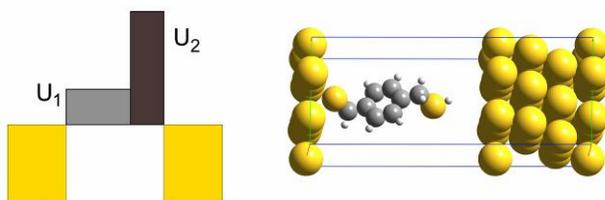


Exploring the Performance of Molecular Rectifiers: Limitations and Factors Affecting Molecular Rectification

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ABSTRACT. There has been significant work investigating the use of molecules as nanoscale rectifiers in so-called ‘molecular electronics’. However, less attention has been paid to optimizing the design parameters of molecular rectifiers or to their inherent limitations. Here we use a barrier tunneling model to examine the degree of rectification that can be achieved and to provide insight for the design and development of molecules with optimum rectification responses.

The original Aviram and Ratner¹ mechanism for rectification by a molecule containing acceptor and donor moieties separated by a sigma-bonded bridge described a three-stage electron tunneling process: cathode to acceptor, acceptor to donor, and donor to anode. Due to the line-up between the acceptor and donor levels, transfer by tunneling would be strongly favored in this forward bias direction. Rectification of current was therefore predicted. Based on this proposal, numerous molecular rectifiers have subsequently been investigated.² Metzger *et al.*³ were able to observe a degree of rectification through a molecular monolayer with an intramolecular tunneling mechanism, similar to the Aviram-Ratner proposal. A number of important experimental and theoretical methods have been developed to probe the electronic characteristics of these devices³⁻¹⁶ not least because they offer the possibility for very densely packed circuitry. For example, Green *et al.* recently reported¹⁷ a 160-kilobit molecular memory device patterned at an unprecedented 10^{11} bits /cm² However it appears that little attention has been paid to the probable limitations of molecular electronic devices. Here we develop a simple model to systematically explore the performance of a molecular rectifier. We apply two methods: an analytical solution to model a double tunneling barrier (which we develop here), and numerical computations based on the well-known Wentzel-Kramers-Brillouin (WKB) approximation. A surprising and significant result is that there appears to be a remarkably low limit to the rectification possible over a single molecule, even under the rather ideal conditions modeled.

The key approximation of our model is to replace the molecule spanning the electrodes by a tunnel barrier. Calculation of the conductance of the molecule is then straightforward by solving the quantum mechanical problem of an electron tunneling through this barrier. Figure 1 shows conceptually how the molecule may be modeled by one or more barriers. In this case we have a situation corresponding to a scanning tunneling spectroscopy experiment where the molecule (1,4-benzenedimethanethiol in this example) is attached to one electrode and there is a vacuum gap to the other electrode, Figure 1b. A density functional theory (DFT) calculation of the electronic structure of this system, made using the SIESTA^{18, 19} code, is shown in Figure 1a. The local density of states (LDOS) is plotted as a function of

the energy relative to the Fermi level (y -axis) and the distance along the transport direction (x -axis), after integration over the transverse directions. Periodic boundary conditions are employed in all dimensions and the unit cell is indicated in Figure 1b. The sulfur atom is adsorbed 0.2 nm from the left electrode after cleavage of an H-S bond. The hydrogen on the right sulfur atom is left in place with a 0.5 nm distance between the sulfur and right electrode. This produces an asymmetric double barrier. The dark lines in the molecular region show areas of high density of states, and can be identified with molecular energy levels. This is clarified in Figure 1c, which shows the corresponding projected density of states (PDOS) onto the molecular orbitals. Conceptually this shows how one may model the molecule by a ‘tunneling barrier’, thereby reducing the complexity of the problem to one involving only a few scalar parameters (which define the barrier ‘shape’). In the example given, the symmetric molecule is separated from one electrode by a vacuum gap, giving rise to a double barrier. Equally, the double barrier may be used to model an asymmetric molecule, with electron donating and accepting moieties at opposite ends and no vacuum gap.

