Are Asymmetric SAM-Induced Work Function Modifications Relevant for Real Molecular Rectifiers?

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Due to the fabrication architecture employed—flat s(substrate) versus sharp t(ip), chemisorption versus physisorption, etc—self assembled monolayers (SAMs) break the forward-backward invariance even in case of homometal molecular junctions; they induce changes in electrodes’ work function different from each other (ΔΦs ≠ ΔΦt). Because differences ΔΦs > ΔΦt translate into internal (Volta) electric fields often exceeding those created by the highest applied biases that real junctions can withstand, one may expect effects relevant for current rectification (RR). Here, they theoretically analyze asymmetric raw I-V data of benchmark junctions. Notwithstanding the large values |ΔΦs − ΔΦt| ≈ 1 eV, they found that the impact on rectification is completely negligible. So, the present theoretical results conveys a word of caution: not any effect that strongly breaks the inversion symmetry necessarily leads to current rectification. While their analysis indicates that per se unequal SAM-induced ΔΦ’s can hardly affect RR-values in general, it does not rule out an indirect effect for junctions where ΔΦ’s affect the charge transfer between the metal layer at interface and the bulk. From this perspective, using interposed narrow-band metal adlayers may be an appealing route toward improving rectification via interface engineering.

1. Introduction

Rational design approaches to achieving basic electronic functions of traditional circuit elements is an important goal for molecular electronics. Applied to the specific case of current rectification, an important sub-field of molecular electronics[1] envisaged in the present paper, attempting to fabricate molecular junctions wherein the forward–backward symmetry is broken appears to be the most straightforward route to be pursued.

The electrostatic coupling of the applied bias V to the eccentric located molecular orbital (MO) that dominates the charge transport and its formalization through the “lever”[11] or “potentiometer”[9,12,13] rule is a nice realization of this symmetry breaking. This turned out to be the mechanism at work in real molecular rectifiers.[7,13,21] In this case, the current rectification is the result of the bias-driven shift of the MO energy $\Delta \epsilon_0 + \epsilon_0(V)$ whose direction changes upon bias polarity reversal

$$\delta \epsilon_0(V) = \epsilon_0(V) - \epsilon_0 = \gamma eV$$ (1)

Used in conjunction with the single level model of charge transport, the bias-driven level shift scenario based on Equation (1) quantitatively explained transport data measured in benchmark molecular junctions exhibiting current–voltage (I–V) asymmetry.[14–16]

Being a possible realization of the broken forward–backward symmetry, the asymmetric coupling of the embedded molecules to the two (“substrate” s and “tip” t) electrodes of a molecular junction could, in principle, give rise to current rectification; this idea based on naive intuition was indeed very popular in the past. It could “in principle”, but not in practice; in line with earlier reports[11,12,17–20] we emphasized recently[21] that the impact of this asymmetric coupling on current rectification is completely negligible in real molecular junctions.

To the best of author’s knowledge, the mechanism that breaks the forward–backward symmetry discussed below has never been analyzed within model studies in conjunction with current rectification of molecular junctions. The effect we are going to examine occurs at the molecule-electrode interfaces. As experiments revealed, molecules adsorbed as a self assembled monolayer (SAM) on metal can make the work function at contact $\Phi = \Phi^0 + \Delta \Phi$ significantly different from that of the bulk metal $\Phi^0$.[22–27] $\Delta \Phi$-values obtained via ultraviolet photoelectron spectroscopy and scanning Kelvin probe microscopy for a variety of SAMs adsorbed on metals used in molecular junctions[15,16,24,28,29] revealed that $|\Delta \Phi|$ can exceed 1 eV.

Let us briefly exemplify why this can yield a broken forward–backward symmetry in real molecular junctions even in cases where both electrodes consist of the same metal ($\Phi^0 = \Phi^0 = \Phi^0$, homometal junctions) to which we restrict throughout for the sake of simplicity.

