Spin-excited states and rectification in an organic spin rectifier*

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Spin-excited states in an asymmetric magnetic organic co-oligomer diode are investigated theoretically. The results demonstrate that the structural asymmetry of the co-oligomer is modulated by the spin-excited states, which is embodied in the wave functions of the eigenstates as well as the spin density wave. By calculating the transport property, a robust spin-current rectification concomitant with a charge-current rectification is observed in all spin-excited states. However, the current through the diode is suppressed distinctly by the spin-excited states, while the rectification ratios may be reduced or enhanced depending on the bias and the excited spins. The intrinsic mechanism is analyzed from the spin-dependent transmission combined with the change of molecular eigenstates under bias. Finally, the temperature-induced spin excitation is simulated. Significant rectification behavior is obtained even at room temperature.

Keywords: organic spintronics, organic ferromagnet, rectification, spin-excited state

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1. Introduction

As a new branch of spintronics, organic spintronics has attracted more and more attention in recent years.[1–3] Organic materials such as single molecules,[4] polymers,[5] and organic single crystals[6] are usually cheap, low-weight, and can be synthesized in large area with chemical methods. It is especially significant that the spin–orbit coupling and hyperfine interactions in organic materials are very weak, resulting in a long spin relaxation time in such materials.[7] Generally, two kinds of organic spintronic devices are of interest now: 1) nonmagnetic molecules sandwiched between two magnetic electrodes, i.e., organic spin valves,[8–10] whose resistance is modulated by an applied magnetic field; 2) organic magnetic molecules as a central medium in which the spintronic functions are designed based on the intrinsic properties of the magnetic molecules.

Organic ferromagnets are particularly fascinating since they combine the advantages of both organic materials and ferromagnets. In recent decades, a variety of organic ferromagnets have been synthesized and measured, such as poly-BIPO,[11,12] m-PDPC,[13] pyro-PAN,[14] V[TCNE]$_X$,[15,16] 2-BIMNN.[17] For example, poly-BIPO can be synthesized from polyacetylene by replacing every other H atom with a heterocycle, which usually contains an unpaired electron and thus has a net residual spin.[11,12] There exists spin coupling between the radical spins and the π electrons along the main chain. As a result, the radical spins form a ferromagnetic order in the ground state.[18,19]

The recent progress in molecular electronics has triggered large interest in designing spintronic devices with organic ferromagnets including spin valves,[20,21] spin filters,[22,23] and spin diodes.[24–26] Among all the spintronic devices, spin diodes are particularly interesting due to their crucial role in logic circuits. As a new concept, molecular spin diodes have also been proposed recently. For example, by coupling a molecular wire with one ferromagnetic and one nonmagnetic electrode, Dalgleish and Kirczenow found that a spin-current rectification may be realized in a molecular junction,[24] where the structural asymmetry arises from the electrodes. On the other hand, the pursuit of *intrinsic* molecular diodes independent of the extrinsic conditions such as electrodes and interfaces has special meaning in the further design of molecular circuit. Analogous studies based on diblock co-oligomer has attracted extra attention in the field of molecular electronics.[27,28] Recently, with the utilization of magnetic co-oligomers we theoretically designed a new *intrinsic* organic spin diode, where the built-in asymmetry originates from the central molecule independent of electrodes.[25,26] It has been demonstrated that both the charge-current rectification and spin-current rectification may be realized, either simultaneously or respectively, with suitable design. This theoretical model is further verified by a recent *ab-intio* calculation about biradical and triradical magnetic molecules.[29]

It should be pointed out that so far, calculations about the proposed spin diodes are limited to the ground state of the molecule. In the presence of temperature, disturbance, photoexcitation or magnetic field, the magnetic molecule may deviate from its ground state. For example, with electron paramagnetic resonance (EPR) measurement, Petukhov has

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demonstrated the existence of spin-excited states in molecular magnets.[30] For a uniform ferromagnetic device, spin-excited states may change the conductance and its spin polarization, according to previous studies.[31,32] However, for an asymmetric magnetic co-oligomer, another issue worth considering is how the structural asymmetry is affected by the spin state of the molecule. Due to antiferromagnetic coupling with the radical spins, the electronic states suffer changes of molecular spin state, and the asymmetric response to the bias will further determine the rectification property.

In this paper, we theoretically investigate the electronic and magnetic properties of the magnetic co-oligomer in the presence of spin-excited states. Then, by calculating the spin-dependent transport, those properties' effects on the rectification are explored. The paper is organized as follows: the model and method are introduced in Section 2. In Section 3, we first calculate and discuss the electronic structure of the magnetic molecule under spin-excited states, and then investigate the transport and rectification properties. A summary is given in Section 4.

