Temperature and field-dependence of hopping conduction in organic semiconductors

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Abstract

Electrical characteristics of the hopping transport in organic semiconductors are studied theoretically. Based on percolation theory of hopping between localized states, an analytical mobility model is obtained. This model is applied to the analysis of both the electric field dependence and the temperature dependence of the mobility. The results agree quantitatively with recent experimental data.
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1. Introduction

Organic semiconductors have witnessed a considerable development in recent years, mainly pushed by the realization of LEDs and displays whose cost and performance are potentially better with respect to more conventional solutions [1,2]. In parallel, understanding the charge-carrier transport properties in these organic materials is of crucial importance to design and synthesize better materials and to improve device performances. Two of the most important parameters are conductivity and mobility of the charge carriers. In particular, the dependence of conductivity on temperature and electric field has been extensively studied in various papers [3–5]. The traditional approach to the analysis of the temperature dependence in disordered organic systems is based on the Miller–Abrahams expression [4]. The electric-field dependence in such systems shows Poole–Frenkel behavior $\ln \mu \propto \exp(\gamma\sqrt{E})$ [3]. However, a mechanism is needed to explain such behavior of conduction. The field effect on the variable range hopping (VRH) at zero temperature was considered by Shklovskii [6]. A more systematic derivation of the temperature dependence based on the VRH and percolation theory was given in [7,8]. Although this model has been applied

successfully to describe the temperature dependence of conductivity in organic materials, it is difficult to account for the experimentally observed electric field dependence.

In the present work, we have derived an expression for electric-field-dependent conductivity based on the VRH theory. In this model, it is assumed that the localized states are distributed randomly in both space and energy coordinates, and the states are occupied according to Fermi–Dirac statistics. The present theoretical calculations are applied to explain recent experiment. A good agreement between theory and experiment is observed.

2. Model theory

For a disordered organic semiconductor system, we assumed that localized states are randomly distributed in both energy and space coordinates, and that they form a discrete array of sites. When an electric field E exists, the transition rate of a carrier hopping from site i to site j is described as [9]

$$\omega_{ij} = \gamma \begin{cases} \exp\left[-\left(2\alpha + \frac{qE}{k_\mathrm{B}T}\cos\theta\right)R_{ij} - \frac{\varepsilon_j-\varepsilon_i}{k_\mathrm{B}T}\right], & \varepsilon_j - \varepsilon_i \geqslant qER_{ij}\cos\theta, \\ \exp(-2\alpha R_{ij}), & \varepsilon_j - \varepsilon_i \leqslant qER_{ij}\cos\theta, \end{cases}$$

(1)

where ϵ_i and ϵ_j are the energy in the absence of electric field at site i and site j, γ depends on the phonons spectrum, α^{-1}

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is the Bohr radius of the localized wave function, k_B is the Boltzmann constant, q is the electrons charge, R_{ij} is the distance between the two sites i and j, and θ is the angle between F and R_{ij}. Assuming no correlation between occupation probability of different localized states, the current between the two sites is given by

$$I_{ij} = \gamma \exp\left[-2\alpha R_{ij} - \frac{|\varepsilon_j - \varepsilon_i + qE\cos\theta R_{ij}|}{2k_B T}\right]$$
$$\sinh\left(\frac{\mu_j - \mu_i}{2k_B T}\right)\left[\cosh\left(\frac{\varepsilon_j - \mu_i}{2k_B T}\right)\cosh\left(\frac{\varepsilon_j - \mu_j}{2k_B T}\right)\right]^{-1},$$
(2)

where μ_i and μ_j are the chemical potentials of sites i and j [10].