Let us first consider the scanning tunneling microscope (STM) architecture. Typical STM break junctions are fabricated and
Table 1. The model parameter values and their standard deviations obtained using MATHEMATICA 12.1.1 for fitting individual $I$–$V$ traces measured for Au/OPT3-Au and Au/Anth-S-Au CP AFM junctions (Figures 3a and 4a). The very large values of the coefficient of determination ($R^2$) demonstrate the very high quality of the data fitting with the aid of Equation (5); the unusually large number of digits presented here aims at showing how small are the differences between the $R^2$ and adjusted $R^2$ values, ruling thereby any over-fitting risk. Negative values of $\varepsilon_0$ mean HOMO- mediated conduction. See the main text for details.

| Quantity | Unit | Au/OPT3-Au | Au/Anth-S-Au |
|----------|------|------------|--------------|
| $t_{\text{ss}}$ | $T_{\text{ss}}$ | eV | 8.93$^{[65,66]}$ | 8.95$^{[65,66]}$ |
| $\varepsilon_0$ | eV | 35.8$^{[65,66]}$ | 35.8$^{[65,66]}$ |
| $\gamma$ | — | 0.069 ± 0.003 | 0.095 ± 0.003 |
| $r_s$ | meV | 289 ± 2 | 931 ± 7 |
| $r_t$ | meV | 71.3 ± 0.6 | 117 ± 1 |
| $\Delta \Phi_s$ | eV | $-1.01^{[15]}$ | $-1.06^{[14]}$ |
| $\Delta \Phi_t$ | eV | 0 | 0 |
| $R^2$ | — | 0.99783 | 0.99941 |
| Adjusted $R^2$ | — | 0.99775 | 0.99935 |

measured by repeated formation wherein the STM tip rapidly crushes toward and recoils from SAMs adsorbed on a metal substrate.$^{[30,31]}$ As said above, because the SAM is chemically adsorbed on the substrate, the associated value $\Delta \Phi$ is substantial. On the other hand, given the formation and the measurement technique, one can expect that the value corresponding to the tip is much smaller ($|\Delta \Phi_s| \gg |\Delta \Phi_t| \approx 0$).

An additional source of symmetry breaking can appear in molecular junctions fabricated under architectures—conducting probe atomic force microscope (CP-AFM) is one thereof—wherein the contact to the top electrode can (also) be physisorbed. Although Pauli forces can cause some reduction ($\Delta \Phi \neq 0$) of the metal work function at a physisorbed contact via the so-called pillow effect,$^{[32–36]}$ the corresponding modifications of the tip’s work function will certainly differ from those at the chemisorbed contact to the substrate electrode. By all means, based on data available for real molecular junctions,$^{[16]}$ it is hard to imagine pillow effect induced values of $\Delta \Phi$ as large as those for $\Delta \Phi_0$ shown in Table 1 for chemisorbed contacts.

In order to investigate the present effect, one can remind that experimental setups wherein the values of the work function at the two molecule-electrode interfaces substantially differ from each other ($\Phi_0 = \Phi + \Delta \Phi_0$, $\Phi \neq \Phi_0 = \Phi + \Delta \Phi_0$) resemble thin semiconducting films sandwiched between dissimilar electrodes extensively studied in the past.$^{[37–44]}$ If molecular junctions behaved as such conventional systems modeled as tunneling barriers, contributions of internal Volta biases $V_i$$^{[37–44]}$ $|eV_i| = |\Phi_0 - \Phi| = |(\Phi_0 + \Delta \Phi_0) - (\Phi_0 + \Phi_0)| = |\Delta \Phi_0 - \Delta \Phi_0| \approx 1$ eV, would need be considered along with the contribution of $V$ to express the MO shift (replace $V \rightarrow V + V_i$ in the right hand side of Equation (1)). Such $V_i$ are comparable with the largest applied biases $V$ that presently fabricated molecular junctions can withstand.

Nowadays multi-MOs NEGF+DFT transport calculations$^{[45–47]}$ for molecular junctions yielding a self-consistent electronic structure at given bias and an overall account of electrostatic effects can routinely be carried out. So, whether a description based on a single level model (like that we are going to employ below) is legitimate, is a question to be briefly addressed below.

Now, let us first note that, when supplemented with accurate ab initio quantum chemical calculations using many-body methods—for example, coupled-cluster (CC) flavors,$^{[48–51]}$ algebraic diagrammatic constructions,$^{[52–54]}$ and outer valence Green’s functions$^{[55,56]}$—that accurately account for (strong) electron correlations, the single level model succeeded to quantitatively explain an impressive body of experimental transport and transport-related data measured in nanojunctions fabricated with various electrodes (Ag, Au, Pt) and various molecules (like oligophenylenes mono- and dithiols,$^{[15,28]}$ alkyl$^{[36]}$ and substituted mono- and dithiols,$^{[57]}$ and oligophenylenedimethanethiols$^{[58]}$).

