Acceleration of polaron induced by site effective mass increment in organic ferromagnets

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Abstract

The polaron dynamics in organic ferromagnets (OFs) is investigated theoretically by considering the increment of site effective mass originating from the attachment of spin radicals. In spite of the increase of polaron effective mass, the results reveal two opposite effects on the polaron velocity caused by the increment of site effective mass. One is the normal decrease of the polaron velocity with the increment of site effective mass. The other is the abrupt acceleration of the polaron from below the sound velocity to the supersonic velocity upon a critical value of the site effective mass increment. Mechanism analysis shows that the acceleration of the polaron is attributed to the reduction of critical decoupling field for optical and acoustic deformations caused by the site effective mass increment. The second effect further depends on the polaron spin due to the existence of spin-dependent intrinsic dipole of the polarons. This work indicates the potential of high polaron mobility and efficient spin filtering effect under low electric fields in OFs.

1. Introduction

Organic spintronics, which uses the freedom degree of electron spin to explore new organic devices, has attracted wide attention in the past decade [1–3]. A unique character of organic materials is the strong electron–lattice (e–l) interaction, which results in a series of nonlinear excitations, such as polarons, bipolarons, or solitons [4, 5]. Theoretical studies have proved that as efficient spin and charge carriers, the polarons may transport along polymers under the applied electric field [6–14]. Therefore, the exploration of polaron dynamics in organic materials is a vital issue for the spin transport of organic spintronics.

Organic ferromagnets (OFs) are the pet of organic spintronics since they combine both the ferromagnetic and organic properties [15–21]. As a typical pure OF containing only C, H, O, N, S light elements, poly-(1,4-bis(2,2,6,6-tetramethyl-4-piperidyl-1-oxyl)-butadiin (poly-BIPO) has been widely studied over the last few decades [22–25]. Poly-BIPO can be obtained from trans-polyacetylene (t-PA) by replacing each other H atom with a spin radical containing an unpaired electron. At the ground state, the radical spins will present a ferromagnetic order due to the spin coupling between the radicals and the π electrons in the main chain [26, 27]. In recent years, polaron dynamics in OFs with spin radicals has been investigated by several groups, where several interesting phenomena caused by spin correlation with radicals were reported, such as asymmetric polaron velocity upon the reverse of electric field [10], ‘intermittent rebound’ under weak fields [10], spin filtering effect [11], spin rectification effects [12] and spin-resolved transport [13]. These studies make OF-based devices promising in the design of intrinsic organic spintronic devices.

A comprehensive description of the effect brought by the spin radicals is crucial to understand the spin transport in OFs. However, the above results are outcomes only by considering the part of electron spin correlation with the spin radicals. When the spin radicals are attached to the carbon atoms of the main chain, the effective mass of the site will be modified, which further affect the effective mass of the polaron...
[28], since a polaron combines an extra electron (or hole) and localized lattice distortions. However, the effect of site effective mass increment on the polaron dynamics in OFs has not been involved. In this paper, based on the extended Su–Schrieffer–Heeger (SSH) model [29] and a nonadiabatic dynamics method, we studied the effect of site effective mass increment on polaron dynamics in OFs. The results demonstrate that the polaron velocity firstly decreases with the site effective mass increment, while an abrupt acceleration of the polaron appears upon a critical value of the site effective mass increment. The paper is organized as follows. In section 2, the model and calculation method are introduced. The results are discussed and analysed in section 3. A brief summary is given in section 4.

2. Model and method

Here we consider a one-dimensional OF such as poly-BIPO. The molecular structure is shown in Figure 1. Spin radicals are attached to the odd sites of the π-conjugated carbon chain. Such model is also valid for other similar OFs with various spin radicals. According to previous literature on the Hamiltonian of OFs with spin radicals [10–13], the effective mass of each site is usually regarded as that of a CH group. However, the substitution of H atoms by spin radicals, which are usually heterocycles, will increase the effective mass of the odd sites. So, the modified Hamiltonian of the OF with site-dependent effective mass can be written as

\[ H = \sum_{n=1}^{N} \left( J_{n,n+1} \delta_{n,\text{odd}} \cdot \sigma_{n} + \left( \frac{K}{2} \right) \sum_{n=1}^{N} \left( u_{n+1} - u_{n} \right)^{2} + \frac{M_{n}}{2} \sum_{n=1}^{N} \frac{\delta_{n,\text{odd}}}{\delta_{n,\text{even}}} \right) \]  