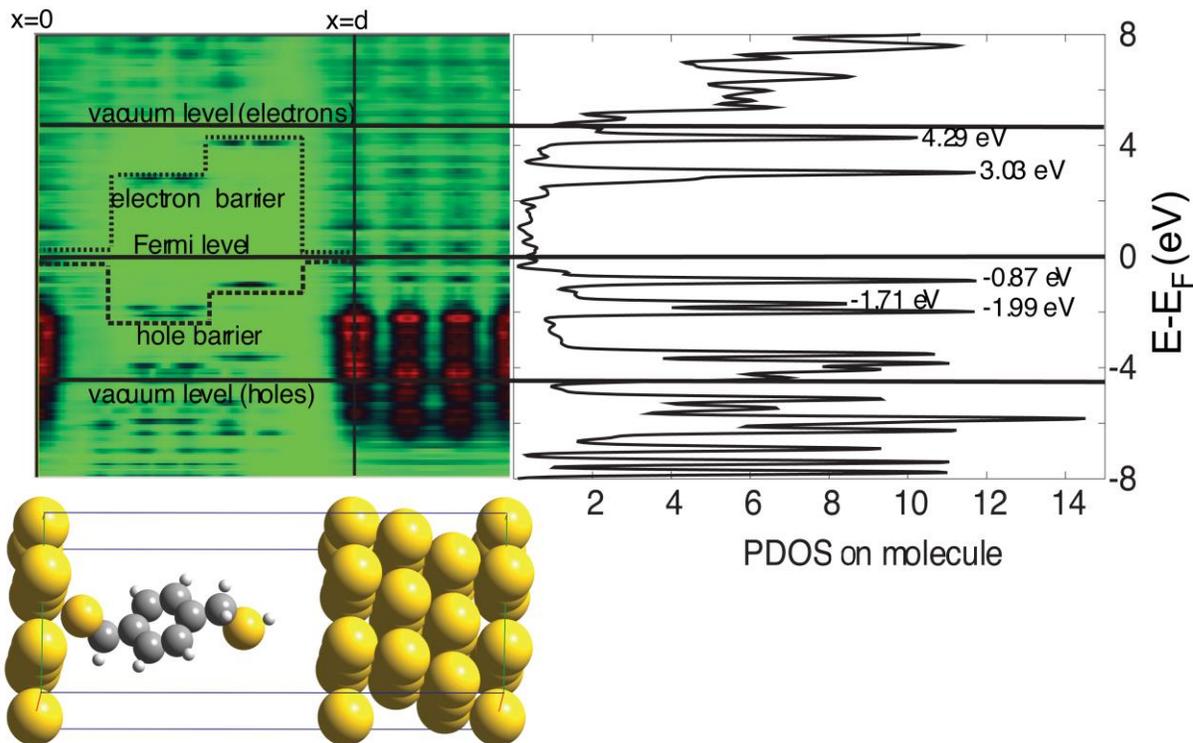


Figure 1. Density of states and corresponding asymmetric double barrier, (a) local density of states for 1,4-benzenedimethanethiol molecule between Au(111) electrodes, calculated with the SIESTA DFT code, (b) schematic diagram showing the electrode-molecule-gap-electrode system, (c) corresponding density of states projected onto the basis orbitals of the molecule. The molecular energy levels closest to the Fermi level can clearly be identified.

The double rectangular barrier system described in Figure 1 can be solved exactly using the time-independent Schrödinger equation (see Supporting Information) and the solution reveals interesting rectifying properties. We propose that the properties derived from this model for a double barrier system can be used to predict the optimal barrier-height and -length ratios for molecular rectification. This exploration of the parameter space provides a useful framework for developing molecules that may exhibit desirable rectification and current-voltage properties. We have also solved the tunneling problem using the WKB approach. This provides a method for finding an approximate solution to the Schrödinger equation, and can be applied to barriers of arbitrary shape. An understanding of the effect of

systematically varying the nature of the molecular barrier can then be achieved, which is not feasible when using more complex theories.

