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Abstract
A new effect called 'charge flipping of spin carriers' is proposed that can be realized in π-conjugated polymeric molecules, where the charge of a spin carrier can be reversed by photoexcitation. The physical mechanism of electron spin resonance, namely spin flipping of charge carriers, is just the complementary effect to charge flipping of spin carriers. The latter phenomenon shows promise for the design of organic optical spin valves.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

In condensed matter physics, according to two degrees of freedom describing the properties of carriers, carriers can be divided into two categories: charge carriers and spin carriers. As is well known, the properties of charge transport are used to fabricate electronic devices. In the 1990s, when microfabrication technology was used to reduce the size of such devices to the nanometre scale, the wave behaviour of charge was clearly exhibited, and simultaneously, the quantum effect of spin then became more apparent. The discoveries of giant magnetoresistance [1] and tunnelling magnetoresistance [2] in metallic spin valves have revolutionized applications in magnetic recording and memory, which has launched the new field of spin electronics, known as 'spintronics' [3].

Different from an inorganic semiconductor, the flexibility of an organic semiconductor induces its carrier to be a composite particle with internal structure characterized by lattice distortion, such as a charged spin polaron and charged spinless bipolaron [4, 5]. Furthermore, by virtue of the extremely weak spin–orbit interaction and weak hyperfine interaction in π-conjugated organic semiconductors (OSEs), the electron spin diffusion length is especially long [6]. All this makes it possible to realize spin-coherent transport in OSEs. Combining

these unique virtues of OSEs with the goal of obtaining spin injection, a planar junction LSMO/T$_6$/LSMO (LSMO stands for La$_{0.7}$Sr$_{0.3}$MnO$_3$ and T$_6$ for sexa-thiophene) has been 'nanostructured' [7]. However, due to the same coercive field in two identical LSMO electrodes, their relative magnetization orientations cannot be altered by an external magnetic field, and it becomes difficult to achieve the pure spin-valve effect. In order to overcome these difficulties, Xiong *et al* have fabricated a vertical organic spin-valve consisting of a three-layer Alq$_3$ spacer (Alq$_3$ stands for 8-hydroxy-quinoline aluminium), most commonly used in organic light-emitting diodes [8], and two ferromagnetic electrode films with different coercive fields. By sweeping an external magnetic field, they completed the injection, transport and detection of spin-polarized carriers at low temperatures [9]. Recently, a series of polyparaphenyl derivatives—embedded composites of La$_{0.7}$Ca$_{0.3}$MnO$_3$ (LCMO)—have been fabricated. By adjusting the conductivity and spin carrier polarization in polymers, spin-polarized carrier transfer from the surfaces of LCMO magnetic particles into polymers can be tuned, leading to tunable negative and positive magnetoresistances [10]. The mechanism of the spin injection process has been determined as follows: when the Fermi level of manganites/manganates, which have giant magnetoresistance, lies below the spinless bipolaron level of a polymer, the completely polarized spin in its Fermi level can be injected into the polymer, forming a spin-polarized polaron [11]. More importantly, these pioneering studies have initiated the new field of 'organic spintronics'.

The strong electron–phonon coupling in organic materials not only forms localized composite carriers, but also makes the carriers very sensitive to external excitation. Once external excitation alters the electron population in an organic material, both the structure of the carrier and its properties are changed [12]. A double-electron excitation can even induce carrier fission [13]. These also make it possible to apply certain photoexcitations to control the properties of spin-polarized carriers in organic materials, leading to tunable polarized-spin transport in OSEs. Thus, this paper predicts a new photoinduced phenomenon in OSEs: without the aid of an external electric field, only under single-electron excitation can the charge of the spin carrier in the polymeric molecule be overturned. If an external electric field is applied, the resulting spin carrier will move in the opposite direction to the electric field.

2. Model

Due to the quasi-one-dimensional structure of a π-conjugated polymeric molecule, its bond structure and energy spectrum strongly depend on the doping and photoexcitation. As far as we know, the prominent self-trapping effect in a conjugated polymer and its resulting carrier, such as a polaron and bipolaron, can be quantitatively described by the extended Su–Schreiffer–Heeger–Hubbard Hamiltonian [5]:

$$H = -\sum_{l,s}\{t_0 + \alpha(u_{l+1} - u_l) + (-1)^l t_e\} \times [a_{l+1,s}^{\dagger}a_{l,s} + \text{H.c.}]$$

$$+ U\sum_{l,s}n_{l,\uparrow}n_{l,\downarrow} + V\sum_{l,s,s'}n_{l,s}n_{l+1,s'} + \frac{K}{2}\sum_{l}(u_{l+1} - u_l)^2. \tag{1}$$

Here, $a_{l,s}^{\dagger}$ ($a_{l,s}$) denotes the electron creation (annihilation) operator at site l with spin s, u_l is the displacement of atom l with mass M, and K is an elastic constant; H_0 describes the electron–lattice interaction; t_0 is a hopping constant and α is an electron–lattice coupling constant; the t_e term in H_0 reflects the confinement effect in polymers with non-degenerate ground state, which ensures that composite particles, such as bipolarons, in the polymer are stable; and H' is the electron–electron interaction. Since the bandwidth $W > 10$ eV of the polymer is much

larger than the strength $U \sim 3$–5 eV of the electron–electron interaction, the polymer is not a strongly correlated system, and H' can be treated by the Hartree–Fock approximation [12, 13].