(1)

Here, \( J_{n,n+1} = J_{0} - \alpha (u_{n+1} - u_{n}) \) is the hopping integral of π electrons between sites \( n \) and \( n + 1 \) with \( J_{0} \) the hopping integral of a uniform lattice, \( \alpha \) is the \( \epsilon \)-1 coupling constant, \( u_{n} \) is the lattice displacement of the carbon atom at the \( n \)th site from the equilibrium site. A driven electric field \( E_{0} = \frac{\gamma}{m_{e} \omega} \) is applied along the main chain in the case of periodic boundary condition, and \( \omega \) is the time-dependent vector potential.

The coefficient \( \gamma \) is defined as \( \gamma = \frac{\epsilon}{\omega} \), and \( \epsilon \) is the charge of an electron and \( a \) the lattice constant. \( c_{n,\sigma}^{+} (c_{n,\sigma}) \) denotes the creation (annihilation) operator of the electron at the \( n \)th site with spin \( \sigma \). The second term is the antiferromagnetic coupling between the radial spin \( \vec{S}_{n} \) and the \( \pi \)-electron spin \( \vec{S}_{n} \) with the strength \( J_{f} > 0 \). \( \delta_{n,\text{odd}} \) means that the radicals only exist at the odd sites with \( \delta_{n,\text{even}} = 0 \) for odd (even) atoms. The last two terms are lattice potential energy and kinetic energy. \( K \) is the elastic constant and \( M_{n} \) the site effective mass at the \( n \)th lattice site. For the even sites without spin radicals, the site effective mass equals to that of CH group as in t-Pt, that is \( M_{n} = M_{0} \). For the odd sites with spin radicals, the site effective mass will be modified due to the substitution of H atoms with heavier heterocycles. The site effective mass of the odd sites are assumed uniform with \( M_{n} = M_{0} \). In spite that the exact increment is hard to know, here we define a site mass increment parameter as \( R_{m} = M_{n} / M_{0} \geq 1 \) to describe the modification of CH group caused by the attachment of spin radicals. According to the relative atomic mass of the reported spin radicals [15, 24, 25] and considering possible relaxation of connecting bonds, the value of \( R_{m} \) is expected to vary from several to several dozens.

The dynamic evolution of the \( \pi \)-electron is given by the time-dependent Schrödinger equation as follows

\[ i\hbar \frac{\partial}{\partial t} Z_{\mu,\alpha}(t) = -t_{n,n+1} e^{i\hbar A} Z_{\mu,\alpha}(t) - t_{n-1,n} e^{i\hbar A} Z_{\mu,\alpha}(t) + \frac{\sigma}{2} J_{f} \delta_{n,\text{odd}} \langle S_{n\alpha}^{2} \rangle Z_{\mu,\alpha}(t), \]  

(2)

where \( \sigma \) is the spin index with \( \uparrow \equiv 1 \) and \( \downarrow \equiv -1 \). \( Z_{\mu,\alpha}(t) \) is the electron wave function expanded in Wannier space. The mean-field (Hartree) approximation is used to treat the spins correlation. \( \langle S_{n\alpha}^{2} \rangle \) is the average value of radical spin along \( z \) direction (perpendicular to the carbon chain), which is set as \( \langle S_{n\alpha}^{2} \rangle = \frac{1}{2} \). The evolution of lattice can be given by the classical Newton equation

\[ M_{n} \ddot{u}_{n}(t) = K(u_{n+1}(t) - u_{n-1}(t) - 2u_{n}(t)) + \alpha \left\{ e^{i\hbar A} \left[ \rho_{\mu,\alpha}^{n+1}(t) - \rho_{\mu,\alpha}^{n-1}(t) \right] + c.c. \right\} \]  

(3)