More specifically, the double barrier is defined by barrier-heights, U_{o1} and U_{o2} , and lengths, d_1 and d_2 , respectively (see Figure 2). These variables define the parameter-space, U_{o1}/U_{o2} and d_1/d_2 , which can be mapped for a range of bias voltages. Upon application of a forward or reverse bias, the double barrier model adopts a trapezoidal configuration and electrons tunnel from left to right, and right to left, respectively — as shown in Figure 1 of the Supporting Information. This produces the necessary asymmetric tunneling, which in turn results in current rectification. Hence, by “tuning” the barrier-heights and lengths, the set of parameters that produces the optimum rectification can be determined.

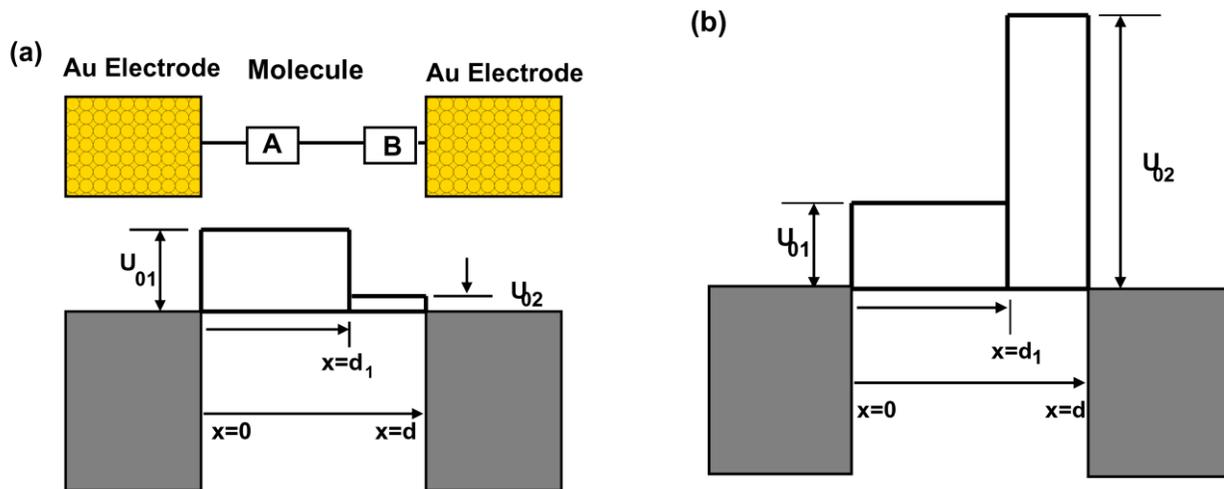


Figure 2. Double barrier system for a single molecule: (a) (top) Au electrodes with a single molecule consisting of components A and B. (below) Example of barrier-height and -lengths for $U_{o2}/U_{o1} < 1$ with zero applied bias. In this configuration, A corresponds to an electron donor group and B to an electron acceptor. (b) Example of barrier-height and -lengths for $U_{o2}/U_{o1} > 1$ in zero bias configuration.

During the analysis of the double barrier system U_{o1} and d_1 remained fixed, while U_{o2} and d_2 were varied. The tunneling current as a function of the applied bias voltage, V_b (or potential, $U_b=e V_b$) reduces to^{14, 20}

$$I(V_b | U_{oj}, d_j) = \frac{2e}{\hbar} \int_0^{eV_b} dE \Pr(E, eV_b | U_{oj}, d_j), \quad \forall j = 1, 2, \dots, N \quad (1)$$