More importantly, it is physical reality that the $I$–$V$ curves measured in the vast majority of the molecular junctions do have shapes not notably differing from those depicted in Figures 3a and 4a. This matter of fact, remarkably formalized in the law of corresponding states (LCS)$^{[59]}$—demonstrated to hold in benchmark classes of molecular junctions qualitatively different from each other, robust against inherent stochastic fluctuations, large variability of contact binding (chemi- or physisorption), geometry (atop, bridge, or hollow), different metallic electrodes (Ag, Au, Pt) architectures of fabrication,$^{[37,39]}$ and even quantum interference$^{[28]}$—unambiguously points toward a universal transport behavior. But a universal behavior would be extremely unlikely if several MOs (characterized by MO-specific couplings to electrodes) gave significant contributions to the charge transport. In this vein, the LCS appears to strongly support the idea that the single level description is rather general and justifies this theoretical framework, especially in studies (like the present one) aiming at gaining conceptual insight into effects which were never considered before.

2. Description of the Model

Previous approaches of the charge transport based on a single conduction channel considered a single energy level (molecular orbital, MO) directly coupled to homogeneous semi-infinite electrodes. The MO energy $\varepsilon_0 \equiv E_{\text{MO}} - E_i$ of the embedded molecule relative to the Fermi energy $E_i$ of the unbiased electrodes (usually set as energy origin, $E_i \equiv 0$) is simply a model parameter. Its value is adjusted by fitting transport data for the specific case investigated. In general, the value of $\varepsilon_0$ thus obtained is different from the energy offset $\varepsilon_0 \equiv E_{\text{MO}} - E_i$ of the isolated molecule. In this way, via $\varepsilon_0 \neq \varepsilon_0$ (image charge effects yield $|\varepsilon_0| < |\varepsilon_0|$)$^{[60]}$ these approaches implicitly allow molecule-electrode couplings to affect the embedded molecule. What these approaches ignore is the opposite effect. If molecular junctions consisted of a single molecule, this opposite effect would certainly be negligible. However, this picture overlooks what is reality in the vast majority of molecular junctions fabricated to date. Even if experimental techniques allow to measure the current through a single molecule—as the case mentioned in Section 1 of repeatedly formed STM break junctions wherein the STM tip crashes into the substrate and is subsequently retracted until a single molecule bridges the nanogap$^{[30,31]}$—the molecules forming extended SAMs substantially change the work function with respect to the bulk metal. Obviously, this is a potentially important effect but, to the best
of our knowledge, it was disregarded in all previous model-based transport studies. To account for the SAM-induced change in electrodes' work function \( \Delta \Phi_{s,t} \equiv \Phi_{s,t} - \Phi^0 \neq 0 \), with respect to the bare metal value \( \Phi^0 \) we will extend the Hamiltonian describing the charge transport mediated by a single energy level\(^{[61-64]} \) as follows

\[
H = \sum_{l \neq \pm} \left[ \mu_{l} c_{l}^\dagger c_{l} - t_{s,l} (c_{l}^\dagger c_{l+1} + H.c.) \right]_H + \sum_{r \neq 2} \left[ \mu_{r} c_{r} - t_{s,r} (c_{r+1}^\dagger + H.c.) \right]_H
\]

\[
+ \left[ \left( \mu_{s} - \Delta \Phi_{s,t} \right) c_{s}^\dagger c_{s} - T_{s} (c_{s}^\dagger c_{s+1} + H.c.) \right]_H
\]

\[
+ \left[ \left( \mu_{t} - \Delta \Phi_{s,t} \right) c_{t}^\dagger c_{t} - T_{t} (c_{t}^\dagger c_{t+1} + H.c.) \right]_H
\]

\[
+ \epsilon_{0}(V) c_{s}^\dagger c_{s} - \tau_{s} (c_{s}^\dagger c_{s+1} + H.c.) - \tau_{r} (c_{r+1}^\dagger + H.c.)
\]

(2)

Above, the subscript 0 refers to the single molecular orbital (MO, “level”) considered. Creation \( c_{s,t}^\dagger \) and annihilation \( c_{s,t} \) operators refer to single electron states in substrate's and tip's conduction band of widths \( W_{s,t} = 4t_{s,t} \), respectively.

The three types transfer integrals \( t_{s,t}, T_{s,t}, \tau_{s,t} \) entering Equation (2) quantify the three distinct microscopic processes of the specific model presently considered:

1) \( t_{s,t} \): charge transfer within the bulk substrate (tip) electrode;
2) \( T_{s}, T_{t} \): charge transfer between the bulk electrode and the adjacent metal interface;
3) \( \tau_{s}, \tau_{t} \): charge transfer between the molecular level and the adjacent metal interfaces.