The coupled equations (2) and (3) can be solved by a Runge–Kutta method of order eight with step size control [30, 31]. In addition, the net charge density of the polaron on the \( n \)th site is defined as

\[ \rho_{\mu,\alpha}^{n}(t) = 1 - \sum_{\nu,\beta} \left\{ \langle Z_{\nu,\beta}(t) \rangle^{2} + \langle Z_{\nu,\beta,-\alpha}(t) \rangle^{2} \right\}. \]

The geometry of the OF is described by the optical order parameter of a smoothed lattice distortion [32]

\[ \nu_{n}(t) = \frac{1}{2} \left( 2u_{n}(t) - u_{n+1}(t) - u_{n-1}(t) \right). \]

The acoustic order parameter is also defined to emphasize the acoustic deformation (compressions or expansions) of the lattice as \( \rho_{\mu,\alpha}^{n}(t) = -u_{n}(t) + u_{n+2}(t) \).

During the calculation, the parameters are chosen as follows according to those widely used for poly-BIPO [27, 33, 34]: \( \hbar_{0} = 2.5 \) eV; \( \alpha = 4.1 \) eV Å\(^{-1} \), \( K = 21.0 \) eV Å\(^{-2} \), \( a = 1.22 \) Å; \( M = 1349.14 \) eV fs\(^{2} \) Å\(^{-2} \), and \( J_{f} = 0.25 \) eV. The total number of carbon atoms in the polymer chain is 160. To ensure the
stability of the system, the driven electric field is applied linearly with $E(t) = \frac{t}{t_0} \cdot E_0$ for $0 < t \leq t_c$ and $E(t) = E_0$ for $t > t_c$. The critical time $t_c$ is chosen as 75 fs.

3. Results and discussion

We first study the time evolution of charge density of the polaron in the OF at different values of the site effective mass increment $R_m$. Here a spin-down polaron is considered, where an extra electron occupying the spin-down lowest unoccupied molecular orbital (LUMO). An external electric field with $E_0 = 0.1$ mV Å$^{-1}$ is applied. As shown in figure 2, the localized polaron moves along the main chain under the electric field. After a short acceleration, the polaron reaches a saturation velocity, and periodically moves along the polymer chain due to the periodic boundary condition. From figure 2, it can be seen that with the increase of $R_m$ from 1 to 5, the movement of the polaron gradually slows down which embodies in the longer time to travel one cycle. This is understandable since according to the previous study [28], the effective mass of the polaron is approximately in proportion to $\sqrt{M}$. The increasing effective mass of the odd sites will enlarge the effective mass of the polaron, and slow down the speed of the polaron.

However, it is unexpected that as $R_m$ increases to 7, as shown in figure 2(d), the polaron suddenly speeds up even over the case at $R_m = 1$. To get a more intuitive sight of the polaron motion, we quantitatively calculated the saturation velocity of the polaron as the function of the site effective mass increment, which is obtained from the chain length divided by the travel time of one cycle. The result is shown in figure 3. We can see that the saturation velocity of the polaron decreases approximately linearly from 0.13 Å fs$^{-1}$ to 0.07 Å fs$^{-1}$ from $R_m = 1$ to $R_m = 6$. The speed is lower than the speed of sound in t-PA defined as $v_s = a\sqrt{K/M}$ [9, 10]. However, at $R_m = 7$, the speed of the polaron abruptly exceeds the speed of sound to 0.34 Å fs$^{-1}$, and thereafter keeps almost unchanged with $R_m$.

