P H Y S I C A L   R E V I E W   L E T T E R S

Rectification Mechanism in Diblock Oligomer Molecular Diodes

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We investigated a mechanism of rectification in diblock oligomer diode molecules that have recently been synthesized and showed a pronounced asymmetry in the measured *I-V* spectrum. The observed rectification effect is due to the resonant nature of electron transfer in the system and the localization properties of bound state wave functions of resonant states of the tunneling electron interacting with an asymmetric molecule in an electric field. The asymmetry of the tunneling wave function is enhanced or weakened depending on the polarity of the applied bias. The conceptually new theoretical approach, the Green's function theory of sub-barrier scattering, is able to provide a physically transparent explanation of this rectification effect based on the concept of the bound state spectrum of a tunneling electron. The theory predicts the characteristic features of the *I-V* spectrum in qualitative agreement with experiment.

In their pioneering paper [1], Aviram and Ratner proposed the idea of a molecular rectifier that contains donor and acceptor π-conjugated segments separated by an insulating σ-bonded segment of molecular wire. Several molecular rectifying systems have been synthesized in the past decade using Langmuir-Blodgett molecular assembly [2–6]. Attempts to provide experimental proof of the molecular rectification were complicated by difficulty in establishing reproducible electrical contacts between metallic electrodes and a single molecule which resulted in uncontrollable interface rectification effects [7].

Recently, a new class of diode molecules has been synthesized based on diblock oligomer molecules [8,9]. These molecules, consisting of thiophene and thiazole structural units, have shown a pronounced rectification effect as a result of built-in chemical asymmetry. By synthesizing diode molecules with different terminal thiol groups, it has become possible to assemble the diode molecules between gold electrodes with a predefined rectification direction [10]. Importantly, it was experimentally proved that the rectification is an intrinsic property of the molecule and not due to asymmetry of the electrodes and/ or molecule-electrode interfaces [8–10]. The effect of rectification in diode molecules has also been independently confirmed by other experimental groups [11].

In this Letter we explain the mechanism of rectification in diblock oligomer diode molecules. We demonstrate that the observed asymmetry of current-voltage characteristics is the result of the resonant character of electron transport in molecular diodes and spatial asymmetry of the wave function of a tunneling electron interacting with an asymmetric molecule in an applied electric field. The asymmetry of the tunneling wave function is enhanced or weakened depending on the polarity of the applied bias.

The diblock oligomer molecule consists of two parts, each containing an equal number of thiophene (C_4N) and thiazole (C_3NS) rings; see Fig. 1(a). A two-terminal mo-

lecular circuit is produced by a sequential assembly between two gold electrodes, and the current-voltage characteristics of an individual molecule are measured by scanning tunneling spectroscopy [8–10]. The characteristic feature of an *I-V* spectrum of molecular diodes is a threshold voltage, i.e., the absence of current below some value of applied bias. The threshold is observed for both polarities of the bias; see Fig. 1(b).

The threshold feature of the experimental *I-V* curve can be explained by considering two fundamental mechanisms of electron transport through single molecules. These
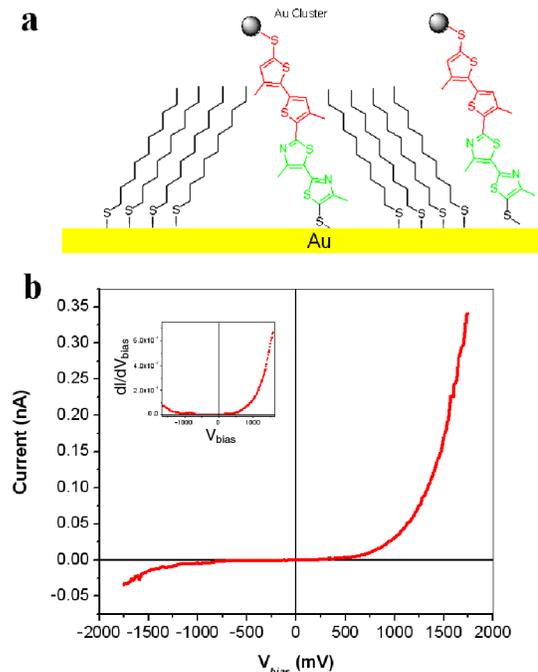