In the absence of magnetic fields, magnetic impurities, etc., all transfer integrals can be taken as real positive numbers \( (t_{s,t}, T_{s,t}, \tau_{s,t} > 0) \). Although by no means critical (see examples in ref. [21]), below we will use throughout the value \( W_s \equiv W_{s,t} = 35.8 \) eV \( ( t_{s,t} = 8.95 \) eV for the width of the gold (s-)band, as it turned out to better fit transport data\(^{[65,66]} \) than the value \( W_s = 20 \) eV \( (t_{s,t} = 5 \) eV) deduced from band structure calculations\(^{[61]} \).

Setting the onsite energies equal to the electrochemical potentials

\[
\mu_{s,t} = \varepsilon_{0} \pm eV/2 \equiv \pm eV/2
\]

(3)

along 1D electrodes is legitimate and mimics real situations wherein the electrodes' transverse dimension by far exceeds the junction's transverse extension\(^{[68]} \). In the same vein, SAM-induced modifications of the electrodes' work function are accounted for by the extra energy contributions \( \Delta \Phi_{s} \) and \( \Delta \Phi_{t} \), to the energies of the sites \( l = -1 \) and \( r = 1 \) at the molecule contacts to the substrate and tip ("interfaces"); the chemically adsorbed molecular layer basically affects the work function of the SAM-covered surface of the metal.

For the sake of simplicity electron spin will not be included explicitly but its contribution (a factor of two) will be accounted for whenever physically relevant (e.g., Equation (5)). Limitations of the model Hamiltonian of Equation (2) similar to those recently noted\(^{[21]} \) for the more particular case \( \Delta \Phi_{s,t} \equiv 0 \), \( T_{s,t} \equiv t_{s,t} \) will not be repeated here.

Obviously, once included into the model, the work function changes \( \Delta \Phi_{s,t} \neq 0 \) can in general significantly impact on transport properties. Equations (17) and (18) presented below may be taken as illustrations of this fact. The latter equation is supported by experiments\(^{[15,16,24,28]} \), which revealed a strong dependence of the conductance \( G \) on \( \Delta \Phi \)'s. What makes current rectification — the main focus of the present study — interesting is just the fact that it is practically not affected by \( \Delta \Phi \)’s.

Putting in more concrete terms, in its general form, the present model Hamiltonian breaks the left-right symmetry. Indeed, as easily seen, Equation (2) is not invariant under the left-right transformation \( \varepsilon_{l} \Rightarrow \varepsilon_{r} \) \( \gamma \Rightarrow -\gamma \). So, the forward current may in principle be different from the backward current \( I(-V) \neq -I(V) \) even in the absence of a bias-driven MO shift (i.e., \( \gamma \equiv 0 \) in Equation (1)). Rephrasing, Equation (2) is compatible with current rectification

\[
RR(V) \equiv -I(V)/I(-V) \neq 1
\]

(4)

even in cases where \( \gamma \equiv 0 \).

However, as was exemplified above and quantitatively analyzed recently\(^{[21]} \) a left-right asymmetry does not automatically imply that the associated current rectification is sufficiently large to be observable. From this perspective, it makes sense to address the specific question formulated in Section 1: can unequal changes \( \Delta \Phi_{s,t} \neq \Delta \Phi_{r} \) significantly impact on and/or give rise to an observable current rectification?

SAMs do not only induce modifications of the work function at interfaces. Making the contact work functions different from the values in the bulk, SAMs can also change the charge transfer efficiency between the metallic layer at interface and the bulk electrode. Rephrasing mathematically, SAMs can alter the values of \( T_{s,t} \) in Equation (2). Does/can this indirect \( \Delta \Phi \)-driven effect, which is another potential source of forward–backward symmetry breaking, quantitatively impact on RR? By allowing \( T_{s,t} \) to be different from \( t_{s,t} \), below we can and do also address this additional question (see Section 4.2).

3. General Formulas

By applying the general Keldysh formalism\(^{[69,70]} \) the zero temperature steady-state current for the specific model of Equation (2) can be straightforwardly obtained\(^{[71]} \)

\[
l = \frac{2e}{h} \int_{\mu_{s}}^{\mu_{t}} d\varepsilon \tilde{f}_s(\varepsilon)G_{s,t}(\varepsilon; V)G_{s,t}(\varepsilon; V)^\dagger(\varepsilon)
\]

(5)