The electron's energy spectrum ε_μ and wavefunction Φ_μ are functionals of the lattice displacement u_l and are determined by the eigenequation

$$H_e \Phi_\mu = \varepsilon_\mu \Phi_\mu. \tag{2}$$

The total energy of the polymer chain, $E[\{u_l\}]$, which is a functional of an atom's displacement u_l, is given by

$$E[\{u_l\}] = \sum_{\text{occ}} \varepsilon_\mu[\{u_l\}] + \frac{K}{2} \sum_l [u_{l+1} - u_l]^2. \tag{3}$$

Assuming electronic wavefunctions $\Phi_\mu = \{Z_{n,\mu}^s\}$ and $\phi_n = (-1)^n u_l$, we can express the Schrödinger as

$$\varepsilon_n Z_{n,\mu}^\sigma = -[t_0 + (-1)^{n-1}\alpha(\phi_{n+1} + \phi_n + t_e)]Z_{n-1,\mu}^s - [t_0 + (-1)^{n-1}\alpha(\phi_{n+1} + \phi_n + t_e)]Z_{n-1,\mu}^s, \tag{4}$$

where μ and s indicate the electronic state and spin, respectively. Applying the Hartree–Fock approximation, we can transform the electron–electron interaction into

$$H_{e-e} = \sum_{n,s} \left\{ U\left(\sum_\mu |Z_{n,\mu}^{-s}|^2 - \frac{1}{2}\right) + V\left[\sum_s \left(\sum_\mu Z_{n-1,\mu}^s|^2 + \sum_\mu |Z_{n+1,\mu}^s|^2 - 2\right)\right] \right\} a_{n,s}^\dagger a_{n,s}$$
$$- \sum_{n,s} \left(V \sum_\mu Z_{n,\mu}^s Z_{n+1,\mu}^s\right)(a_{n,s}^\dagger a_{n,s} + \text{H.c.}). \tag{5}$$

Since atoms are much heavier than electrons, based on the Hellmann–Feynman theorem, an atom's movement can be described by classical dynamics as

$$M\frac{d^2 u_l}{dt^2} = -\sum_\mu^{\text{occ}} \frac{\partial \varepsilon_\mu}{\partial u_l} + K(2u_l - u_{l+1} - u_{l-1})$$

$$= \begin{cases} 2\alpha \sum_n W_0^s - K(\phi_0 + \phi_1) - K'\alpha, & n = 0 \\ 2\alpha \sum_n W_{N-1}^s - K(\phi_{N-1} + \phi_N) - K'\alpha, & (n = N) \\ 2(-1)^n \alpha \sum_n (W_n^s - W_{n-1}^s) \\ \quad - K[(\phi_{n-2} + \phi_{n-1}) + (\phi_{n-1} + \phi_n)] & 0 < n < N. \end{cases} \tag{6}$$

Thus, the charge distribution can be represented as

$$\rho_n^s = \sum_\mu |Z_{n,\mu}^s|^2 - n_0, \tag{7}$$

and the spin distribution is

$$S_n = \frac{\hbar}{2} \sum_\mu |Z_{n,\mu}^s|^2 - \frac{\hbar}{2} \sum_\mu |Z_{n,\mu}^{-s}|^2, \tag{8}$$

where n_0 is the density of the positively charged background. These coupled equations can quantitatively describe the dynamics of a conjugated polymer chain.
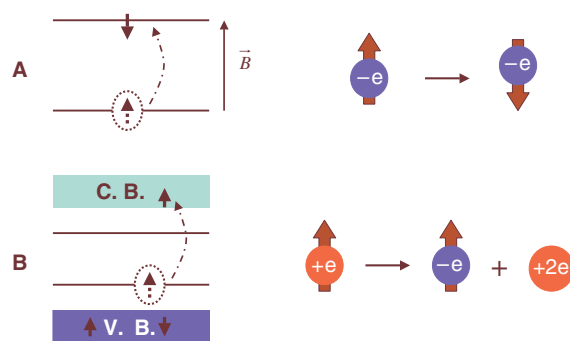
Figure 1. Two complementary effects: (A) spin flipping of a charge carrier and (B) charge flipping of a spin carrier.

