Molecular rectification: why is it so rare?

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Abstract

Although conductance measurements of single molecule and few molecules junctions are currently being reported, there is a striking rarity of molecular rectification in these reports. Molecular rectification can be defined as the absence of inversion symmetry, $I(V) = -I(-V)$, where I and V are the measured current and applied voltage. In molecular junctions of the form metal/molecule/metal, there is generally an absence of structural mirror symmetry. One might then expect rectification arising from this asymmetrical structure. We suggest here that molecular rectification in tunneling junctions is generally difficult to achieve, essentially because deformation of the structure in the presence of finite voltage will result in effectively symmetric voltage profiles for forward and reverse biases. © 2002 Elsevier Science B.V. All rights reserved.

1. Introduction

The effect of molecular rectification consists in an asymmetric current response of a molecular junction to an external voltage bias and was theoretically predicted in 1974 [1]. Many different transport regimes may occur for a given molecular interface. They include tunneling, hopping and diffusion; the interplay among these mechanisms is temperature dependent [2]. Charge carrying particles in these junctions are either electrons or holes and the current, in the coherent tunneling regime to which we limit our attention, depends strongly on at least four factors: (i) The nature of the molecular

bridge and the contacts; (ii) The strength of the electrode–molecule interaction; (iii) The position of the Fermi energy; and (iv) The spatial profile of the electrochemical potential across the interface.

A whole host of molecular junctions has been designed, both consisting of individual molecules and molecular films [3]. Some of these junctions show rectification behavior [4–6], but a general criterion to predict whether a specific junction will rectify depends on our understanding of the crucial elements that determine the current and how they combine to produce asymmetries in the I–V characteristic. The dominant factors in inducing rectification are some geometric asymmetry in the molecular junction and in the electrostatic potential spatial profile. If no voltage drop occurs across the molecular bridge, asymmetries in the energy spectrum (or the geometry) of the isolated

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molecule, or even of the junctions, will not suffice to produce an asymmetric *I–V* curve.

It follows that the molecular synthetic voltage engineering to achieve rectification must assure both that not all voltage drop occur at the interfaces, and that the molecule itself has no inversion symmetry. One way to achieve this is to provide both very strong mixing between at least one end of the molecule and the contact electrode, and an obvious molecular asymmetry. This has indeed been achieved by Reed and co-workers [7], who report very strong rectification. A second strategy would be to provide one or more "weak links" (places of highly reduced local electronic coupling along the longitudinal axis of the junction) and one or more local electrostatic defect sites, all within an asymmetric structure [8].

2. Tunneling current

Although the quantitative calculation of the non-linear tunneling current through a molecule is facilitated by considering a *supermolecule* that includes the bridge and some of the atoms that form the electrodes, for discussion of rectification it is simpler to define the system as a molecule interacting with continuum metallic electrodes. The current in the elastic regime can be written as [9–11]

$$I = \frac{2e}{h} \int_{\mu_L}^{\mu_R} d\epsilon \text{Tr}[\mathbf{G}(\epsilon, V)\mathbf{\Delta}_L(\epsilon, V)\mathbf{G}^\dagger(\epsilon, V)\mathbf{\Delta}_R(\epsilon, V)].$$
(1)

Here μ_L and μ_R are the electrochemical potentials in each contact, left (L) or right (R); $V = (\mu_R - \mu_L)/e$, the bias voltage; $\mathbf{\Delta}_{L(R)}$ the spectral density corresponding to each contact, and $\mathbf{G}$ the Green function matrix defined by

$$\mathbf{G}(z) = (z\mathbf{S} - \mathbf{H}_M - \mathbf{\Sigma})^{-1},$$
(2)

where $\mathbf{S}$ and $\mathbf{\Sigma}$ are the overlap and self-energy matrices, respectively, and $\mathbf{H}_M$ is the molecular Hamiltonian. The self-energy matrix is defined by

$$\mathbf{\Sigma}(z) = \mathbf{V}_{ME}(z - \mathbf{H}_E)^{-1}\mathbf{V}_{EM},$$
(3)

where $\mathbf{V}_{ME}$ is the matrix specifying the coupling between the molecule and the electrodes, whereas