2. Model and method

We use a quasi-one-dimensional chain to model the device. As shown in Fig. 1, an organic magnetic molecule is sandwiched between two noninteracting semi-dimensional metallic chains. The molecule is composed of two segments, the left organic ferromagnetic part (poly-BIPO) and the right nonmagnetic one (polyacetylene). The Hamiltonian of the device can be written as

$$H = H_{\rm m} + H_l + H_r + H_{\rm coup} + H_E. \tag{1}$$

The first term is the Hamiltonian of the central molecule, which is described by an SSH (Su–Schieffer–Heeger) model combined with a Kondo term [18,33]

$$\begin{aligned} H_{\rm m} &= -\sum_{n,s}[t_0 - \alpha(u_{n+1}-u_n)](c^{\dagger}_{n,s}c_{n+1,s} + c^{\dagger}_{n+1,s}c_{n,s}) \\ &\quad + \frac{K}{2}\sum_n (u_{n+1}-u_n)^2 + J_f\sum_n^{N_1}\delta_{n,e}\boldsymbol{S}_{nR}\cdot\boldsymbol{S}_n, \end{aligned} \tag{2}$$

where t_0 is the hopping integral of π electrons between the n-th and $(n+1)$-th sites in a uniform chain, α is the electron–lattice coupling constant, u_n is the lattice displacement at site n and $c^{\dagger}_{n,s}$ $(c_{n,s})$ denotes the creation (annihilation) operator of a π electron at the n-th site with spin s. The second term is the lattice elastic energy with elastic constant K. The last term describes the spin correlation between the π-electron spin $\boldsymbol{S}_n$ and the residual spin $\boldsymbol{S}_{nR}$ of the radical R with coupling strength $J_{\rm f}$. The spin correlation occurs only on the even sites of the left magnetic part with total N_1 sites. With a mean-field approximation, the radical spin $\boldsymbol{S}_{nR}$ is further treated as $\langle S^z_{nR}\rangle$, where $\langle S^z_{nR}\rangle$ means the average value of the spin along the z axis.

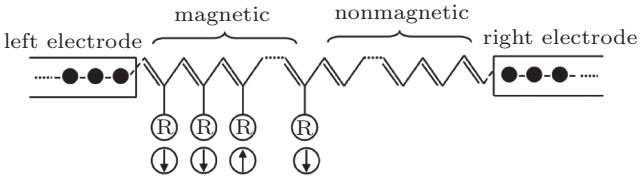


Fig. 1. Schematic structure of a metal/magnetic-nonmagnetic co-oligomer/metal spin diode. The arrows denote the spin orientation of the radical spins.

The two semi-infinite electrodes are identical normal metals described by the following Hamiltonian

$$H_{l(r)} = \sum_{m,s}\varepsilon_{l(r)}a^{\dagger}_{m,s}a_{m,s} + \sum_{m,s}t_{l(r)}(a^{\dagger}_{m,s}a_{m+1,s} + a^{\dagger}_{m+1,s}a_{m,s}), \tag{3}$$

where $\varepsilon_{l(r)}$ is on-site energy of a metal atom, $t_{l(r)}$ is the closest transfer integral and $a^{\dagger}_{m,s}$ $(a_{m,s})$ is the creation (annihilation) operator of an electron at the m-th site with spin s.

The coupling between electrodes and molecules is assumed to take place only at the nearest connecting atoms,

$$\begin{aligned} H_{\rm coup} &= \sum_s t_{lm}(a^{\dagger}_{l,s}c_{1,s} + c^{\dagger}_{1,s}a_{l,s}) \\ &\quad + \sum_s t_{rm}(a^{\dagger}_{r,s}c_{N,s} + c^{\dagger}_{N,s}a_{r,s}), \end{aligned} \tag{4}$$

where $t_{l(r)m}$ is the interfacial coupling strength and N is the number of the total sites in the interlayer molecule. For simplicity, only spin-independent interfaces are considered here.

The last term is the contribution from an external field E caused by the applied bias V between the two electrodes,

$$\begin{aligned} H_E &= -\sum_{n,s}|e|E\left[\left(n - \frac{N+1}{2}\right)a + u_n\right]c^{\dagger}_{n,s}c_{n,s} \\ &\quad + \sum_n |e|E\left[\left(n - \frac{N+1}{2}\right)a + u_n\right], \end{aligned} \tag{5}$$

where e is the electronic charge and a the lattice constant. The two terms correspond to the electric potential energy of π electrons and lattice ions respectively. Here a uniform electric field along the main chain is used with $E = V/[(N-1)a]$ when the applied bias V is not too large.