The physical mechanism for the acceleration of the polaron induced by site effective mass increment is further explored by investigating the optical order parameter and acoustic order parameter. The results with $R_m = 1, 7, 9$ are compared at three different times $t = 50, 500, \text{and} 1500$ fs. As shown in figures 4(a)–(c) with $R_m = 1$, one can see that the two order parameters are always coupled together and move along the OF. With the increase of time, the optical order parameter remains almost unchanged in the process of polaron motion. However, the acoustic deformation became more and more compressed. Besides, an expanded region ahead of the polaron ($y_n > 0$) is developed and included in the acoustic deformation, which forms a potential barrier to impede the polaron motion. The electron cannot gain enough energy to overcome the potential barrier of the expanded region, and thus moves below the speed of sound. The results are consistent with previous studies about the order parameter of polaron dynamics in t-PA [32]. Then, we turn the attention to figures 4(d)–(f) with $R_m = 7$. One can see that during the acceleration process shown in figure 4(d), the optical and acoustic deformations are also coupled together, which is the same as figure 4(a). With the increase of time to 500 fs, the acoustic deformation is compressed and accompanied by the generation of an expanded region. However, as we can see from figure 4(f), the acoustic deformation is decoupled from the polaron and remains behind the polaron at $t = 1500$ fs. At the same time, the optical phonons are emitted by the polaron, which can be seen from the rapid oscillating trajectory of the optical and acoustic order parameters. Note that the electron stays with the optical deformation, which may drift in supersonic velocity. This explains the abrupt acceleration of the polaron in figure 2. The acoustic and optical deformations with $R_m = 9$ are also shown in figures 4(g)–(i). The picture is similar to that of $R_m = 7$, where the acoustic deformation is also decoupled from the polaron and remains behind the polaron at the time of 1500 fs. Thus, the polaron keeps the supersonic velocity and only a slight decrease of the velocity is observed with the further increase of $R_m$.

The nature of the decoupling between the acoustic and optical deformations caused by the site effective mass increment can be understood as follows. The decoupling of the optical deformation from the acoustic deformation needs extra energy from the electric field to overcome the barrier generated by the ahead expanded region. If the saturation velocity of the polaron is below the speed of sound, all the energy gained from the electric field is consumed to support the polaron motion. With the increase of $R_m$, the actual speed
of sound will be decreased according to $v_s = a \sqrt{K/M^*}$, where $M^*$ is the average site effective mass and of course increases with $R_m$. After a critical value, the actual speed of sound turns smaller than the saturation velocity at the present electric field. As a result, extra energy from the electric field can be provided to overcome the expansion barrier from the acoustic deformation. Thus, the optical deformation owns the ability to decouple from the acoustic deformation, and hence the acceleration of the polaron happens.
According to above analysis, the increase of site effective mass increment will lower the speed of sound, and hence the critical value of the decoupling field. This can be used to achieve high polaron mobility under low bias. In the following, we investigated the dependence of the critical decoupling field on $R_m$. As shown in figure 5, it is found that the critical decoupling field gradually decreases from 0.16 mV Å$^{-1}$ to 0.09 mV Å$^{-1}$ with the increase of $R_m$ from 1 to 10, which may be much smaller than the value of 0.14 mV Å$^{-1}$ in t-PA [28]. It means that by taking into account the site effective mass increment from the spin radicals, the polaron mobility in OFs will be much larger than that in t-PA under some specific fields, e.g., from its decoupling field to 0.14 mV Å$^{-1}$.

Due to the spin nondegeneracy in the OF, the case of a spin-up polaron is also examined, where the extra electron occupies the spin-up LUMO. As shown in figure 6, at the same driven electric field of $E = 0.1$ mV Å$^{-1}$, the acceleration is not observed for the spin-up polaron, where its saturation velocity keeps decreasing from 0.13 Å fs$^{-1}$ to 0.05 Å fs$^{-1}$ with $R_m$ from 1 to 12. As a result, once $R_m$ is beyond 6, the speed of the spin-down polaron will be much larger than the spin-up one, which indicates a distinct spin filtering effect at the present field. The reason can be understood as follows. According to previous studies [10, 13, 34, 35], there exists an intrinsic dipole for the polarons in the OF due to the asymmetric charge density, which further works on the polaron velocity. The direction of the dipole is opposite for the polarons with different spins. By examining the charge density, we find that the dipole of the spin-up polaron is opposite to the external electric field. In this case, the saturation velocity of the spin-up polaron is lowered relative to the spin-down polaron. Hence, the decoupling of the optical and acoustic deformations is suppressed. But if a larger electric field of $E = 0.25$ mV Å$^{-1}$ is applied, the abrupt acceleration of the spin-up polaron can be also observed at $R_m = 10$, while the spin-down polaron moves with supersonic speed in all the range of $R_m$. This means that a larger $R_m$ is advantaged to realize the spin filtering effect at low field.