3. Results and discussion

3.1. Spin flipping of a charge carrier (SFCC) and charge flipping of a spin carrier (CFSC)

As is well known, spin flipping of a charge carrier (SFCC) is the physical mechanism of electron spin resonance (ESR). With application of a magnetic field to paramagnetic molecules, the coupling between the field and unpaired electron spin $\overrightarrow{\mu_s} \cdot \overrightarrow{B}$ can split carrier spin levels by an amount proportional to the magnetic field: one corresponds to the spin-up state and the other to spin down. Therefore, the applied electromagnetic microwave can excite a single electron or hole from a low to a high state, reversing the spin's direction, whose physical process is shown in figure 1(A). The resultant absorption spectra is described as ESR, which is a common investigative tool to study the structure of the molecules.

The complementary effect to SFCC, i.e., charge flipping of a spin carrier (CFSC), can be viewed as the following: by single-electron excitation, the positive sign of charge of a spin carrier can be reversed to negative. However, during the charge flipping of the spin carrier, in order to conserve the total charge, the system has to emit a new spinless carrier with two positive charges, as shown in figure 1(B). While double-electron-excitation-induced polaron fission on conducting polymers has been reported [13], as a complementary effect to SFCC, CFSC must be completed by single-electron excitation. Thus, we hope to find polaron fission, which is a result of single-electron excitation, one of whose resultant carriers is a stable bipolaron.

As mentioned above, once the polarized spin is injected into the polymer from the magnetic layer, a polarized-spin polaron can be formed [9–11]. Meanwhile, two localized states, Φ_u and Φ_d, of the polaron lie in the centre of the gap, where Φ_u is empty and Φ_d is occupied by only one spin-polarized electron.

Now, let the spin-polarized positive polaron be photoexcited; i.e., a single electron in Φ_d is excited to the conduction band by absorbing a photon, as shown in figure 1(B). The process of single-electron excitation can be described by the time-dependent charge and spin distribution during its relaxation process, as shown in figure 2. Remarkably, along with the relaxation, the original charge distribution is no longer symmetrical about the centre. The positive charge shifts to the left side, and simultaneously the negative charge emerges on the right side. Meanwhile, as shown in figure 2(B), after carrier splitting occurs, the resulting polaron is always bonded with a spin, but the bipolaron cannot possess spin. Finally, the spin-polarized positive polaron is split, forming two new stable carriers, where one is a positive spinless bipolaron, and the another is a spin-polarized negative polaron in the ground state. This kind of carrier fission is the result of symmetry breaking.
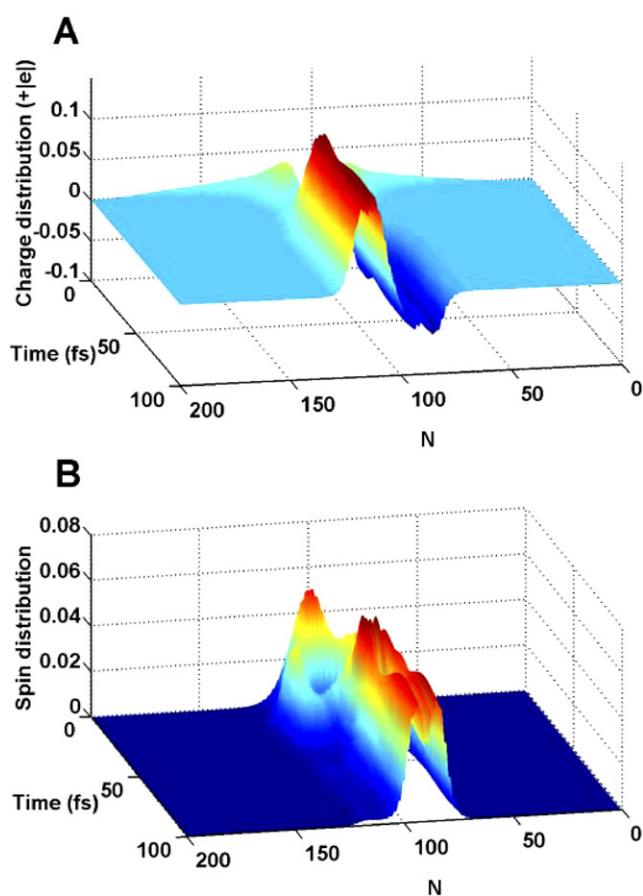
Figure 2. (A) Charge distribution. (B) Spin distribution in the polymer chain after photoexcitation. The vertical axis is the distribution at the Nth site of the polymer chain, whose unit is a single positive charge $+|e|$.