Under a bias, the lattice configuration and electronic structure of the magnetic molecule will be determined firstly by solving the electronic eigenequation and minimizing the total energy of the molecule, which is performed with a self-consistent method.[18,25] After obtaining the stable structure of the molecule, the spin-dependent current through the device can be calculated with the help of Landauer–Büttiker formula,[34]

$$I_s(V) = \frac{e}{h}\int_{-\infty}^{+\infty}[T_{ss}(E,V)]\,[f_l(E) - f_r(E)]\,{\rm d}E. \tag{6}$$

$T_{ss}(E,V)$ is the spin-dependent transmission coefficient, which can be obtained from the Lattice Green Function through the Fish–Lee relation[34] $T_{ss}(E,V) = {\rm Tr}\,[\Gamma_l G_{ss}(E,V)\Gamma_r G^{+}_{ss}(E,V)]$,

where $G_{ss}(E,V) = 1/(E - H^s_{\rm m} - H^s_E - \Sigma_l - \Sigma_r)$ with $\Sigma_{l(r)}$ being the self-energy operator due to the coupling to the left (right) electrode. $\Gamma_{l(r)}$ is the broadening matrix. $H^s_{\rm m}$ and H^s_E are the electron Hamiltonians with spin s in Eqs. (2) and (5). $f_{l(r)}(E) = 1/\{1+\exp[(E-\mu_{l(r)})/K_{\rm B}T]\}$ is the Fermi distribution function of the left (right) electrode with chemical potential $\mu_{l(r)} = E_{\rm F} \pm eV/2$ and Fermi energy $E_{\rm F}$.

In the numerical calculation, the parameters are chosen as follows: $t_0 = 2.5$ eV, $\alpha = 4.1$ eV/Å, $K = 21.0$ eV/Å^2, $J = J_{\rm f}/t_0 = 1.5$, and $\langle S^{\rm z}_{nR}\rangle = -1/2$, which may describe the co-oligomer of the organic ferromagnet poly-BIPO and polyacetylene properly.[18,25,35] The lengths of the two moieties are set equal, with $N_1 = N_2 = 16$. The parameters of electrodes are taken as $\varepsilon_{l(r)} = 0$, $t_{l(r)} = 2.5$ eV. The coupling between the molecule and the electrodes is set to be symmetric with $t_{lm} = t_{rm} = 1.0$ eV.

3. Results and discussion

Before calculating the transport property, we first investigate the electronic and magnetic properties of the isolate magnetic co-oligomer under spin-excited states. For the present magnetic co-oligomer, there are eight spin radicals in the left magnetic moiety ($N_1 = 16$). At the ground state, all the radical spins point in the same direction (assumed to be the z axis) and the spin number of the system is 8 in the unit of $\hbar/2$. Note that the total spin of the π electrons in the main chain remains zero.[33] An antiferromagnetic spin density wave exists along the molecule, mainly distributed in the left magnetic segment.

Spin-excited state in organic ferromagnets means one or more radical spins are flipped, which makes the molecule lie in higher energy. For a finite asymmetric molecule with a fixed boundary condition, the spin excitation will depend on the number of excited spins as well as their positions. If one radical spin is excited, we found that it costs the least energy when the first radical spin nearest to the left end of the molecule is flipped; while when two or more radical spins are flipped, the excited spins will form a coupled excitation rather than separate ones, which is similar to those in an organic ferromagnet oligomer.[32] If the number of flipped spins does not exceed the half (here $N_s \leq 4$), the coupled excitation tends to appear near the left end of the molecule. If $N_s > 4$, the low-energy excitation will appear near the right end of the magnetic moiety, which is due to the degeneracy of the molecule with $\langle S^z_{nR}\rangle = \pm 1/2$. For simplicity, in this context we consider only the low-energy excitation for a given number of flipped spins. In Fig. 2(a), we show the spin-excited energy, defined as $\Delta E(N_s) = E(N_s) - E_0$, in different spin-excited states. $E(N_s)$ is the total energy of the molecule with N_s flipped spins and E_0 the energy of the ground state. Obviously, the excited energy increases with N_s when $N_s \leq 4$, and then decreases with N_s. The curve is symmetric with $N_s = 4$ due to the spin degeneracy for $\langle S^z_{nR}\rangle = \pm 1/2$.

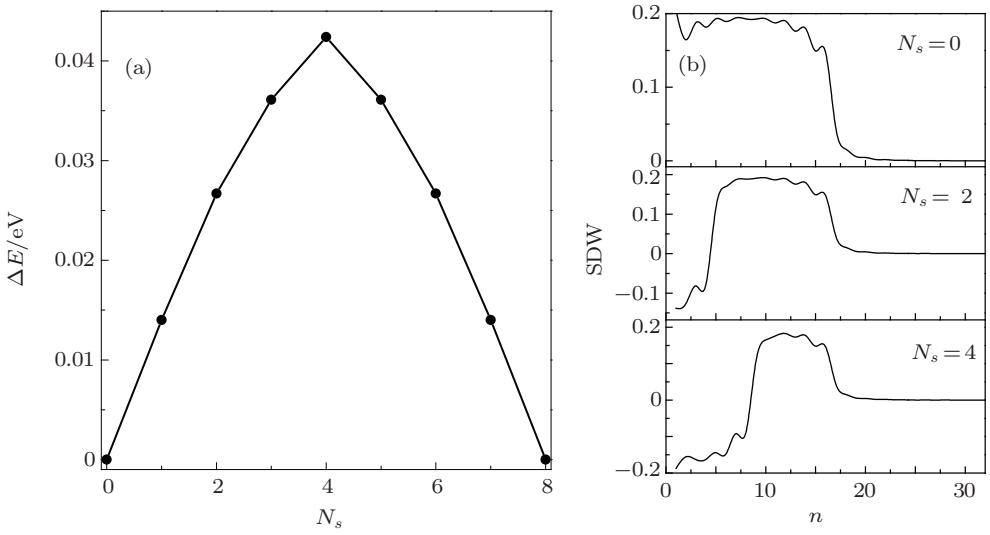


Fig. 2. (a) Spin excitation energy ΔE versus the number of flipped radical spins. (b) Spin density wave (SDW) at different spin-excited states.