FIG. 1 (color online). (a) Atomic structure of diblock oligomer diode; (b) measured *I-V* spectrum.

mechanisms are ordinary tunneling, when the bound states of a tunneling electron are above the Fermi level of the negatively biased electrode, and resonant electron transfer, when part of the spectrum is within the energy interval $\varepsilon_F^l - |V| \leq \varepsilon_s \leq \varepsilon_F^l$ (following the experiment [8–10], we assume that the left and right electrodes have the same values of the work function $W = |\varepsilon_F^l|$). The amplitude of ordinary tunneling transition is much smaller then the resonant amplitude, which results in exponentially small values of current at the applied bias $|V| < V_{th}$. As the bias increases, the band of the bound states of the tunneling electron is lowered towards the Fermi level of the left electrode ε_F^l. The current instantaneously jumps at the moment when the resonant condition is realized, i.e., when the lowest state s from the band aligns with ε_F^l at a specific threshold bias V_{th}; see Fig. 2. In Fig. 2, the positive bias is applied to the right electrode so that the electrons of the left electrode are transferred to the right electrode via the resonant energy levels of the negative ion.

An important question is concerned with the nature of the bound state energy spectrum of the tunneling electron. Usually, the electron orbitals of a neutral molecule are calculated and used for the interpretation of the transport mechanisms. However, the energy spectrum of a neutral molecule is very different from the energy spectrum of an extra electron interacting with the molecule, i.e., the energy spectrum of the negative ion. In order to address this issue, we have recently developed a theory of the bound states of the tunneling electron in a molecular wire [12] based on the concepts of sub-barrier scattering [13,14]. Here we apply this theory to explain the asymmetry of resonant tunneling current-voltage characteristics in the case of chemically asymmetrical diode molecules.
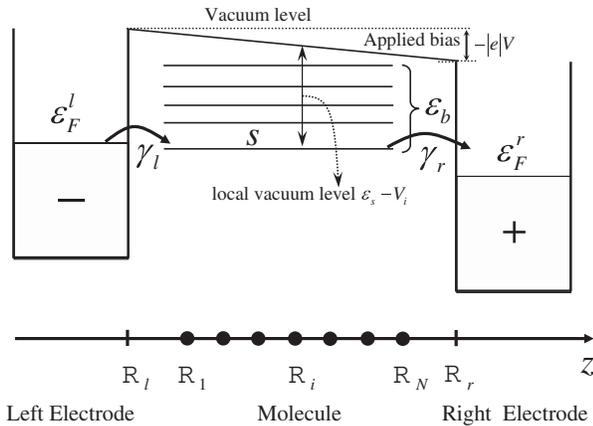

FIG. 2.   Energy diagram of the left-electrode–molecule–right-electrode junction in the case of a positively biased right electrode. The resonant state below ε_F^l contributing to resonant electron transfer has label "s." Local vacuum level is shown for ith scattering center; γ_l and γ_r are the probabilities of electron transfer from the left electrode to bound state s and from bound state s to the right electrode.

Taking into account the resonant character of electron transport in molecular diodes substantiated by the experimentally observed threshold in the *I-V* spectrum, one might ask what the factors are that contribute to the asymmetry of the current with respect to the polarity of applied bias. The expression for the resonant current due to the resonant state s is symmetric with respect to the left and right electrodes:

$$I_{res}(\varepsilon_s) = \frac{1}{2} \frac{\gamma_l \gamma_r}{\gamma_l + \gamma_r}, \tag{1}$$

where $\gamma_{l,r} = 2\pi |\langle \psi_{l,r} | U | \psi_b \rangle|^2 \rho_{l,r}(\varepsilon_s)$ are the probabilities of electron transfer from the bound state $\psi_b(\varepsilon_s)$ to one of the states ψ_l or ψ_r of the continuous spectrum of the left or right electrode, respectively, $\gamma_s = \gamma_l + \gamma_r$ being the inverse lifetime of the resonant energy level. U is the electronic potential at the electrode-molecule interface (we use the atomic system of units $\hbar = e = m_e = 1$). Therefore, (1) will give approximately the same value of current at small applied voltages $\pm V$, $|V| \ll 1V$, even if there is some small dependence of the bound state wave function ψ_b on the applied electric field E.