3. Low electric field regime

To determine the conductivity of an organic system, one can use percolation theory regarding the system as a random resistor network [11]. In the case of low electric field, the resulting voltage drop over a single hopping distance ($\Delta\mu \ll k_B T$) is small. The conductance between sites i and j can be simplified from Eq. (2) to the form

$$\sigma_{ij} = \sigma_0 \exp(-s_{ij})$$
(3)

and

$$s_{ij} \approx 2\alpha R_{ij} + \frac{|\varepsilon_i - \varepsilon_F| + |\varepsilon_j - \varepsilon_F||\varepsilon_j - \varepsilon_i + qE\cos\theta R_{ij}|}{2k_B T}, \quad (4)$$

where ϵ_F is the Fermi-energy and σ_0 is prefactor. In this model, we assume an exponential density of states (DOS) for organic semiconductors as

$$g(\varepsilon) = \frac{N_t}{k_B T_0}\exp\left(\frac{\varepsilon}{k_B T_0}\right) \quad (\varepsilon \leqslant 0),$$
(5)

N_t is the number of states per unit volume and T_0 is a parameter that indicates the width of the exponential distribution. According to [8], the Fermi-energy ϵ_F is fixed by the condition

$$\delta \cong \exp\left(\frac{\varepsilon_F}{k_B T_0}\right)\Gamma(1 - T/T_0)\Gamma(1 + T/T_0),$$
(6)

here δ is the fraction of occupied states and Γ is the gamma function. According to percolation theory [7], at the onset of percolation the critical number B_c can be written as

$$B_c = \frac{N_b}{N_s}.$$
(7)

$B_c = 2.8$ for a three-dimensional amorphous system, N_b and N_s are respectively the density of bonds and density of sites in this percolation system, which can be calculated as [8,12]

$$N_b \int d\mathbf{R}_{ij}\, d\varepsilon_i\, d\varepsilon_j g(\varepsilon_i)g(\varepsilon_j)\theta(s_c - s_{ij})$$
(8)

and

$$N_s = \int d\varepsilon g(\varepsilon)\theta(s_c k_B T - |\varepsilon - \varepsilon_F|).$$
(9)

Here $\mathbf{R}_{ij}$ denotes the distance vector between sites i and j, and s_c is the exponent of the conductivity given by the relation $\sigma = \sigma_0 e^{-s_c}$ [13].

Substituting (8) and (9) into (7) results in a percolation criterion for an organic system as

$$B_c \approx N_t \frac{\pi k_B T}{2qE}\left(\frac{T_0}{T}\right)^3 \exp\left(\frac{\varepsilon_F + s_c k_B T}{k_B T_0}\right)$$
$$\left[\left(2\alpha - \frac{qE}{k_B T}\right)^{-2} - \left(2\alpha + \frac{qE}{k_B T}\right)^{-2}\right].$$
(10)

This yields the expression for conductivity as

$$\sigma = \sigma_0\left\{\frac{\pi k_B T \delta N_t}{2qEB_c}\left(\frac{T_0}{T}\right)^3 \exp\left(\frac{1}{\Gamma(1 - T/T_0)\Gamma(1 + T/T_0)}\right)\right.$$
$$\left.\left[\left(2\alpha - \frac{qE}{k_B T}\right)^{-2} - \left(2\alpha + \frac{qE}{k_B T}\right)^{-2}\right]\right\}^{T_0/T}.$$
(11)

Eq. (11) is obtained assuming

- that the site positions are random,
- the energy barrier for the critical hop is large,
- and the charge carrier concentration is very low.

To describe the mobility, we use the mobility definition given by [14]

$$\mu = \sigma(\delta, T)\frac{T_0}{T}\frac{1}{q\delta N_t}.$$
(12)