$\mathbf{H}_E$ is the Hamiltonian matrix for the electrodes. $\mathbf{\Delta}_L$ is related to the self-energy by

$$\mathbf{\Delta}_L = -\frac{1}{\pi}\text{Im}(\mathbf{\Sigma}_L)$$
(4)

and a similar expression holds for the right electrode. The trace in the integral in Eq. (1) is taken over all molecular orbitals.

At zero bias, the common Fermi energy of the system electrode–molecule–electrode is determined by a subtle balance of charge transfer at the interface. At finite bias, the voltage dependence of the contact spectral density can be approximated as a shift in the electrochemical potential that displaces the Fermi levels of the electrodes without changing the electronic structure of the contacts. The important voltage dependence, the one that determines the occurrence of the rectification phenomenon, is that of the reduced Green function of Eq. (2) corresponding to the molecular Hamiltonian modified by the self-energy.

2.1. Rectification

Once equilibrium has been established at zero bias, increasing the voltage may or may not provoke an additional distortion in the energy spectrum. If the voltage drop occurs completely at the molecule–electrode interfaces, the electronic structure of the molecule is only slightly perturbed and it is a good approximation to neglect the voltage dependence of the Green function. Under such conditions, we will show that rectification will not occur regardless of asymmetries either in the molecular structure or in the contacts. On the other hand, if the voltage drop occurs, at least partially, through the molecular region, rectification will be observed if there is asymmetry, either in the molecular geometry or in the contacts.

In the absence of the molecular bridge, the spatial profile of the potential is a ramp as determined by Poisson equation. There exists accumulating evidence that molecules in the junction gap behave to a large extent as a polarizable dielectric, hence the primary effect of the bias is to produce a charge redistribution of opposite sign to the voltage difference [12,13]. This redistribution of the charge density causes, to a first approximation,

important changes in the potential profile, that adopts a sigmoid-like shape where the potential drops primarily at the interface.

A simple model to represent the potential drop, which is assumed to occur only at the interfaces, consists in introducing a voltage division factor η, to take into account asymmetries due to the nature of the contacts. For a total voltage bias V the drops at the two interfaces would be ηeV and $(1 - \eta)eV$, respectively. For $\eta = 1/2$ the symmetric case is recovered. Previous analysis has focused on this situation [11,14].

A key element in understanding the rectification behavior in the coherent tunneling regime is that for electrified molecular interfaces the voltage division factors may need essentially to be exchanged between the two interfaces under inversion of the voltage bias. This is a counterintuitive behavior for interfaces with constant geometry (effectively, constant resistance) because then the division factor is only a function of the geometry and remains invariant under bias inversion. The two different profiles are schematically represented in Fig. 1. For adsorbed molecules, charge transfer creates a dipolar structure that is very sensitive to the local electrode potential, thereby inducing a variable interfacial resistance due to adjustments in the equilibrium distance between the molecule and the electrode upon biasing. A theoretical analysis of realistic tip-sample geometries in STM-imaging of

adsorbed molecules shows exactly this kind of behavior [15]. Moreover, the series of experiments in which bonds are broken by STM tips [16–19] shows the ability of the local fields at tip junctions to modify bond lengths. Without a formal proof, and based on these physical considerations, we argue that upon inversion of the bias, besides changing V into $-V$, it is appropriate (because of geometric reorganization in molecular junctions) to interchange $1 - \eta$ and η.