The above results of the spin-up polaron can be verified by figure 7, where the optical order parameter and acoustic order parameter of the spin-up polaron with $R_m = 6$ and $R_m = 10$ are given at a long time of 1000 fs. From figures 7(a) and (b) with the low field of $E = 0.1$ mV Å$^{-1}$, one can see that, for $R_m = 6$ and $R_m = 10$ the two order parameters are always coupled together and move along the OF. However, at the
Figure 5. Critical decoupling field of the polaron as a function of the site effective mass increment.

Figure 6. Polaron velocity with different spins as a function of the site effective mass increment. The black (red) line indicates the low (high) field of $E = 0.1 \ (0.25) \ \text{mV} \ \text{Å}^{-1}$. The blue line is the speed of sound. The inset is the enlarged view of the velocity below the speed of sound.

high field of $E = 0.25 \ \text{mV} \ \text{Å}^{-1}$, as shown in figures 7(c) and (d), the optical and acoustic order parameters are coupled together with $R_m = 6$, but is decoupled with $R_m = 10$.

Finally, the effects of parameter strength on the critical value of $R_m$ are discussed based on the spin-down polaron. Here the spin correlation strength $J_f$ and the e–l coupling constant $\alpha$ are considered, since they are usual variables in OFs. As shown in figure 8(a), we can see that the critical value of $R_m$ keeps unchanged as 7 when $J_f$ is not too large ($J_f = 0.25 \ \text{eV} \ \text{and} \ 0.5 \ \text{eV}$), while the value reduces to 6 for a large $J_f$ of 1.0 eV. It means that the critical value is not sensitive to $J_f$. The reason for the decrease of the critical value at the strong $J_f$ is that the large spin correlation strength decreases the dimerization in the main chain, accompanied by a decrease of the effective mass of polarons. This is helpful for achieving the acceleration of polaron in the case of a relatively smaller $R_m$. The effect of the e–l coupling constant is given in figure 8(b), where an obvious increase of the critical value of $R_m$ with $\alpha$ is obtained. This is because that the effective mass of the polaron increases with $\alpha$ [28], and hence the velocity of the polaron becomes slower and a larger $R_m$ is required. Based on above results, we would like to point out several possible situations to achieve the proposed polaron acceleration in the case of a relatively smaller $R_m$. For example, one may increase the driving electric field to speed up the polaron as demonstrated in figure 5, or alternatively reduce the effective mass of the polaron by adopting OFs with a relatively small e–l coupling and improving the spin correlation strength.
Figure 7. The optical and acoustic order parameters of spin-up polarons with $R_m = 6$ and $R_m = 10$ at $t = 1000$ fs. (a) and (b) are the low field with $E = 0.1 \text{mV Å}^{-1}$ (c) and (d) are the high field with $E = 0.25 \text{mV Å}^{-1}$.

Figure 8. (a) Polaron velocity with different spin correlation strengths as a function of the site effective mass increment. Here the electric field is fixed to $E = 0.1 \text{mV Å}^{-1}$. (b) The critical value $R_m$ as a function of the e–l coupling constant with a fixed field of $E = 0.15 \text{mV Å}^{-1}$.

4. Conclusions

In conclusion, using the extended SSH model and the nonadiabatic dynamical method, we have studied the effect of site effective mass increment on the polaron dynamics in OFs. It is found that the velocity of the polaron firstly decreases with the site effective mass increment due to the increase of effective mass. However, after a critical value, the polaron accelerates sharply to a supersonic velocity. The mechanism can be understood from the decoupling between the acoustic and optical deformations, where the critical decoupling field is reduced by the site effective mass increment. Such effect further shows dependence on the polaron spin. A larger electric field is required to observe the acceleration for the spin-up polaron. The reason is that the intrinsic dipole of the spin-up polaron is opposite to the spin-down one. In addition, the effects of spin correlation strength and the e–l coupling constant on the critical value of the site effective
mass increment are discussed. Some possible situations to achieve the polaron acceleration in the case of a relatively small $R_m$ are point out. This study is helpful to understand the polaron dynamics in OFs, and further design OFs-based devices with high polaron mobility and efficient spin filtering effect under low fields.

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Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

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