystal) and 2D (i.e., the molecular layer within the ab plane) temperature-dependent hole mobility both with and without thermal fluctuation of the transfer integrals (see Fig. 2.23). For the 1D case, due to the fluctuating nature of the transfer integrals, the charge transfer rates between some of the molecular dimers become less than those at the equilibrium geometry and the charge becomes oscillating between dimers with larger charge transfer rate, becoming bottle necks for charge transport. It is noted that even at low temperature (100 K), the disorder effect is remarkable. This is due to the fact that the dominant intermolecular mode is around 50 cm^{-1} , which can be converted to about 72 K. The ratio between the simulated mobility with and without dynamic disorder decreases with temperature due to the larger fluctuation of transfer integrals and thus more pronounced “bottleneck effect” at higher temperatures. For the 2D case, it is interesting to see that the temperature dependence of mobility does not depend on the dynamic disorder of the transfer integrals. In 2D systems, there are much more hopping pathways than in 1D case. If the transfer integral of one path is small, the hole can always choose another pathway with larger transfer integrals, thus the mobility is less affected. Note that here the charge transfer rates are temperature independent below room temperature, similar with the case of tetracene shown in Fig. 2.20. As a result, the “band-

Fig. 2.24 Ratio of the hole mobility along a axis in 2D with dynamic disorder with respect to that of disorder-free, as a function of σ_V over the mean transfer integral $\langle V \rangle$. Here, σ_V is kept at the value in 300 K, while $\langle V \rangle$ is varied. The phonon-assisted current starts at about $\sigma_V / \langle V \rangle = 1$. Reproduced from Ref. [42] by permission of the PCCP Owner Societies



like” behavior of temperature dependence of mobility is solely a nuclear tunneling effect. In an extreme case, when the fluctuation in transfer integral is larger than its average, the dynamic disorder can even increase the hole mobility for 2D (see Fig. 2.24). This indicates an intrinsic transition to the phonon-assisted transport by dynamic disorder. More details about the role of such non-local electron–phonon couplings will be talked about in Chap. 3 within the polaron picture.

2.9 Conclusion

In this chapter, we have talked about the general methodology of the hopping mechanism as well as two improvements incorporating the nuclear tunneling effect from the high-frequency modes for the local electron–phonon couplings and the dynamic disorder effect from the low-frequency modes for the nonlocal electron–phonon couplings. Applications of these approaches have been performed to various star organic semiconducting materials, e.g., the siloles, triphenylamines, oligothiophenes, and oligoacenes. Several clear conclusions can be drawn: (1) The transfer integrals between neighboring molecules and the reorganization energy during the charge transfer processes are key to determine the charge transport efficiencies in molecular crystals. The former requires tight crystal packing and nice intermolecular matching between frontier molecular orbitals, while the latter favors long conjugated, planar, and rigid molecules with less flexible degrees of freedom. (2) At low temperatures, the nuclear tunneling effect can be very important for charge transport. Because of this, the “band-like” temperature dependence of mobility is possible within the hopping picture when the major contribution comes from the high-frequency modes. We note that when the external reorganization, which is mostly of low-frequency environment mechanisms, is very strong, the overall temperature dependence may be changed

completely, and then the high-frequency modes will only generally reduce the mobility, without any impact on temperature dependence. (3) The dynamic disorder coming from the thermal fluctuation of the transfer integrals is very important for one-dimensional systems. For higher dimensions, the effect becomes significant only when the fluctuation is larger than the mean transfer integral itself. Therefore this effect should be considered for loosed packing crystals and high temperatures. There, a phonon-assisted term will be added to the temperature dependence of mobility, and can be of great importance to the overall transport behavior. In [Chap. 3](#), we will talk about the Holstein–Peierls polaron model, which is principally more general than the present hopping model. More basic understandings concerning the role of different electron–phonon couplings on the temperature dependence of mobility will be revealed.

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