In the specific case of Equation (2), the key quantity entering Equation (5), \( G_{s,t} = G_{r,c}^* \), is the corner matrix element \( G_{23} \) of the
(3 × 3) retarded Green’s function matrix $G$

$$G^{-1}(\epsilon; V) = \epsilon 1 - H$$

$$= \begin{pmatrix}
\epsilon - \mu_s + \Delta \Phi_s & \tau_s & 0 \\
\tau_s & \epsilon - \epsilon_0(V) & \tau_t \\
0 & \tau_t & \epsilon - \mu_t + \Delta \Phi_t - \Sigma_s(\epsilon)
\end{pmatrix}$$

(6)

expressed by means of the embedding self-energies $\Sigma_s (x = s, t)$

$$\Sigma_s(\epsilon) \equiv \Delta_s(\epsilon) - \frac{i}{2} \Gamma_s(\epsilon)$$

(7)

Above and whenever possible, we suppress full listing of function’s arguments for the sake of simplicity. For the energy range of interest $|\epsilon - \mu_s| < 2t_s$, the broadening and the shift functions are given by

$$\Gamma_s(\epsilon) = \frac{T_s^2}{4t_s^2} \sqrt{4t_s^2 - (\epsilon - \mu_s)^2}$$

(8a)

$$\Delta_s(\epsilon) = \frac{T_s^2}{2R_s}(\epsilon - \mu_s)$$

(8b)

Notice that we used the tilde symbol above to avoid confusing $\Gamma_s$ with the quantities

$$\Gamma_s \equiv 2\tau_s^2/t_s$$

(9)

entering the conventional single level model in the wide band limit.$^{[62,64]}$

In addition, for the intuitive physical interpretation of the numerical results for RR, the local density of states projected onto the molecular state

$$\text{LDOS}(\epsilon; V) = -\frac{1}{\pi} \text{Im} G_{22}(\epsilon; V)$$

(10)

is also a quantity of interest. The renormalized bias-dependent MO energy $\epsilon_0(V)$ can easily be deduced from Equation (10) as the LDOS maximum location

$$\epsilon_0(V) = \text{LDOS}^{-1}(\text{max} \text{LDOS}(\epsilon; V))$$

(11)

As the inversion of the (3 × 3) matrix of Equation (6) can be done analytically, some tedious algebraic effort (similar to that of ref. [21]) eventually allows to derive closed analytical approximations for some of the results reported below. However, because those formulas are rather lengthy, with a single exception (namely, Equation (15)), we prefer not to present them here but merely show exact numerical results obtained using MATHEMATICA 12.1.1. Numerically solving Equation (11) and computing the integral of Equation (5) do not pose any special problem nowadays.

### 4. Results and Discussion

#### 4.1. $\Delta \Phi$-Induced Renormalization of the MO Energy

Within the present single-level model of charge transport, current rectification can arise in cases where reversal of the applied bias polarity ($V \to -V$) yields different shifts in the MO energy. As noted in Section 3, the renormalized MO energy $\epsilon_0(V)$ can be obtained from Equation (11). The applied bias shifts the MO energy $\epsilon_0(V)$ of the embedded molecule

$$\epsilon_0(V) = \epsilon_0 + \gamma eV + \delta \epsilon_0 + \overline{\gamma} eV + \mathcal{O}(V^2)$$

(12)

Notice that within the present model the bias-driven MO shift, Equation (12), is split into two distinct parts. The SAM-induced part (approximately) characterized by the dimensionless strength $\overline{\gamma}$ represents an additional contribution to the bias-driven shift of Equation (1). The latter traces back, for example, to eccentric MO location (cf. Section 1) or intramolecular Stark effects$^{[9,12]}$ and quantified by the dimensionless strength $\gamma$.

In its turn, the MO energy shift $\Delta \epsilon_0(V)$ due to the presently considered SAM-induced changes in electrodes’ work function can be disentangled into a bias dependent contribution $\delta \epsilon_0(V)$ and a bias independent contribution $\delta \epsilon_0$

$$\Delta \epsilon_0(V) = \epsilon_0(V) - \epsilon_0(V) = \delta \epsilon_0(V) + \delta \epsilon_0(V)$$

(13a)

$$\delta \epsilon_0 = \left. \epsilon_0(V) \right|_{V \to 0} - \epsilon_0$$

(13b)

$$\delta \epsilon_0(V) = \left. \epsilon_0(V) - \epsilon_0(V) \right|_{V \to 0} = \overline{\gamma} eV + \mathcal{O}(V^2)$$

(13c)

The bias-independent MO shift $\delta \epsilon_0$ does not directly impact on current rectification. To single out the effect of the unequal changes in the work function on rectification, let us assume that no other source of forward–backward asymmetry exists, that is: $\Delta \Phi_s \neq \Delta \Phi_t$, $\epsilon_0(V) \equiv \epsilon_0$ (i.e., $\gamma \equiv 0$ in Equation (11)), $\tau_s = \tau_t = t, \tau_{s,t} = t$. Excepting Section 4.3, we will also assume $\Gamma_s = \Gamma_t = t$.