Using expression (11), σ has been calculated as a function of T at an electric field of $100\,\text{V/cm}$, as shown in Fig. 1. One can see the linear dependence of conductivity on $T^{-1/4}$ (the dashed line is a guide to the eye). We also use the presented
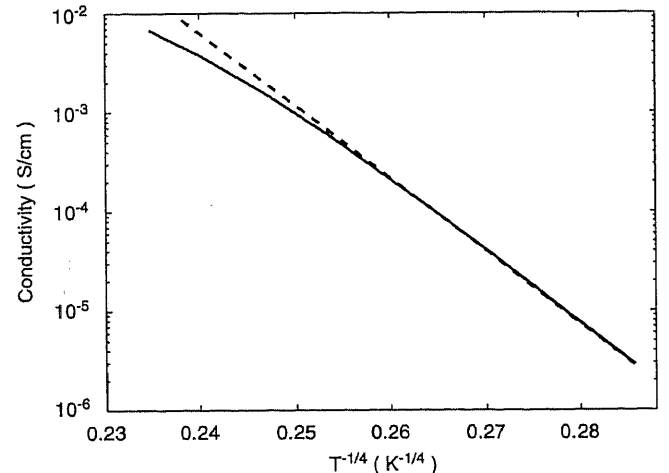

Fig. 1. Plot of $\log\sigma$ versus $T^{-1/4}$ with the electric field $100\,\text{V/cm}$.

model to calculate the temperature and electric field dependences of the conductivity and mobility of ZnPc. In Fig. 2, the curves are obtained from (11) using $\sigma_0 = 12.5 \times 10^5$ S/m, $T_0 = 485$ K and $\alpha = 0.3$ Å^{-1}. The experimental data are from [14].

Figs. 3 and 4 show the mobility plotted semilogarithmically vs. T^{-1} and T^{-2}. Symbols are TOF experimental data from [15] and the solid lines are the results of the analytical model. The dashed line is to guide the eye. In both presentations a good fit is observed. But when plotted as log μ versus T^{-2}, when temperature is lower than the transition temperature $T_c = 210$ K, the slope is reduced. This transition has also been observed by Monte–Carlo simulation [16].

The field dependence of the conductivity is presented in Fig. 5. The conductivity is approximately constant for very low fields, and increases as we increase E. This is the result of the fact that fields can decrease the activation energy for forward jumps, enabling the motion of carriers. We also
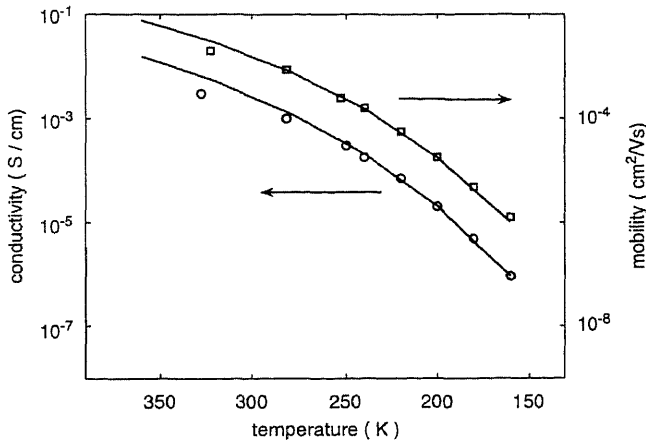

Fig. 4. The data of Fig. 3 versus T^{-2}.

Fig. 2. Conductivity and mobility versus temperature.
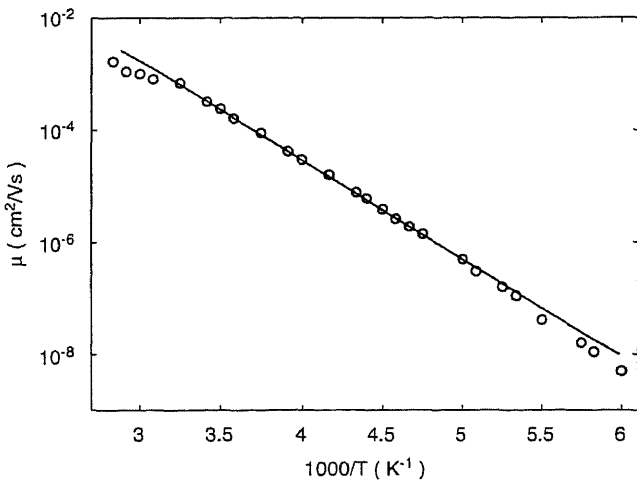

Fig. 5. Plot of log σ versus $E^{1/2}$ at $T = 204$ K.