For the sake of simplicity, we use a simple one-dimensional tight-binding picture to show the mathematical expressions that support our explanation, but the conclusions are quite general. For this case, and taking into account the effect of the division factor, Eq. (1) reduces to

$$I(V) = \frac{2e}{h} \int_{E_F - \eta eV}^{E_F + (1-\eta)eV} d\epsilon |G_{1N}(\epsilon, V)|^2 \Delta_1$$
$$\times (\epsilon + \eta eV)\Delta_N(\epsilon - (1 - \eta)eV). \quad (5)$$

This equation can be written, using an obvious notation, as

$$I(V) = \frac{2e}{h} \int_{E_F - \eta eV}^{E_F + (1-\eta)eV} d\epsilon T(\epsilon, V), \quad (6)$$

where $T(\epsilon, V)$ is a dimensionless transmission function describing the effective coupling between the electrodes mediated by the molecular bridge.

Under voltage inversion (6) becomes

$$I(-V) = \frac{2e}{h} \int_{E_F - (1-\eta)(-eV)}^{E_F + (\eta)(-eV)} d\epsilon T(\epsilon, -V)$$
$$= \frac{2e}{h} \int_{E_F + (1-\eta)eV}^{E_F - (\eta)eV} d\epsilon T(\epsilon, -V)$$
$$= -\frac{2e}{h} \int_{E_F - \eta eV}^{E_F + (1-\eta)eV} d\epsilon T(\epsilon, -V), \quad (7)$$

where it has been assumed that the functional dependence of Δ_1 and Δ_N on the voltage is the same. This assumption is certainly true within Newns model [20], where voltage dependence arises because of the shift in the Fermi energies of the contacts. It may break down in more realistic models that take into account voltage-induced charge transfer or band bending in semi-conductor contacts.
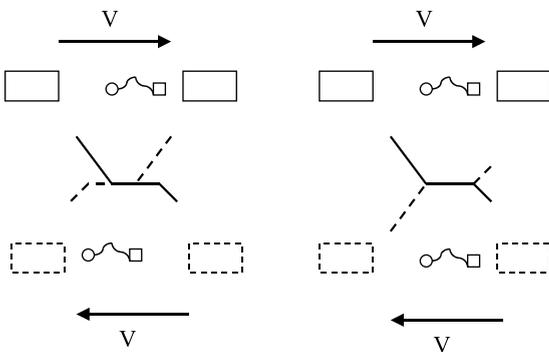
Fig. 1. Schematic structure of molecular wires and associated voltage profiles, in a tunneling junction. The upper sketch shows the geometry for forward bias corresponding to the solid line voltage profile in the middle. The reverse bias geometry and profile are shown with dashed lines. The left (right) side corresponds to a non-rectifying (rectifying) junction.

The question of the symmetry under inversion of the $I(V)$ curve now reduces to examining the symmetry of the function $T(\epsilon, V)$. The symmetry property $I(V) = -I(-V)$ means that there will be no rectification: changing sign of the applied voltage simply changes sign, not magnitude, of the conductance $g(V) = \partial I(V)/\partial V$.

In the case we are considering, the Hamiltonian of the molecule is voltage independent. The only source of bias dependence in $T(\epsilon, V)$ is the self energy, that is a property of the metal contacts. In simple models that consider semi-elliptical band shapes for the metal, as in Newns theory [20], the self-energy is a symmetric function of V, $\Sigma(\epsilon, -V) = \Sigma(\epsilon, V)$. For voltage-symmetric self-energies, one has, $I(-V) = I(V)$, and there will be no rectification.

3. Conclusions

The symmetry arguments show that, even for different contacts leading to arbitrary voltage division factors, if the voltage drops entirely at the interfaces rectification should be absent in coherent molecular junctions.

Our finding provides a rationale to the search for rectifying unions. These must create asymmetric voltage drops across the molecular bridge. Conditions that could favor such a behavior are linked to asymmetries in the molecule, local weak links, the presence of strongly electronegative or electropositive substituents, and nearly ohmic contacts.

The dynamical geometric reorganization for electrified interfaces would prohibit rectifying behavior in molecular tunneling junctions unless some voltage drop occurs along the molecule.

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