where a constant density of states and zero temperature is assumed. In Eq.1,

$\Pr(E, eV_b | U_{oj}, d_j)$ is the transmission probability for an N -trapezoidal barrier. (The transmission probability function is determined from the exact solution of time-independent Schrödinger equation. The full derivation for this function of a multi-trapezoidal ($N \geq 2$) barrier system is given in Supporting Information text.) We apply Eq. 1 to a double barrier ($N=2$) system using a bias voltage, V_b , range of $\pm 2V$. Current rectification, $|I_r/I_f|$, was also evaluated over a range of bias voltage corresponding to $V_b = \pm 2V$, where I_r and I_f are the reverse and forward tunneling currents, respectively. The parameter space is defined in terms of the barrier-height ratio, $U_{o2}/U_{o1} \in [10^{-3}, 10]$ and barrier-length ratio $d_2/d_1 \in [10^{-1}, 1]$. The first barrier-height and -length were fixed at $U_{o1} = 3.0\text{eV}$ and $d_1 = 0.9\text{nm}$, a typical molecular length¹⁴, while the second barrier-height, U_{o2} , and -length, d_2 , were varied over specified ranges. (The calculations have also been repeated for $U_{o1} = U_{Au} = 5.13\text{eV}$ and -length, $d_1 = 0.9\text{nm}$, see Supporting Information text, Table 2 and Figures 11 to 17.) The values for U_{o1} were chosen to mimic the typical barrier-heights^{15, 16}.

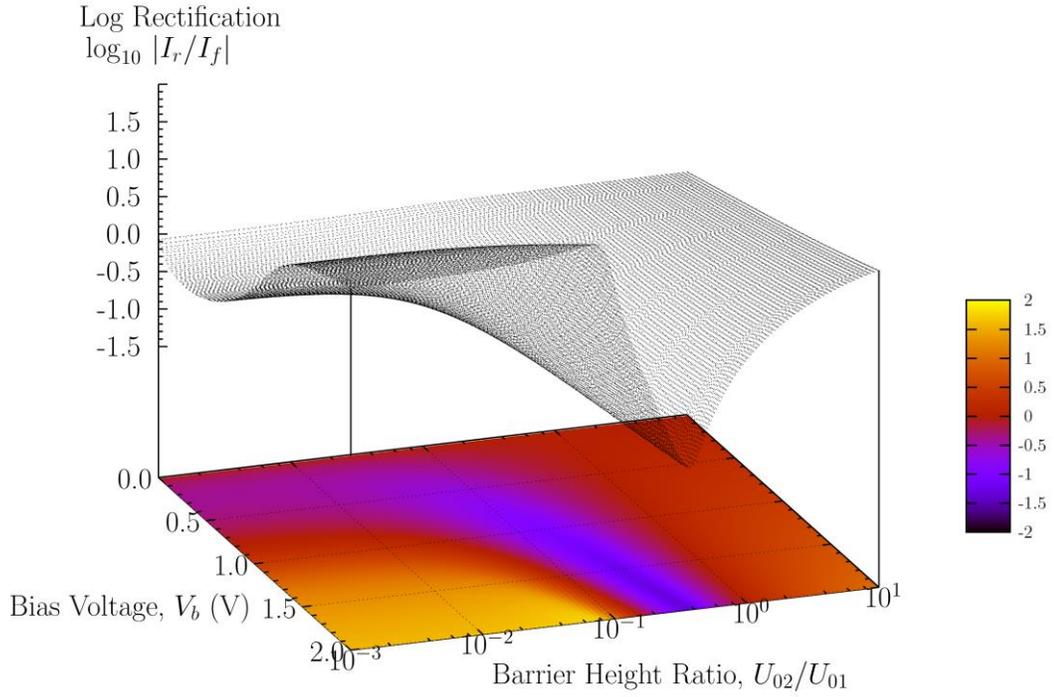


Figure 3. Rectification of double barrier system (z -axis) for barrier-height ratios, U_{02}/U_{01} (x -axis), and bias voltage V_b (y -axis). Calculations carried out for $U_{01}=3.0\text{eV}$ and $d_1/d_2=1$, where $d_1=0.9\text{ nm}$. Note that the z -axis and palette is shown on a \log_{10} -scale.