Fig. 3. Logarithm of the mobility versus T^{-1}. The electric field is 1.0×10^5 V/cm. $\sigma_0 = 1.1 \times 10^9$ S/cm, $T_0 = 340$ K, $\alpha = 0.5$ Å^{-1}.
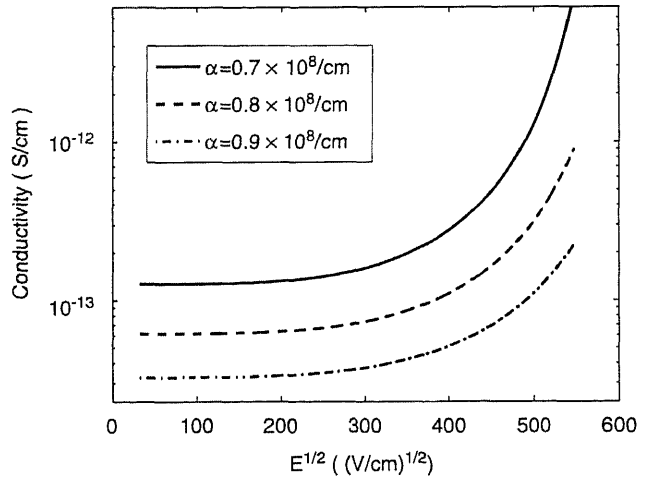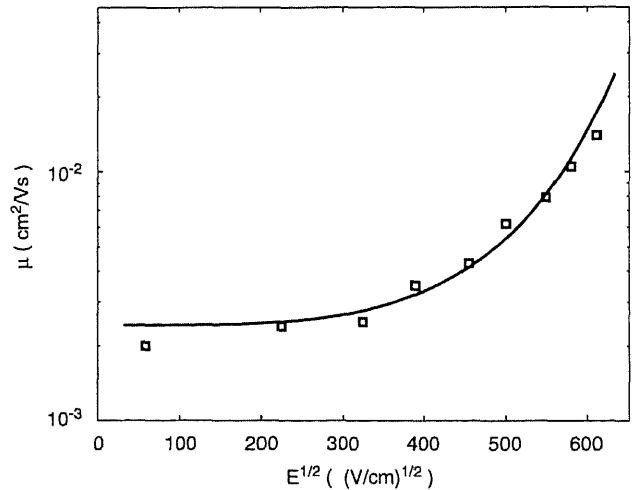

Fig. 6. Electric field dependence of mobility at 290 K. Symbols represent Monte–Carlo results [17], the line represents our work with parameters $T_0 = 852$ K.

compare (12) to the Monte–Carlo result for μ versus $E^{1/2}$ [17], the comparison is shown in Fig. 6.

4. High electric field regime

With increasing electric field, the voltage drop over a single hopping distance increases. If this voltage drop is of the order of $k_B T$ or larger, the approximate expression (4) for conductivity does no longer hold. The current between the two sites depends on the chemical potential of the sites, which in turn depends on the strength and direction of the electric field. Therefore, a percolation model is usually adopted, assuming site-to-site hopping currents instead of conductance [10].

However, in this case, a conductivity model for the high electric field regime can only be obtained after some approximations. According to percolation theory, the critical percolation cluster of sites would comprise a current carrying backbone with at least one site-to-site current equal to the threshold value. Since a steady-state situation would prescribe a constant current throughout the whole current carrying backbone, the charge will redistribute itself along the path, thus changing the chemical potentials of sites. Hapert omitted this rearrangement by optimization of the current with tunneling [10]. Potentially, the redistribution of charge would change the tunneling current, but this effect seems negligible compared to large spread I_{ij}. As a result, the conductivity between two sites is given by

$$\sigma_{ij} \approx \exp(-s_{ij}) \tag{13}$$

with

$$s_{ij} = 2\alpha R_{ij} + \ln\left(\frac{qE}{2k_B T} R_{ij}\right). \tag{14}$$

Combining (7)–(10) and (15), the following expression for the percolation criterion is obtained:

$$B_c \approx \frac{N_t}{2}\left[1 + \frac{\delta}{\Gamma(1 - T/T_0)\Gamma(1 + T/T_0)}\right] \int dR_{ij}\theta(s_c - s_{ij}). \tag{15}$$