Results obtained in this way by means of Equation (10) using typical parameter values are depicted in Figure 1. The MO offset values $|\epsilon_0| = 0.5$ eV and $|\epsilon_0| = 1$ eV used Figures 1 and 2 are comparable to those for various benchmark molecular junctions$^{[15,16,28,29]}$. The value $\tau \approx 0.119$ eV used there corresponds to an ohmic conductance value $G / G_0 \approx 10^{-3}$ ($G_0 \equiv 2e^2/h = 77.48$ $\mu$S is the conductance quantum) typical for real (few-membered rings) molecular junctions$^{[15,16,24,28,30,72–75]}$.

Inspection reveals that the quantities $\delta \epsilon_0$, $\delta \epsilon_0(V)$, and $\overline{\gamma}$ depicted in Figures 1 and 2 for values $0 \leq |\Delta \Phi| < |\Delta \Phi| < 2.5$ eV—safely covering the experimental range measured for real molecular junctions$^{[15,16,24,28,29]}$—are very small. The “largest” thereof is the bias-independent MO shift $\delta \epsilon_0$. To leading order, it can be expressed as follows

$$\delta \epsilon_0 \approx \left( \epsilon_0 + 2\Delta \Phi_s \right) \frac{\Gamma_s}{W_s} + \left( \epsilon_0 + 2\Delta \Phi_t \right) \frac{\Gamma_t}{W_t}$$

(14)

For values of $\Delta \Phi_s, t$-values of practical interest, the difference between the values of $\delta \epsilon_0$ calculated exactly via Equation (10) and
Figure 1. In cases where the SAM-induced changes in the work function of the two \(s\) (substrate) and \(t\) (tip) electrodes differ \((\Delta \Phi_s \neq \Delta \Phi_t)\), an applied bias \(V\) yields an MO energy shift \(\delta \varepsilon_0(V)\) exhibiting an approximate linear dependence in broad \(V\)-ranges: (a) case of \(\Delta \Phi_s\) and \(\Delta \Phi_t\) having the same sign; (b) case of \(\Delta \Phi_s\) and \(\Delta \Phi_t\) having opposite sign. It is somewhat larger in cases where \(\varepsilon_0\) and \(\Delta \Phi_s\) (\(\Delta \Phi_t\)) have the same sign (compare panels (a) and (b) among themselves).

those obtained by means of the approximate analytical form of Equation (14) are negligible; see Figure 1a.

As visible in Figure 1a, the bias-dependent MO shift \(\delta \varepsilon_0(V)\) linearly depends on \(V\) in cases where \(\varepsilon_0\) and \(\Delta \Phi_s\) \((|\Delta \Phi_s| > |\Delta \Phi_t|)\) have the same sign—which more interesting because it is the typical experimental situation\(^{[15,16,24,28]}\)—where it is larger than in cases of opposite signs (cf. Figure 1b). Approximately, the slope \(\tilde{\gamma}\) of this line (cf. Equation (13c)) is constant. A high asymmetry of the SAM-induced work function changes \((|\Delta \Phi_s| > |\Delta \Phi_t|)\) favors a large bias-dependent MO shift \(\delta \varepsilon_0(V)\). In this limiting (from the point of view of rectification very advantageous) case, the leading order contribution to the slope \(\tilde{\gamma}\) of the lines \(\varepsilon_0(V)\) versus \(V\) has the form

\[
\tilde{\gamma} \underset{\Delta \Phi_t \to 0}{\approx} \left( \frac{k_\varepsilon_0}{W_s} \right)^{1/4} \left( \frac{\Gamma_s}{W_s} \right) \left( \frac{|\Delta \Phi_s|}{W_s} \right)^{3/2} \tag{15}
\]

where \(\Gamma_s\) is expressed by Equation (9).

Figure 2 depicts graphically exact numerical results in agreement with the dependence expressed in approximate analytical form by Equation (15).

4.2. Impact of \(\Delta \Phi\)'s Asymmetry on Current Rectification in Benchmark Molecular Junctions

Based on the generic results shown in the preceding section, one can conclude that unequal values \(\Delta \Phi_s \neq \Delta \Phi_t\) can indeed make positive and negative biases shifting the MO energy in opposite direction and hence current rectification.