However, an important feature of molecular rectification is the resonant character of electron transfer through the diode molecule which results in a threshold voltage $V_\pm^{th} \sim 1$ eV. At such bias the spatial behavior of the bound state wave function of the tunneling electron becomes highly asymmetric because of a small penetration of the bound state wave function under a triangular potential barrier $U(z) = -Vz/d$ (d is the distance between left and right electrodes). Then, the probability of electron transfer from the left electrode to the resonant bound state γ_l is very small compared to that from the bound state to the right electrode γ_r; see Fig. 2. This creates a bottleneck at the left electrode for electron transfer at positive bias. For negative bias, electrons are transferred from the right electrode to the left electrode and the bottleneck is created at the right electrode $\gamma_r \ll \gamma_l$. Therefore, the expression for resonant current (1) reduces to

$$I(\varepsilon_s) = \begin{cases} 1/2\gamma_l, & V \geq V_+^{th} > 0 \\ 1/2\gamma_r, & V \leq V_-^{th} < 0 \end{cases}. \tag{2}$$

As seen from (2) the asymmetry in the current as the polarity of the bias changes will be due to the inequality $\gamma_l \neq \gamma_r$. The probabilities γ_l and γ_r of electron transfer to the left and right electrodes are proportional to $|\psi_b(\mathbf{R}_{l,r}; \varepsilon_s)|^2$. As is shown below, the tunneling electron interacts differently with chemically different parts of the molecule which results in inequality $\psi_b(\mathbf{R}_l, +V) \neq \psi_b(\mathbf{R}_r, -V)$, the latter being the source of *I-V* asymmetry.

We have recently developed a theory of electron transfer in single molecular systems based on the Green's function theory of electron sub-barrier scattering off the structural units (or functional groups) constituting the molecule [13,15]. The fundamental building block of this theory is

the scattering operator $t_i(\varepsilon, \theta)$ of a structural unit of the molecule or scattering center i. The scattering operator $t_i(\varepsilon, \theta)$ is calculated using a variational-asymptotic approach that explicitly takes into account the electron-electron and electron-nuclei interactions between the tunneling electron and the molecule [14]. All of the complexity of the many-body interactions between the tunneling electron and the molecule is coarse grained into the dependence of the scattering operator on the energy ε and the scattering angle θ. Once the $t_i(\varepsilon, \theta)$ are known for all structural units of the molecule, the total Green's function G of the tunneling electron is easily obtained. The poles of G comprise the bound energy spectrum of the tunneling electron, the energies and the corresponding wave functions being obtained in the course of solving a system of linear equations for the partial scattering operators $\vec{T}(s) = \{T_1(s), T_2(s), \ldots, T_N(s)\}$ [12,13].

The effects of an external electric field are explicitly taken into account by parametric referencing of the local vacuum levels of the scattering centers by the local electrostatic energy $V = -V(R_i/d)$ because the functional form of the scattering operators $t_i(\varepsilon, \theta)$ is almost independent of the applied electric field. In fact, the calculated change in total energy of neutral polythiophene molecule consisting of eight thiophene rings in an electric field of 0.07 V/Å (which corresponds to bias of 2 V applied to the ends of the molecule) is small, ~0.2 eV/molecule. The charge redistribution due to external electric field is also negligible. An additional electrostatic effect that we took into account in our calculations is the interaction of the tunneling electron with its image charges in the left and the right electrodes which results in an additional contribution to the local vacuum levels of the scattering centers.