Figure 3 shows the parameter-space for the double-barrier model for a range of U_{02}/U_{01} , and V_b values for $d_2/d_1=1$ and $V_b < 2\text{ V}$. For small bias voltages, and over the U_{02}/U_{01} -range, the rectification ranges from ~ 0.32 to ~ 3.2 (or ± 0.5 on the \log_{10} z -scale). As V_b increases, the rectification increases considerably to ~ 50 for $U_{02}/U_{01} \leq 10^{-2}$, while it inverts in direction to about 0.045 for $0.1 < U_{02}/U_{01} < 1$. These regions reveal some interesting properties that can be explored further if the rectification is evaluated at a specific bias voltage.

For example, Figure 4 shows the results of the simulations over a range of U_{02}/U_{01} and d_2/d_1 values. As expected, for equal barrier-heights ($U_{02}/U_{01} = 1$) no rectification occurs as the system is acting as a single symmetrical barrier of total length $d = d_1 + d_2$. Also in the limit of $U_{02}/U_{01} \rightarrow 0$ and $d_2/d_1 \rightarrow 0$, the rectifying behavior disappears as the double barrier reduces to a single barrier. However, there is a

‘sweet spot’ for rectification in the region where $0.1 < U_{o2}/U_{o1} < 1$. (We note that the lack of symmetry about $U_{o2}/U_{o1} = 1$ (vertical line) is a consequence of the calculation method, since U_{o1} remains fixed, while U_{o2} is varied — see Figure 2). We have also explored the same system using the WKB method, which yields similar results – see Supporting Information, Figure 9. This confirms that the sweet spot we describe is not an artifact of our analytical solution.

In Figures 3 and 4 for the region $\sim 0.1 \leq U_{o2}/U_{o1} \leq 1$, the reverse bias current dominates the forward bias current and the rectification produced is $|I_r/I_f| \sim 10$, which is marginal considering the large range of barrier-height and -length ratios. In the range of barrier-height ratios $U_{o2}/U_{o1} = 1.0 \pm 0.2$, negligible rectification is observed indicating that only molecules with a substantial difference between U_{o1} and U_{o2} will produce sizeable rectification.

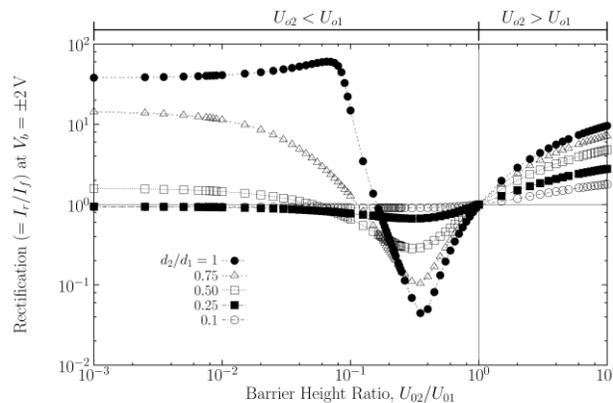


Figure 4. Rectification for double barrier system in terms of barrier-height ratios, U_{o2}/U_{o1} , for a range of barrier-length ratios, d_2/d_1 . The rectification was evaluated at $V_b = \pm 2V$ and $U_{o1} = 3$ eV.

The region $0.1 < U_{o2}/U_{o1} < 1$ reveals some interesting properties. Firstly, minima exist for $|I_r/I_f|$ of the d_2/d_1 values investigated. The minima effectively define *resonances* in the rectification for specific U_{o2}/U_{o1} and d_2/d_1 values. Furthermore, this range defines the ‘sweet spot’ or optimum rectification. Interestingly, the forward current dominates the reverse current at these resonances, i.e. $|I_r/I_f| < 1$. The optimum rectification for this set of parameters is $|I_r/I_f| \approx 0.045$ for $U_{o2}/U_{o1} = 0.35$ and $d_2/d_1 = 1.00$, corresponding to a forward bias current gain of ~ 22 over reverse bias current. The data curves shown in