Still, the problem of practical importance is whether the ensuing difference between \(\varepsilon_0(V)\) and \(\varepsilon_0(-V)\) is sufficiently large to make current rectification observable in real molecular
rectifiers. And this is indeed the essential point; the inspection of the small numbers on all γ-axes in Figures 1 and 2 reveals that these differences hardly exceed or even reach a few meV.

In a more friendly analytical form, Equation (15) once more makes it clear that the strength of the SAM-induced bias-driven MO shift $\gamma$ is a very small quantity. For real molecular junctions, values estimated from experiments for $|s_0|$ can hardly exceed $\approx 1$ eV, $\Gamma$s are at most $\approx 0.1$ eV, and the largest $|\Delta \Phi|$‘s are smaller than $\approx 2$ eV.$^{[15,16,24,28,29]}$ Because each of these quantities are substantially smaller than electrodes’ conduction bandwidth $W \approx 20 – 36$ eV$^{[15–67]}$ the value of each fraction entering the right hand side is much smaller than unity.

To interrogate the practical relevance of the forward–backward symmetry breaking arising from SAM-induced work function changes, we will examine below, as specific examples, asymmetric molecular junctions based on the three-membered rings of the oligoacene and oligophenylene families: triphenylene thiol (Au/OPT3-Au$^{[16]}$) and anthracene thiol (Au/Anth-S-Au$^{[24]}$). In CP-AFM junctions fabricated with gold electrodes, these molecules are chemically adsorbed via thiol groups on the substrate and physisorbed on the tip.$^{[16,24]}$ For this reason, substantial changes in the tip’s work function are unlikely, so, already said above, we set $\Delta \Phi_t = 0$.

Individual $I$–$V$-traces measured for CP-AFM Au/OPT3-Au and Au/Anth-S-Au junctions are depicted in Figures 3a and 4a along with the fitting (red) curves based on the present single level model, wherein the impact of $\Delta \Phi_t$ is explicitly accounted for. In order to reduce the number of free parameters for $I$–$V$ data fitting by means of Equation (5)—desirable for avoiding over-fitting—we followed a procedure utilized recently$^{[21]}$ and checked a posteriori (see below). Namely, we fixed the ratio $\tau_c/\tau_i$ of the molecule-electrode transfer integrals using the information available for the ohmic conductance of the diithiol counterparts (Au-OPD3-Au and Au-S-Anth-S-Au) of the presently considered (Au/OPT3-Au and Au/Anth-S-Au, respectively) monothiol junctions. In this way, with three adjustable parameters ($s_0$, $\tau$, and $\gamma$) and $\Delta \Phi$‘s set to the available experimental values,$^{[16,24]}$ the present approach has the same number of fitting parameters as the single level model employed recently$^{[16]}$ for comprehensive investigations of Au/OPTn-Au junctions.$^{[15]}$ There, $\Delta \Phi$-induced effects were (implicitly) accounted for via (renormalized) parameter values fitted to transport data.

Table 1 collects the values of the model parameters used in Figures 3a and 4a along with their standard deviations. The high quality of the aforementioned fitting procedure is witnessed by the very large, extremely close to unity of the $R^2$-values.

Furthermore, the extremely small differences between the values of $R^2$ and adjusted $R^2$ rule out the risk of over-fitting that could occur if too many independent fitting model parameters were employed.$^{[78]}$ And because pitfalls of merely using $R^2$, which misses a straightforward mathematical basis in cases of nonlinear fit models, for quantifying the goodness of fit are well documented,$^{[77–81]}$ the reasonable residuals’ scattering around zero depicted in Figures 3b and 4b adds further confidence to the fitting approach employed.

To reiterate, the theoretical fitting (red) curves of Figures 3a and 4a assume two independent contributions to the bias driven MO shift: one contribution expressed by Equation (1) and related to $\gamma$ and another contribution arising from $\Delta \Phi \neq \Delta \Phi_t = 0$ related to the strength of the SAM-induced bias-driven MO shift $\gamma$, a quantity distinct from $\gamma$.

To single out the SAM-induced contribution to the $I$–$V$-asymmetry of the experimental curves, we will set $\gamma \equiv 0$ (cf. Equation (1)) while using the values of the other parameters from Table 1 (implying $\gamma \neq 0$). These results for $\gamma \equiv 0$ are depicted as green curves in Figures 3a and 4a. Clearly, the $I(V)$ asymmetry of these curves cannot be seen within the drawing accuracy of Figures 3a and 4a. The SAM-induced impact to rectification due to $\Delta \Phi \neq \Delta \Phi_t \approx 0$ has indeed no practical importance. At the highest experimental bias shown, the RR-values for the Au/OPT-Au and Au/Anth-S-Au curves are $RR=0.987$ and $RR=0.970$, respectively.