The modulation of the structural asymmetry by the spin-excited states can be first reflected from the spin density wave (SDW). In Fig. 2(b), we depict the SDW of the co-oligomer at three different spin states. Here, the SDW order parameter is defined as $\mathrm{SDW}(n) = (-1)^n(n_{n\uparrow} - n_{n\downarrow})$, where n_{ns} is the electronic charge density at the n-th site with spin s ($\uparrow$ or $\downarrow$). In the ground state, the SDW mainly appears in the left segment and is highly asymmetric about the center of the molecular chain. At $N_s = 2$, the SDW near the flipped radical spins is reversed to negative. The negative region is broadened at $N_s = 4$. The

different spatial configurations of the asymmetric SDW are expected to generate distinct rectification property, which will be calculated later.

A more detailed investigation of the structural asymmetry can be performed by calculating the molecular eigenstates and their spatial distribution. Figure 3 shows the spin-dependent eigenvalues of the frontier molecular orbitals at different spin-excited states. Specifically, we calculate the energy gap and the spin-splitting energy in Fig. 3(b). Here, the energy gap is defined as $E_{\rm g}(N_{\rm s}) = \varepsilon^{\uparrow}_{\rm LUMO}(N_{\rm s}) - \varepsilon^{\downarrow}_{\rm HOMO}(N_{\rm s})$ and the spin-splitting energy is defined as $E_{\rm s}(N_{\rm s}) = \varepsilon^{\downarrow}_{\rm LUMO}(N_{\rm s}) - \varepsilon^{\uparrow}_{\rm LUMO}(N_{\rm s})$, where $\varepsilon^{s}_{\rm LUMO(HOMO)}(N_{\rm s})$ is the eigenvalue of the lowest unoccupied molecular orbital (LUMO) or the highest occupied molecular orbital (HOMO) with spin s. It is found that with the increase of flipped radical spins from 0 to 4, the energy gap increases about 0.18 eV while the spin splitting is reduced about 0.13 eV. In Fig. 4, we further plot the wave functions of the spin-up LUMO and spin-down LUMO, which are two frontier orbitals to the Fermi energy. We found that at the ground state the spin-up LUMO mainly distributes in the left magnetic segment and the spin-down one in the right non-magnetic segment. In the presence of spin-excited states, the orbital tends to be more delocalized, especially for the spin-down LUMO at a high spin-excited state ($N_s = 4$).

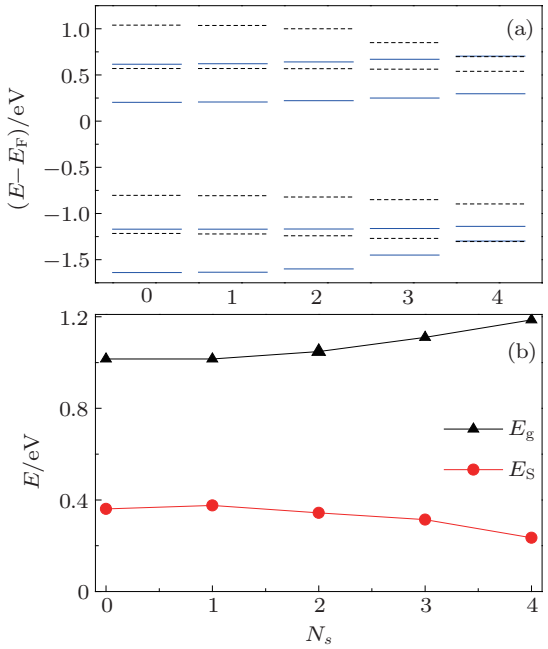


Fig. 3. (color online) (a) Spin-dependent molecular eigenvalues at different spin-excited states. Solid lines denote spin-up orbitals and dashed lines represent spin-down ones. (b) Energy gap ($E_{\rm g}$) and spin splitting ($E_{\rm s}$) of the energy spectrum with the number of flipped radical spins.