The wave function for the resonant bound state s that determines the probabilities of γ_l and γ_r is obtained as

$$\psi_b(\mathbf{r}; \varepsilon_s) = \sum_n T_n(s)\tilde{\varphi}(\mathbf{r} - \mathbf{R}_n; \varepsilon_s), \qquad (3)$$

where $\tilde{\varphi}(\mathbf{r} - \mathbf{R}_n; \varepsilon_s)$ are additional contributions to the exponential tail of the electron wave function of the tunneling electron due to its interaction with scattering center n. The partial scattering operators $T_n(s)$ are determined via solution of the homogeneous system of linear equations:

$$T_n(\varepsilon, V) = \sum_{k \neq n} t_n(\varepsilon - V_n)G_V(\mathbf{R}_n, \mathbf{R}_k; \varepsilon)T_k(\varepsilon, V), \qquad (4)$$

where $G_V(\mathbf{R}_n, \mathbf{R}_k; \varepsilon)$ is the vacuum Green's function in the external electric potential V that connects centers $\mathbf{R}_n$ and $\mathbf{R}_k$.

The determinant of system (4) is the secular equation for the eigenspectrum of the bound states

$$\det|\delta_{ik} - t_i(\varepsilon - V_i, \theta)G_v(\mathbf{R}_i, \mathbf{R}_k; \varepsilon)| = 0. \qquad (5)$$

As is seen from (4) and (5), the quantity $h(\varepsilon, V_i) = |t_i(\varepsilon - V_i, \theta)G_V(\mathbf{R}_i, \mathbf{R}_{i\pm1}; \varepsilon)|$ serves as an "effective"

hopping integral that can be used to relate the properties of individual scattering centers to the local properties of the wave function of the resonant state $\psi_b(\varepsilon_s)$ as a function of applied bias. Qualitatively, the larger the effective hopping integral $h(\varepsilon, V_i)$, the stronger the localization of the tunneling electron at center i. The effective hopping integral $h(\varepsilon, V_i)$ is a decreasing function of the absolute energy $|\varepsilon|$ due to an exponential reduction of the Green's function. Therefore, when the positive bias is applied, the right end of the molecule experiences an effective reduction of the local vacuum level $\varepsilon - V$, $\varepsilon, V < 0$ and the wave function is strongly localized at the right end of the molecule. At the left end of the molecule, the electrostatic potential and a corresponding reduction of the local vacuum level are small, which results in a relatively small value of the wave function at the left end of the molecule $\psi_b(\mathbf{R}_l, \varepsilon_s)$. When the polarity of bias is reversed, localization occurs at the left end of the molecule, which experiences a larger reduction of the local vacuum level. Then, the resonant current is determined by $\psi_b(\mathbf{R}_r, \varepsilon_s)$ at the right end of the molecule.

The energy dependence of the scattering operators $t_i(\varepsilon)$ is the key factor in explaining the physics of the rectification effect. In general, when the energy of a tunneling electron decreases with respect to the vacuum level ($|\varepsilon|$ increases), $|t_i(\varepsilon)|$ grows substantially due to an appreciable contribution to the exchange interaction of the tunneling electron with the electrons of the molecule at tunneling energies close to the energies of the molecular orbitals. Let us assume that the left half of the molecule consists of scattering centers which have larger values of the scattering operator $t_i(\varepsilon)$ than scattering centers on the right half of the molecule, $|t_l(\varepsilon)| > |t_r(\varepsilon)|$. This difference is due to different number of valence electrons in thiazole and thiophene structural units. At zero bias $|h_l(\varepsilon_s, 0)/h_r(\varepsilon_s, 0)| = |t_l(\varepsilon_s)/t_r(\varepsilon_s)| > 1$, consequently, $|\psi_b(\varepsilon_s, \mathbf{R}_l)| > |\psi_b(\varepsilon_s, \mathbf{R}_r)|$. As the bias is increased, this ratio is reduced due to the trend for wave function localization at the right end by a rate which is determined by the ratio $|h_l(\varepsilon_s, V)/h_r(\varepsilon_s, V)|$. Eventually, this ratio becomes less than 1 at any bias above the threshold value, but the localization of the bound state of the tunneling electron at the right end of the molecule is greatly reduced because of the initial dominance of the scattering operators at the left end. Therefore, the probability γ_l is appreciable and the direct current is substantial.