This gives the conductance as

$$\ln(\sigma/\sigma_0) = -2\alpha\eta - \ln\left(\frac{qE\eta}{2k_B T}\right), \tag{16}$$

where

$$\eta = -\frac{2k_B T}{qF}\ln\left[1 - \left(\frac{qE}{2k_B T}\right)^3 \frac{B_c}{4\pi N_t(1 + \delta/\Gamma(1 - T/T_0)\Gamma(1 + T/T_0))}\right]. \tag{17}$$

For high electric field, the conductivity $\ln\sigma$ is presented as a function of $E^{1/2}$ in Fig. 7. In this case, a field-saturated drift velocity, i.e., $\sigma \propto E^{-1}$ is observed in accordance with the simulation work [18] and experiment [19]. At very high fields the effective disorder seen by a migrating carrier vanishes and backward transitions are excluded [20]. The temperature dependence of conductivity at the electric field
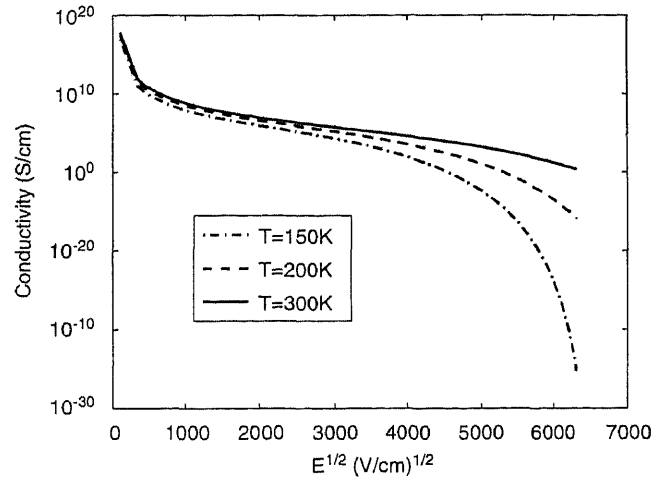

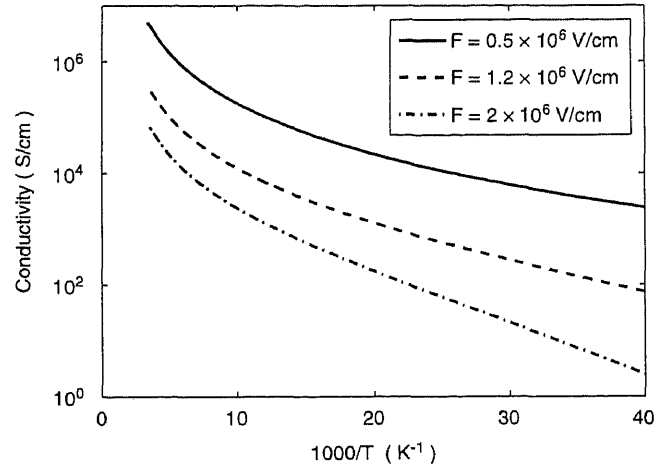Fig. 7. Field dependence of the conductivity at different temperatures.

Fig. 8. Temperature dependence of the conductivity at different electric field.

of 1×10^5 V/cm is presented in Fig. 8. An Arrhennius-like temperature dependence $\ln\sigma \propto -E_a/(k_B T)$ is also observed at low temperature.

5. Conclusion

An analytical model to describe both the temperature and electric field dependence of conductivity in organic semiconductors has been derived. This model predicts the usual $T^{-1/4}$ relationship at low electric fields and Arrhennius-like temperature dependence at high electric fields. The field-saturated drift velocity has also been observed at high electric field.

Acknowledgments

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