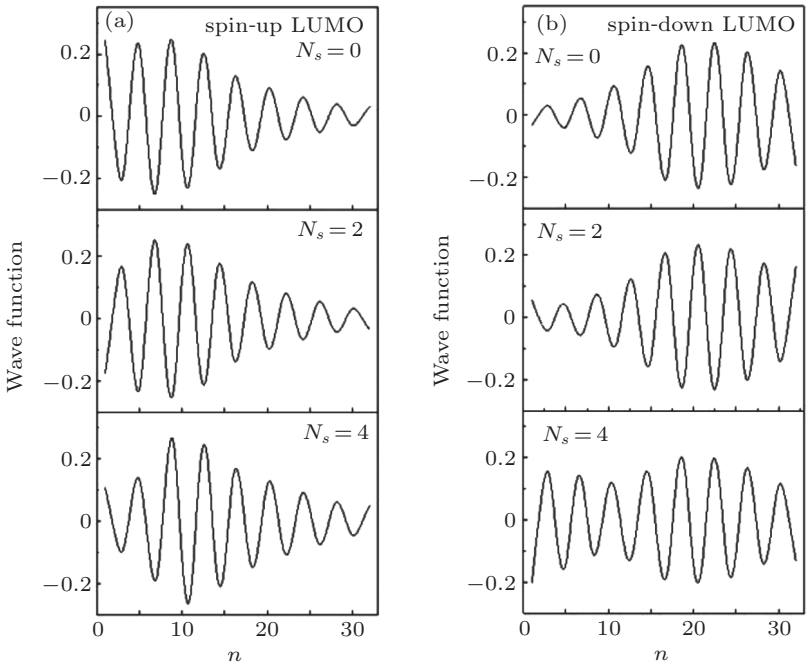


Fig. 4. Wave functions of the (a) spin-up LUMO and (b) spin-down LUMO at different spin-excited states.

In the following, we begin to study the transport property of the molecular spin diode at different spin-excited states. Figure 5 shows the current–voltage characteristics of the device. Apparently, both the charge current and spin current are rectified simultaneously at either ground state or spin-excited states. The currents in the positive bias region are much larger than those in the negative region. The present form of the spin-current rectification is parallel spin-current rectification,[25] where the spin-polarized orientation keeps unchanged while the magnitude of the spin current is asymmetric. Furthermore, it can be found that, in the presence of spin-excited states, the magnitude of the current at positive bias is depressed gradu-

ally with the flipped spins, while the current at negative bias changes little. The charge (spin) current at 1 V with $N_s = 4$ drops to about one-third of the ground state. The current suppression is consistent with experimental measurements of molecular magnets.[36] The threshold voltage of the device also increases slightly at spin-excited states, which may be understood from the energy gap evolution mentioned above.

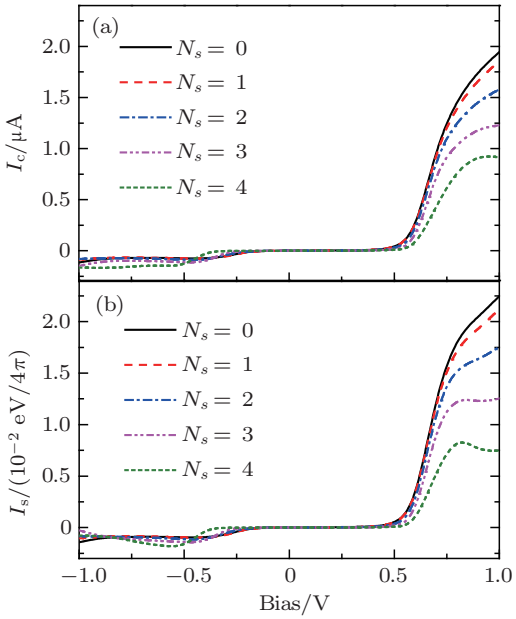


Fig. 5. (color online) (a) Charge current and (b) spin current as the function of bias voltage at different spin-excited states.

Figure 6 gives the bias-dependent charge-current ratio and spin-current rectification ratio at different spin-excited states, which are defined as $\mathrm{RR(V)} = -I_c(\mathrm{V})/I_c(-\mathrm{V})$ and $\mathrm{SRR(V)} = -I_s(\mathrm{V})/I_s(-\mathrm{V})$ respectively. Obviously, the RR and SRR change nonlinearly with the bias. It is found that if the applied bias is not too large (< 0.8 V), the RR and SRR decrease with the number of flipped radical spins. It looks reasonable since the spin-excited state tends to reduce the spin splitting of the electronic states, and hence reduces the structural asymmetry of the present co-oligomer. However, it is interesting that at a larger bias (> 0.8 V), the rectification ratio at some spin-excited states may be larger than the ground state. For example, at 1.0 V the RR and SRR in low-energy spin-excited states ($N_s = 1, 2$) is slightly larger than $N_s = 0$. In particular, a strongly enhanced SRR (about 47) appears at $N_s = 3$ in spite of the decreased RR. These results indicate that despite the suppression of the current, the rectification ratio at some bias may be improved by several specific spin-excited states.

