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Molecular Rectification through Electric Field Induced Conformational Changes

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The idea of employing single molecules as ultimate miniaturized components of electronic circuits, which sounded provocative in the 1960's[1] and was a matter of purely theoretical speculation in the 1970's,[2] has become, in the past decade, one of the principal motifs in the research of many groups.[3]

Although hypotheses on the future design of nanocircuits are probably premature, it is clear that the realization of molecular rectifiers is a necessary step for the entrance of chemistry in the world of electronics. First attempts[4] to obtain molecular rectification were driven by a theoretical proposal of 1974,[2] where it was noted that a molecule, containing a donor (D) with low ionization potential and an acceptor (A) with high electron affinity, separated by a saturated bridge (B), may act as a rectifier when located between two metallic leads. The molecular rectifying behavior was proven for the first time for the $C_{16}H_{33}Q$-3CNQ molecule assembled in ordered Z-type multilayers sandwiched between Pt and Ag electrodes.[4] Metzger improved this approach using different electrodes,[5] showing that the rectification was due to the molecule itself and not only to the metallic interface. Rectification was demonstrated also in several few molecules experiments.[6−8]

Recent improvements in the theory of electrical conduction through molecules[9] allowed for a fairly good understanding of the rectification observed in these cases.[10] At low bias, the Fermi energies of the two electrodes are not in resonance with any molecular level. With the increasing external bias, molecular energy levels and Fermi energies of the two electrodes move with respect to each other, and when they go into resonance a strong increase in current is observed, due to the enhanced effective coupling between the metal leads. For asymmetric interfaces (the D−B−A molecules maximize this effect), the resonance for positive and negative potentials occurs at a very different bias, and the resulting *I*/*V* curve is strongly asymmetric. However, rectification based on this principle is rare, as discussed in ref 11, and presents several inconveniences. In resonance condition, the molecule is charged and may undergo irreversible reactions. Moreover, resonance causes an enhancement of the inelastic contribution to the electron transfer,[12] resulting in the heating of the molecule and perhaps its decomposition. In Metzger's experiments, in fact, the current decreases each time the *I*/*V* curve is measured, revealing an irreversible damaging of the monolayer.

Nuclear motions of the molecule, causing the incoherent contribution to the coupling, have been often considered an unpleasant complication of the system, and theoretical and experimental research in the field have been focused so far in the study of molecules without flexible nuclear degrees of freedom. We show here that rectification may be realized in off resonance regimes by exploiting the conformational change in the molecule driven by the external electric field. The conductance switching in single molecules due to thermal conformational changes was recently observed by Donhouser et al.[13] W. Ho and co-workers observed, in several STM measurements, conformational changes induced both by inelastic tunneling[14a] and by the electric field[14b] altering the relative stability of the adsorbate conformations.

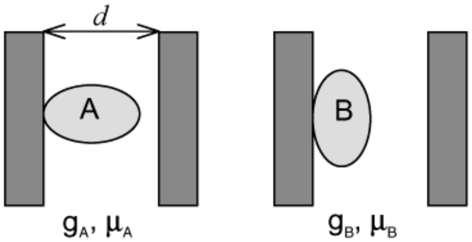

Figure 1. A schematic of a molecule sandwiched between two electrodes, bonded to one and stable in two conformations with sufficiently different conductance (*g*) and dipole moment (μ).

We will describe a very simple model to define molecular junctions that may lead to off resonance rectification. We consider a number of molecules, located between two electrodes, that may each assume two conformations of comparable stability (say **A** and **B**). In general, the conductance of these two conformations ($g_{\mathbf{A}}$ and $g_{\mathbf{B}}$) will be different, and not infrequently the difference is very large. Conductance is extremely sensitive to geometrical changes mainly because the electronic coupling between the molecule and the leads generally decays exponentially with the molecule−electrode distance. Figure 1 depicts a typical case where a large difference in conductance may be observed, corresponding to a molecule, chemically bonded to an electrode, which may lie horizontally or vertically with respect to the metal surface (compare for example the experiment described in ref 14a).

If the molecule contains polar bonds, a change in dipole moment $\Delta\boldsymbol{\mu} = \boldsymbol{\mu}_{\mathbf{A}} - \boldsymbol{\mu}_{\mathbf{B}}$ is expected when going from one conformation to the other. Indicating with $\Delta U = U_{\mathbf{A}} - U_{\mathbf{B}}$ the difference in energy of the two conformers at zero voltage, we can easily express the ratio between the populations ($P_{\mathbf{A}}$, $P_{\mathbf{B}}$) of the two conformers in the presence of an external electric field **E** at temperature *T*:

$$P_{\mathbf{A}}/P_{\mathbf{B}} = \exp(-(\Delta U - \Delta\boldsymbol{\mu}\mathbf{E})/k_BT) \qquad (1)$$

$$P_{\mathbf{A}} + P_{\mathbf{B}} = 1 \qquad (2)$$

Polarization effects can be neglected if $\Delta\mu$ is sufficiently large.[15] For planar electrodes perpendicular to the *z* axis $\Delta\boldsymbol{\mu}\mathbf{E} = \Delta\mu_z V/d$, indicating with *V* and *d* the electric potential and the distance between the electrodes, we have:

$$P_{\mathbf{A}}/P_{\mathbf{B}} = \exp(\alpha V + \beta) \qquad (3)$$

$$\alpha = \Delta\mu_z/dk_BT; \quad \beta = -\Delta U/k_BT \qquad (4)$$

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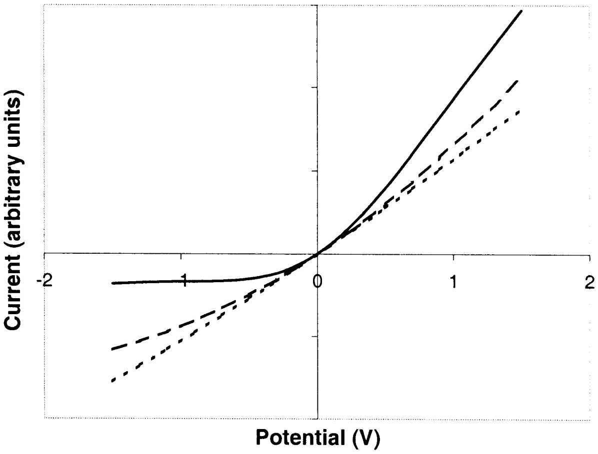

Figure 2. $I(V)$ curve calculated from eq 6 with parameters $g_B/g_A = 0.1$, $\beta = 0$, $\alpha = 2.5\ V^{-1}$ (solid line), $\alpha = 0.5\ V^{-1}$ (dashed line), and $\alpha = 0.1$ (dotted line). Conformation **A** is more populated at positive bias.

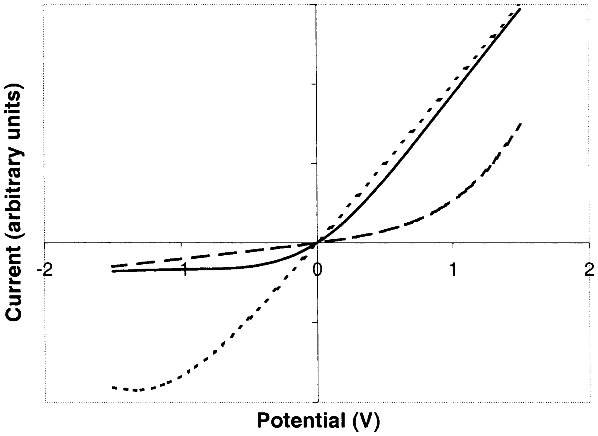

Figure 3. $I(V)$ curve calculated from eq 6 with parameters $g_B/g_A = 0.1$, $\alpha = 2.5\ V^{-1}$, $\beta = 0$ (solid line), $\beta = -4$ (dashed line), and $\beta = 4$ (dotted line). For such parameters, **A** and **B** populations are equal at 0 V (solid line), 1.6 V (dashed line), and −1.6 V (dotted line).

For small voltage (typically <0.5 V), a linear relation between current and voltage for the two conformers may be assumed[16] ($I_A = g_A V$, $I_B = g_B V$), and the total current I is essentially a linear combination of the two contributions:

$$I = P_A I_A + P_B I_B = g_A(P_A + g_B/g_A P_B)V \tag{5}$$

$$I = g_A\left(\frac{1 + \exp(-\alpha V - \beta)g_B/g_A}{1 + \exp(-\alpha V - \beta)}\right)V \tag{6}$$

The $I(V)$ shape in this model is then determined simply by the g_B/g_A ratio and by the α and β parameters which in turn depend on the molecular characteristics and on the temperature. Some illustrative $I(V)$ curves are shown by Figures 2 and 3.

Figure 2 displays the $I(V)$ curve for several values of α with $\beta = 0$ (the case of exactly isoenergetic conformations **A** and **B**), and the g_B/g_A ratio is fixed to 0.1. Strong rectification is shown by the model curve with $\alpha = 2.5\ V^{-1}$. This corresponds for example to the reasonable values of $d = 10$ Å, $\Delta\mu_z = 3.2$ D, and $T = 300$ K. The α parameter measures the tendency of the molecule to change conformation upon an applied external field. Rectification is improved by increasing $|\alpha|$, that is, either increasing $|\Delta\mu_z|$ or decreasing the temperature. For sufficiently high $|\alpha|$, the rectification properties are entirely determined by the g_B/g_A ratio.

The effect of the different energy of the two conformations at zero bias is analyzed in Figure 3, where parameter β is changed with $\alpha = 2.5$ and $g_B/g_A = 0.1$. The effect of increasing β is to reduce the rectification around 0 V, moving the nonlinear region toward positive ($\beta < 0$) or negative ($\beta > 0$) potential regions. For the voltage range we are interested in, rectification may be observed for $|\beta| < 2$, corresponding, at $T = 300$ K, to a difference in the two conformations' energy of about 1 kcal/mol.

These results show that is possible to prepare a rectifying junction based on field induced conformational change. Equation 6 can be used to determine whether a given molecule is likely to show a rectifying behavior. Simulations on realistic systems are subject to current investigation. Particularly promising molecules for this purpose seem to be characterized by strongly polar groups, which rearrange in space by rotation around σ bonds. Note that the molecule must be anchored (e.g., chemisorbed) to at least one of the electrodes to preserve the junction asymmetry.

This model is valid if a fast thermal equilibrium between conformations **A** and **B** is assumed. Consequently, such a device must operate on a time scale longer than the interconversion rate between the two isomers. For devices containing few or just one molecule, random switching would cause an increased noise, a problem, however, shared with any kind of molecular scale device.

It is worthwhile to point out, in conclusion, that molecular electronics is something more than conventional electronics done with molecules. Nuclear degrees of freedom, in fact, give to molecular devices substantially different properties from the solid-state analogues, and many solutions for new component design[17] might exploit these properties instead of reproducing on a smaller scale the ideas of conventional electronics.

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