In the case of negative bias applied to the molecule, the localization at the left end of the molecule is greatly assisted due to the initial imbalance $|\psi_b(\varepsilon_s, \mathbf{R}_l)| > |\psi_b(\varepsilon_s, \mathbf{R}_r)|$. As bias is increased, localization at the left end occurs at a much higher rate due to the increased energy dependence of the scattering operator $t_l(\varepsilon_s)$. As a consequence, the wave function $\psi_b(\varepsilon_s, \mathbf{R}_r)$ at the right end at negative bias is much smaller than $\psi_b(\varepsilon_s, \mathbf{R}_l)$ at the left end at the positive bias of the same value of $|V|$. Therefore,
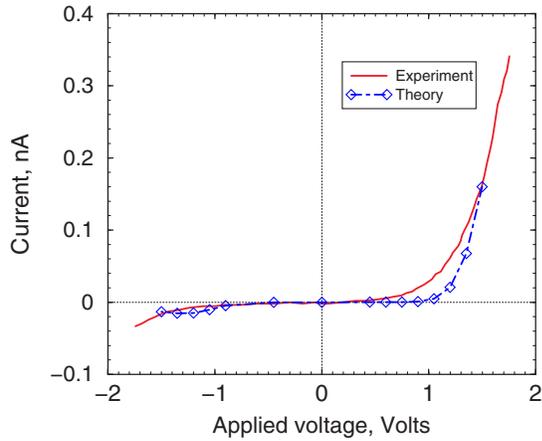
FIG. 3 (color online). The *I-V* spectrum of diode molecule predicted by theory and compared with experiment.

due to the much smaller value of γ_r, $\gamma_r < \gamma_l$, the resonant current at negative bias above the threshold will be much smaller than that at the same bias but of positive polarity; see Eq. (2).

In order to confirm this qualitative picture, we have performed calculations of diode *I-V* characteristics for a diblock oligomer molecule consisting of four thiophene and four thiazole units. Each ring is modeled as a single structural unit, i.e., scattering center, and is represented by the scattering operators $t_1(\varepsilon)$ or $t_2(\varepsilon)$ for thiazole and thiophene rings, respectively. The parametrization of $t_1(\varepsilon)$ or $t_2(\varepsilon)$ used in simulations is

$$t(\varepsilon)/2\pi = a/(\varepsilon - \varepsilon_0) + b + c\varepsilon \qquad (6)$$

where $a/(\varepsilon - \varepsilon_0)$ and $b + c\varepsilon$ are the pole and potential terms of the scattering operator, respectively. The numerical values of $a_1 = a_2 = 1.0$; $\varepsilon_{0,1} = \varepsilon_{0,2} = -0.037$; $b_1 = b_2 = 10.0$; $c_1 = 2500$; $c_2 = 1500$ were chosen based on our previous calculations of scattering operators for various molecular systems and by taking into account the specific conditions of the experiment. In particular, the values of the coefficients in (6) are an order of magnitude larger than that for simple systems such as the hydrogen atom, which is quite reasonable when taking into account the fact that the scatterers are molecular systems consisting of several atoms connected by conjugated bonds. The distance between the scatterers is 4 Å $\approx$ 8 a.u.

The calculated *I-V* spectrum for a molecular diode is shown and compared with experiment in Fig. 3. This simple model of a molecular diode predicts threshold values of the voltage $V_l^{\text{th}} \approx 1.0$ eV and a rectification ratio $I(+1.5 \text{ V})/I(-1.5 \text{ V}) = 10$ that is in qualitative agreement with experiment.

As stressed above, the substantial rectification effect in diode molecules is the consequence of resonant electron transfer in diblock oligomer systems. Interestingly, a similar but smaller asymmetry in the *I-V* spectrum with respect to the polarity of applied bias can be observed in the regime of direct tunneling through single molecules, i.e., when the energy levels of the tunneling electron are above the Fermi level of the negatively biased electrode.

In conclusion, we have investigated the mechanism of rectification in diblock oligomer diode molecules and have shown that the observed rectification effect is due to both the resonant nature of electron transfer in the system and the localization properties of bound state wave functions of the resonant states of the tunneling electron in an electric field.

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