A deeper understanding can be achieved by investigating the spin-dependent transmission. As a representative, figure 7 compares the bias-dependent transmission between the ground state and the spin-excited state with $N_s = 3$. Under a low bias of ± 0.7 V, we found that the current is dominated by the spin-up transmission peak nearest to the Fermi energy, which is contributed by the spin-up LUMO by checking the molecular eigenstates. The spin-up LUMO transmission peak is enhanced at positive biases, while it is much suppressed at negative biases, and thus generates the rectification. The intrinsic reason is the bias-dependent orbital hybridization,[25,37] where spatial distribution of the wave function is asymmetric under the bias. We further noticed that at the spin-excited state, the transmission peak under the negative bias is a little enhanced, which leads to a smaller RR. This is because the wave function of the orbital is more delocalized under the spin-excited state as demonstrated above. Under a larger bias of ± 1.0 V, besides the spin-up LUMO the high-energy orbitals also contribute slightly to the current, such as the tails of spin-down LUMO and spin-up LUMO + 1. For example, at the ground state, the tail of spin-up LUMO + 1 transmission peak enters the bias window at -1.0 V. But at the spin-excited state of $N_s = 3$, the tail of spin-down LUMO transmission peak enters the bias window instead of the spin-up LUMO + 1. As a result, the spin current at -1.0 V is very small under the spin-excited state distinct from the charge current, which induces a very large SRR in spite of a small RR. By checking the spin-dependent transmission at other spin-excited states (not shown here), we found that the contribution from the high-energy orbitals is also responsible for the increase of RR and SRR at $N_s = 1$ and $N_s = 2$ under large bias. This means that the presence of spin-excited states modifies the uniform mechanism for rectification into a mixed one, that is, asymmetric wave function combined with the asymmetric eigen levels shift upon the reversal of the bias, as has been well analyzed in a previous study.[38]

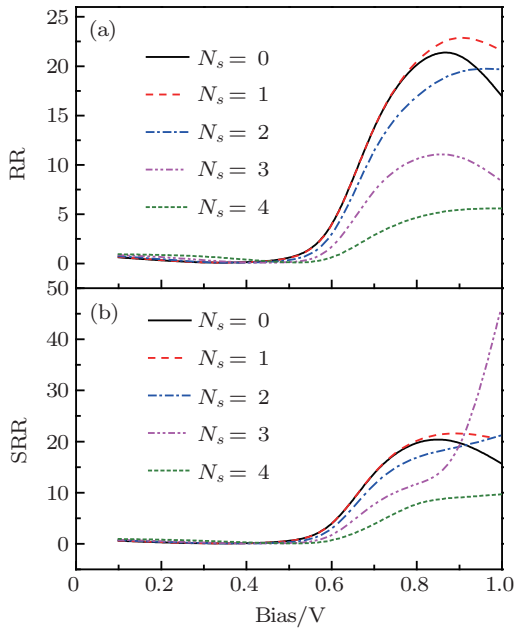


Fig. 6. (color online) Dependence of charge-current rectification ratio RR and spin-current rectification ratio SRR on the bias at different spin-excited states.

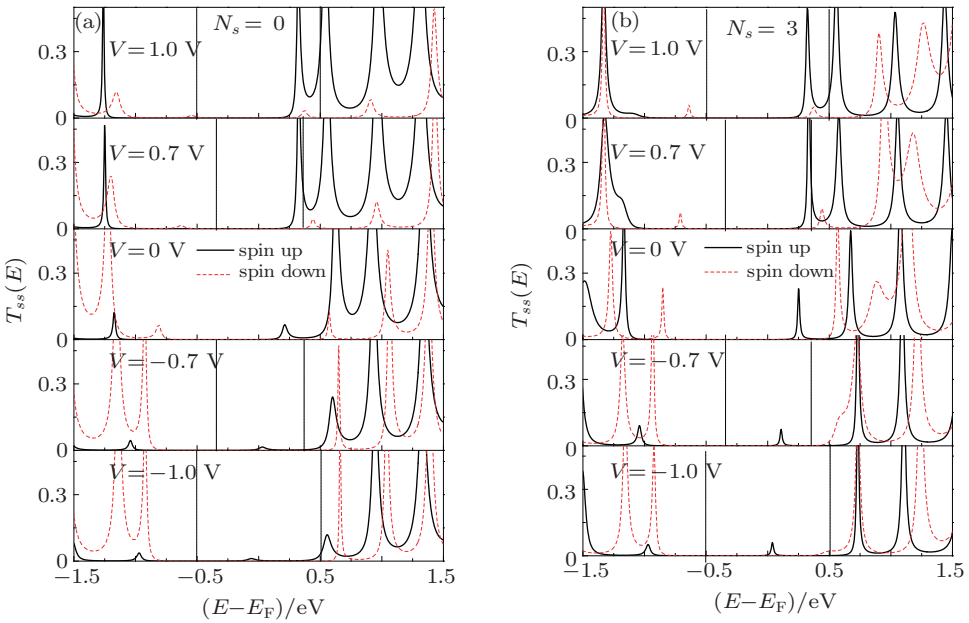


Fig. 7. (color online) Spin-dependent transmission near the Fermi energy with (a) $N_s = 0$ and (b) $N_s = 3$ at the bias voltage of 0 V, ± 0.7 V, and ± 1.0 V respectively.