Figure 2, especially $d_2/d_1 = 1.00$, are clear indications of an optimum matching between the barrier-height and length, and result in tunneling currents that could be technologically useful. The rectification resonance drops off by a factor of ~ 2 with a 25% reduction in d_2 relative to d_1 , from $|I_r/I_f| \approx 0.045$ for $U_{o2}/U_{o1} = 0.35$ to $|I_r/I_f| \approx 0.045$ to $|I_r/I_f| \approx 0.104$. This suggests that the matching of the barrier-lengths is an important factor in single molecule rectification. As d_2/d_1 decreases further, $|I_r/I_f|$ approaches unity as expected, and the system approaches a single-barrier model.

Another feature of this region is the range of barrier-height ratios about the optimum values that produce significant rectification, $|I_r/I_f| \leq 0.1$. The range $U_{o2}/U_{o1} \approx 0.2$ to 0.55 provides a window in which some useful rectification could be achieved in practice. (Also see Supporting Information, Tables 1 and 2, and Figures 2, 9 and 11.) The rectification in this region also produces nonlinearities in the $I(V_b)$ and dI/dV_b -plots, as shown in Figure 5a and 5b for specified d_2/d_1 -values at the rectification resonance. In the case of $d_2/d_1 = 1.00, 0.75$ the nonlinearity is noticeably stronger for the forward relative to the reverse bias current. In particular, dI/dV_b increases considerably towards 2V compared to the reverse bias case. These results suggest that differential current gain can be produced for these sets of parameters — see Supporting Information text.

In the region $0.001 < U_{o2}/U_{o1} < 0.1$ and for $d_2/d_1 = 0.25, 0.10$, we notice $|I_r/I_f| \rightarrow 1$, but the rectification ostensibly increases as d_2/d_1 increases. Also, it is dominated by reverse current, i.e. $I_r/I_f > 1$. However, caution should be exercised in interpretation of this region as $U_b \gg U_{o2}$ and non-tunneling conduction through U_{o2} becomes probable. The extent of the rectification in this region of Figure 4 is therefore unreliable, since in practice conduction and thermal effects will overwhelm tunneling when $U_b \gg U_{o2}$. There is also significant rectification in the region where $U_{o2}/U_{o1} > 1$. However, this also cannot be exploited for devices because the overall conductance of the corresponding systems is extremely low on account of the significant barrier that they present to tunneling.

Finally, we note that, for $U_{o2} < U_{o1}$ there is no single point that the rectification curves pass through and “flip” from $|I_r/I_f| < 1$ to $|I_r/I_f| > 1$, as is the case at $U_{o2}/U_{o1} = 1$. This is essentially due to the difference in

barrier lengths. The rectification for $d_2/d_1=1.00, 0.75, 0.5$ plateau to $|I_r/I_f| \approx 40, 16$ and ~ 1.5 , at $U_{o2}/U_{o1} \approx 0.02, U_{o2}/U_{o1} \sim 0.01$ and $U_{o2}/U_{o1} \sim 0.01$, respectively.