3.2. Organic optical spin valve

After the polarized spin is injected into the polymer to form a positive spin-polarized polaron, an applied electric field $\vec{E} = 5.0 \times 10^{-4}$ V cm^{-1} drives the spin-polarized polaron to move in the same direction as the field. Once this polaron absorbs a photon in 300 fs, the positive charge of the original polaron is reversed to form a negative spin-polarized polaron, as shown in figure 3, where the resultant negative spin-polarized polaron reverses to move in the opposite direction.

In electronics, the familiar application of SFCC is electron spin resonance. As for the complementary effect, CFSC provides a new venue for possible applications in spintronics. Here, based on the physical mechanism of CFSC, we design an organic optical spin valve as shown in figure 4. This valve is composed of two materials, A and B, where A is a low-dimensional organic solid, and B is another conductor. The application of a bias voltage between A and B makes the voltage in A higher than in B, and consequently the positive spin polaron cannot be injected into B and remains in A. By means of photoexcitation, the charge of the spin polaron is reversed, namely, the positive spin polaron transforms into a negative spin polaron. Finally, the bias voltage in the junction can easily inject the spin of a negative polaron
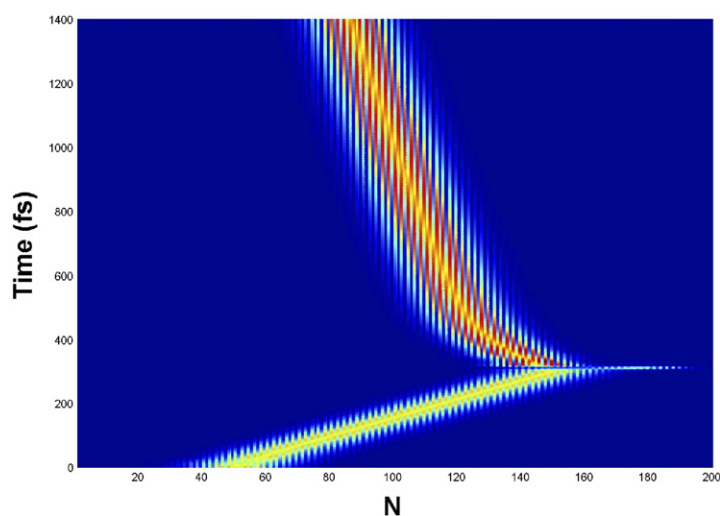
Figure 3. Motion of a spin polaron under an external field $\vec{E} = 5.0 \times 10^{-4}$ V cm^{-1}. After the polymeric molecule absorbs a photon, the charge of the positive spin polaron is reversed to form a negative spin polaron moving in the opposite direction. The vertical axis measures time in the unit fs, and N refers to the sites.
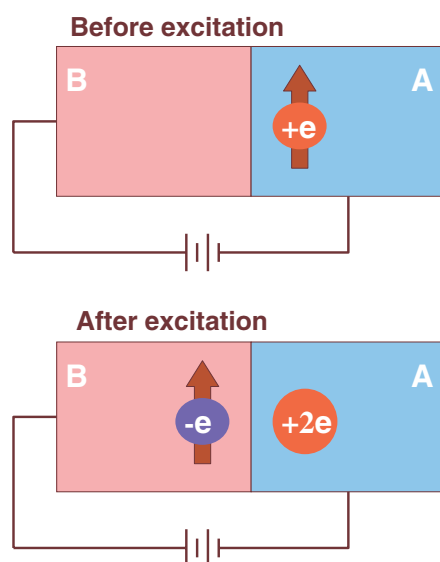

Figure 4. Organic optical spin valve. Before photoexcitation the positive spin polaron remains in organic material A, and after photoexcitation the charge of the original spin polaron is reversed, and a new negative spin polaron is injected into material B.

from A into B, and the spinless positive bipolaron remains in A. Here, we must emphasize that due to the energetic degeneracy of positive and negative polarons the polarons with opposite spins should be equally populated, which could make it difficult to create and inject spin carriers into organic materials. In order to overcome this difficulty, by applying an external magnetic field, the energetic degeneracy of opposite polarons can be eliminated, leading into

different populations of the spin carriers, and then the applied external electric voltage can inject net spin into organic materials.

4. Summary

We have demonstrated the possible effect of charge flipping of spin carriers in conjugated polymers, which is complementary to spin flipping of charge carriers, where the latter is the physical mechanism of electron spin resonance. Through photoexcitation, the charge of a positive spin polaron in a conducting polymer is reversed to form a negative spin polaron. Thus, under an external electric field, the resultant spin carrier will move in the opposite direction to the electric field. Based on this effect, a new spintronic device—an organic optical spin valve—is designed. Moreover, the lifetime of the excited states is on the nanosecond timescale, combining femtosecond spectroscopy with giant magnetoresistance technology, so that it is possible to detect this effect in a polymeric molecule [14].

Acknowledgments

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