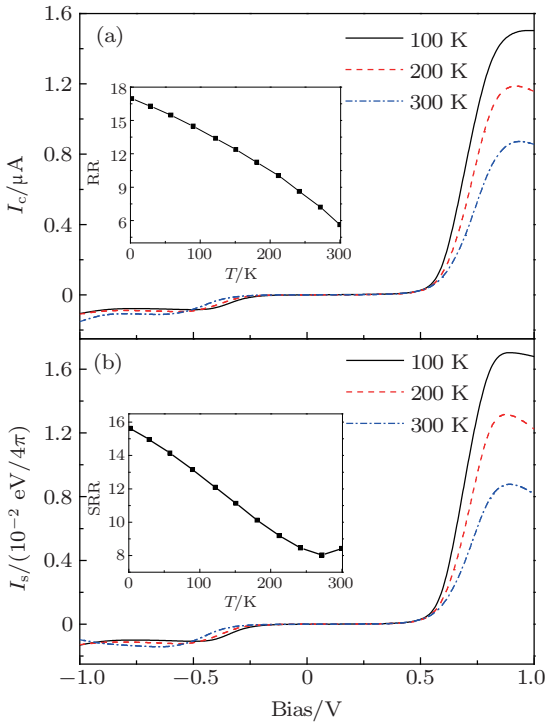


Fig. 8. (color online) (a) Calculated charge current and (b) spin current as functions of bias voltage at different temperatures. The insets are the dependence of rectification ratio on the temperature at $|V| = 1.0$ V.

At last, we further simulate the temperature excitation on the radical spins as thermal fluctuation from the ferromagnetic ground state. It is assumed that at a temperature T, the random deviation of each radical spin from the ground state is described by an angle θ. All the deviation angles obey a square-random distribution from 0 to θ_0, where θ_0 is the maximum deviation angle related to the temperature with a simple Boltzmann relation $\Delta\varepsilon \approx K_B T/2$. $\Delta\varepsilon$ is the energy difference per site between the disturbed states and the ground state. In Fig. 8, we first show the charge-current and spin-current curves at three different temperatures, 100 K, 200 K, and 300 K, where the Fermi distribution function is also adjusted according to the temperature. It is found that significant rectification exists even at room temperature. The maximum value of the charge (spin) current at 300 K drops to about half of that at 100 K. The dependence of the rectification ratio on the temperature is given in the insert plot, which is calculated at ± 1.0 V. With increasing temperature the RR and SRR decrease almost linearly. The value of RR (SRR) decreases from 17 (16) to 4 (8) when temperature increases to room temperature. This means that robust charge-current rectification and spin-current rectification can be obtained, even at room temperature.

To conclude this paper, let us make some comments on the mean-field approximation for the radical spins of the organic ferromagnet. In our mean-field treatment, the z component of the radical spins is predetermined with fixed values of $\langle S^z_{nR} \rangle = \pm 1/2$. Although this treatment works well for the magnetism of organic ferromagnets, an expected more rigorous calculation is to determine the spin order of the radicals self-consistently under the nonequilibrium situation with an applied bias. For example, in the frame of a more complex Anderson-type model where the electron hopping between the π electrons and unpaired radical electrons are included,[39,40] the probability distribution of the radical electrons may be solved with the exact diagonal method. This issue will be taken into account in our future work.

4. Summary

In summary, we have performed a theoretical study on the spin-excited states' effect in an organic magnetic co-oligomer diode by calculating the electronic and magnetic properties of an isolated molecule and the spin-dependent transport property through the device. It is found that the spatial asymmetry of the spin density wave along the magnetic co-oligomer is modulated by the spin-excited states. With the increase of excited radical spins the molecular energy gap is increased while the spin-splitting energy is reduced. The wave functions of the frontier orbitals tend to be more delocalized at spin-excited states. By calculating the transport property, we found that significant rectification is still obtained for both the charge current and spin current in the case of spin-excited states, although the magnitude of current is suppressed. At a low bias, the rectification ratio keeps decreasing when more and more radical spins are excited. But at a larger bias, we found that both the charge-current and spin-current rectification ratios may increase at several spin-excited states. By analyzing the spin-dependent transmission the intrinsic mechanism can be tracked from the modulation of the eigenstates by the spin-excited states. We further discussed the temperature-induced spin excitation on the rectification. The results showed that the rectification ratios decrease with temperature. The spin diode effect is robust even at room temperature. The work indicates a possible way to modulate the rectification behavior of an organic spin diode with a magnetic mode, i.e., manipulating the molecular spin states.