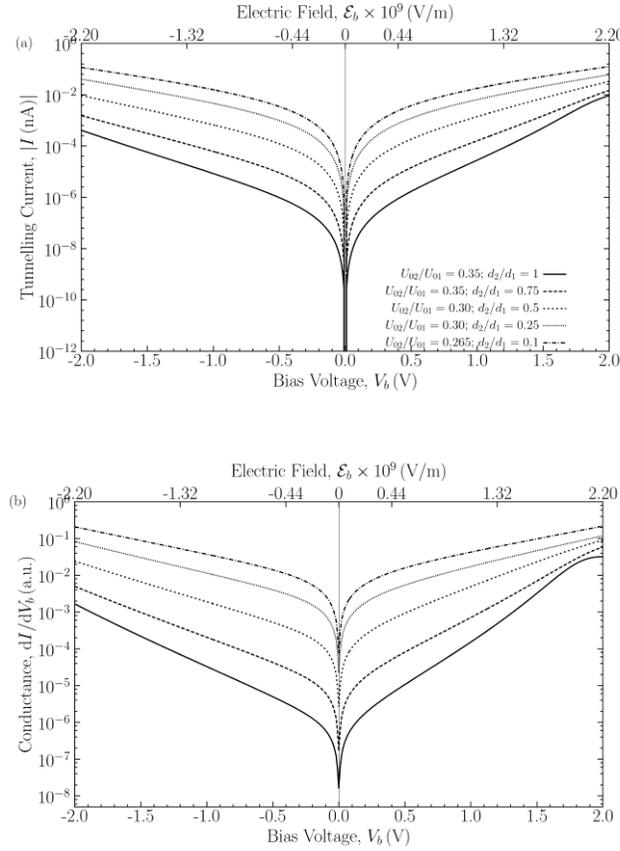


Figure 5. Current-voltage and conductance-voltage characteristics at optimum rectification: (a) Current-voltage for the resonance in rectification at the barrier-heights and -lengths corresponding to the minima in Figure 4. (b) The corresponding conductance-voltage characteristic.

The results given in Figures 3 and 4 define the limitation on the response of a single molecular rectifier. That is, by parameterising the double barrier model in terms of U_{o2}/U_{o1} , we have clearly demonstrated that the maximum extent of rectification is limited to less than 100, even under the ideal conditions assumed by the models. This rectification is significantly lower than that displayed by present silicon and solid-state devices, which usually have rectification ratios of in excess of 1×10^5 . A high rectification ratio is desirable or even essential in order to minimize leakage of current under reverse

bias conditions. The difference in capability between a molecular electronics junction and a solid state p-n junction is due to the fact that they operate on rather different principles. In broad summary, current flow through a p-n junction at relatively low bias can be explained without recourse to tunnel barriers. It is controlled by the movement of charge in the depletion layer between the two types of material and by a step-like configuration of Fermi levels. As a first approximation, the junction is fully conductive in the forward bias direction but current cannot even flow when it is reverse biased, except as a result of thermal activation. This is not the case for a molecular electronics diode. In this case, there is a physically-defined tunnel barrier which impedes the passage of charge in both directions. The shape of this barrier is primarily determined by the size and structure of the organic molecule making up the barrier, while movement of charge onto or off the molecule and direction of bias have a less pronounced effect. This explains why less rectification is possible. Given these factors and the limitations demonstrated above, we submit that it is unreasonable to expect that single molecule rectifiers could match the performance of their solid-state counterparts.

In conclusion, examination of rectification described by a double barrier tunneling model shows that maximum rectification is approached as the barrier length ratio approaches an optimum value in the vicinity of $d_2/d_1 \approx 1$, and results in tunneling currents that are physically and technologically plausible. Furthermore, three rectification regimes have been identified based on the barrier-height ratio. For $U_{o2}/U_{o1} > 1$, rectification is small, $1 \leq |I_r/I_f| \leq 10$. For $U_{o2}/U_{o1} \leq 0.1$, rectification of $|I_r/I_f| \sim 40$ is indicated by the models, however an extreme barrier-height ratio is needed, which may be impractical, and in any case thermal and conductive effects may dominate and diminish any rectification. Promising behavior is observed in the region $0.1 < U_{o2}/U_{o1} < 1$; a forward bias gain of ~ 22 over reverse bias current can be achieved for a practical ratio of barrier-heights. On one hand, the exploration of the double barrier model in terms of U_{o2}/U_{o1} and d_2/d_1 parameter space is useful, as it provides insight for the design and development of molecules with optimum rectification responses. On the other hand, the results presented here demonstrate some fundamental limitations in the rectification responses of single molecules.

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Supporting Information Available. Derivation of the analytical expression for tunneling over a double barrier. Plots showing rectification possible for different barriers. Results from a numerical implementation of the WKB model for comparison to the analytical solution. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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