References

[1] Naber W J M, Faez S and van der Wiel W G 2007 *J. Phys. D: Appl. Phys.* **40** R205

[2] Dediu V A, Hueso L E, Bergenti I and Taliani C 2009 *Nat. Mater.* **8** 707

[3] Sugawara T and Matsushita M M 2009 *J. Mater. Chem.* **19** 1738

[4] Liang W, Shores M P, Bockrath M, Long J R and Park H 2002 *Nature* **417** 725

[5] Dediu V, Murgia M, Matacotta F C, Taliani C and Barbanera S 2002 *Solid State Commun.* **122** 181

[6] Podzorov V, Menard E, Borissov A, Kiryukhin V, Rogers J A and Gershenson M E 2004 *Phys. Rev. Lett.* **93** 086602

[7] Pramanik S, Stefanita C G, Patibandla S, Bandyopadhyay S, Garre K, Harth N and Cahay M 2007 *Nat. Nanotechnol.* **2** 216

[8] Xiong Z H, Wu D, Vardeny Z V and Shi J 2004 *Nature* **427** 821

[9] Zhan Y Q, Bergenti I, Hueso L E, Dediu V, de Jong M P and Li Z S 2007 *Phys. Rev. B* **76** 045406

[10] Wang H, Hu G C and Ren J F 2013 *Chin. Phys. B* **22** 058504

[11] Korshak Y V, Medvedeva T V, Ovchinnikov A A and Spector V N 1987 *Nature* **326** 370

[12] Cao Y, Wang P, Hu Z, Li S Z, Zhang L Y and Zhao J G 1988 *Synth. Met.* **27** B625

[13] Iwamura H, Sugawara T, Itoh K and Takui T 1985 *Mol. Cryst. Liq. Cryst.* **125** 379

[14] Katulevskii Y A, Magrupov M A and Murninov A A 1991 *Phys. Status Solidi A* **127** 223

[15] Manriquez J M, Yee G T, McLean R S, Epstein A J and Miller J S 1991 *Science* **252** 1415

[16] Raju N P, Savrin T, Prigodin V N, Pokhodnya K I, Miller J S and Epstein A J 2003 *J. Appl. Phys.* **93** 6799

[17] Sugano T, Blundell S J, Lancaster T, Pratt F L and Mori H 2010 *Phys. Rev. B* **82** 180401

[18] Fang Z, Liu Z L and Yao K L 1994 *Phys. Rev. B* **49** 3916

[19] Guo J Y, Chen Y G and Chen H 2005 *Chin. Phys.* **14** 821

[20] Yoo J W, Edelstein R S, Lincoln D M, Raju N P, Xia C, Pokhodya K I, Miller J S and Epstein A J 2006 *Phys. Rev. Lett.* **97** 247205

[21] Li B, Zhou M, Lu Y, Kao C K, Yoo J W, Prigodin V N and Epstein A J 2012 *Org. Electron.* **13** 1261

[22] Hu G C, Guo Y, Wei J H and Xie S J 2007 *Phys. Rev. B* **75** 165321

[23] Wang W Z 2006 *Phys. Rev. B* **73** 235325

[24] Dalgleish H and Kirczenow G 2006 *Phys. Rev. B* **73** 235436

[25] Hu G C, He K L, Xie S J and Saxena A 2008 *J. Chem. Phys.* **129** 234708

[26] Hu G C, Wang H and Ren J F 2011 *Chin. Phys. B* **20** 077306

[27] Jiang P, Morales G M, You W and Yu L 2004 *Angew. Chem. Int. Ed.* **43** 4471

[28] Díez-Pérez I, Hihath J, Lee Y, Yu L, Adamska L, Kozhushner M A, Oleynik I I and Tao N 2009 *Nat. Chem.* **1** 635

[29] Zhu L, Yao K L and Liu Z L 2012 *Chem. Phys.* **397** 1

[30] Petukhov K, Hill S, Chakov N E, Abboud K A and Christou G 2004 *Phys. Rev. B* **70** 054426

[31] D'Amico I and Vignale G 2000 *Phys. Rev. B* **62** 4853

[32] Jiang H, Hu G C, Guo Y and Xie S J 2009 *Org. Electron.* **10** 809

[33] Hu G C, Wang H, Ren J F, Xie S J and Timm C 2014 *Org. Electron.* **15** 118

[34] Datta S 1995 *Electronic Transport in Mesoscopic Systems* (New York, Oxford University Press) p. 148

[35] Xie S J, Zhao J Q, Wei J H, Wang S G, Mei L M and Han S H 2000 *Europhys. Lett.* **50** 635

[36] Heersche H B, de Groot Z, Folk J A, van der Zant H S J, Romeike C, Wegewijs M R, Zobbi L, Barreca D, Tondello E and Cornia A 2006 *Phys. Rev. Lett.* **96** 206801

[37] Hu G C, Wei J H and Xie S J 2007 *Appl. Phys. Lett.* **91** 142115

[38] Hu G C, Zhang G P, Ren J F, Wang C K and Xie S J 2011 *Appl. Phys. Lett.* **99** 082105

[39] Li Z J, Lin H Q, An Z and Yao K L 1998 *J. Chem. Phys.* **109** 10082

[40] Fu H H and Yao K L 2011 *J. Chem. Phys.* **134** 054903