So, even substantial asymmetric SAM-induced changes in the electrodes’ work function like those characterizing the presently investigated CP-AFM Au/OPT3-Au and Au/Anth-S-Au junctions ([$|\Delta \Phi - \Delta \Phi_t| \approx 1$ eV, among the largest ever measured$^{[15,16,24,29]}$], cannot have a significant contribution or explain very modest rectification values like those measured for the presently considered junctions (RR $\approx 2$, cf. red curves in Figures 5a and 6a).
Figure 4. a) Accounting for a bias driven HOMO shift, Equation (1), the single level model can excellently reproduce raw I–V-data (courtesy of C. D. Frisbie) measured in CP-AFM anthracene thiol molecular junctions with gold electrodes (Au/Anth-S-Au). This is demonstrated by the very large values of $R^2$ and adjusted $R^2$ indicated in the inset. Values and standard deviations of the model parameters are presented in Table 1. b) The data fitting yields residual errors exhibiting a reasonable scattering around zero. See the main text for details.

Figure 5. a) Neither the (green) curve obtained by merely accounting for the forward–backward symmetry breaking stemming from $\Delta \Phi_s \neq \Delta \Phi_t = 0$ (i.e., setting $\gamma = 0$ and using the other parameter values of Table 1) nor the (blue and magenta) curves computed to allow $\Gamma_s$ be different from $\Gamma_t = t$ (i.e., setting $\gamma \equiv 0$ and using $\Gamma_s$ as indicated in the inset along with the values for the other parameter of Table 1) can reproduce the (red) curve for rectification $RR(V) = -I(V)/I(-V)$ obtained by recasting the fitting I–V-curve in excellent agreement with measurements on Au/OPT3-Au junctions. b) SAM-induced bias driven MO energy shifts pertaining to the curves depicted in panel (a). See the main text for details.

4.3. Impact of an Additional $\Delta \Phi$-Induced Forward–Backward Asymmetry on Current Rectification

Let us now consider the possibility that the transfer integrals $T_s$ can differ from the transfer integrals within the bulk electrodes $t_s$. This might be an indirect result of the SAM-induced modifications of electrode’s work function. So, the asymmetry $\Delta \Phi_s \neq \Delta \Phi_t \approx 0$ could then indirectly induce an additional forward–backward symmetry breaking relevant for current rectification.

Because the inequality $T_s \neq t_s$ turned out to yield a novel mechanism for current rectification (see below), we undertook the effort of deriving an analytical formula for the quantity $\tilde{\gamma}$ entering Equation (13c). To leading order, it reads

$$\tilde{\gamma} = \frac{1}{2} \left( \frac{t_s^2}{T_s^2} - 1 \right) \frac{\Gamma_s}{W_s} - \frac{1}{2} \left( \frac{t_i^2}{T_i^2} - 1 \right) \frac{\Gamma_i}{W_i}$$

Here, $\Gamma_{s,i}$ are expressed by Equation (9). Equation (16) shows that, rather then the unequal values $\Delta \Phi_s \neq \Delta \Phi_t \approx 0$, it is the difference between $T_{s,i}$ and $t_{s,i}$ that yields the largest contribution to $\tilde{\gamma}$, which eventually may make RR-values significantly different from unity. Quantities containing $\Delta \Phi$’s explicitly, like those entering the right hand side of Equation (15), represent higher-order terms whose contribution to $\tilde{\gamma}$ is altogether negligible; they were omitted in the right hand side of Equation (16). Differences between exact numerical values for $\tilde{\gamma}$ and those obtained from Equation (16) are too small to be visible within any reasonable drawing accuracy.
An analytic expression for the bias independent MO energy shift can be also be deduced

$$\delta \varepsilon_0 \approx \frac{t_i}{f_s} \left[ \varepsilon_0 \left( 2 \frac{t^2}{f_s^2} - 1 \right) + 2 \frac{2 t^2}{f_s^2} \Delta \Phi \right] \frac{\Gamma_s}{W_s} + \frac{t_i^2}{f_t} \left[ \varepsilon_0 \left( \frac{t^2}{f_t^2} - 1 \right) + 2 \frac{t^2}{f_t^2} \Delta \Phi \right] \frac{\Gamma_t}{W_t} \tag{17}$$

It recovers Equation (14) as a particular case ($\Gamma_t \rightarrow t_t$).

For completeness, we also present below the expression of the low bias conductance

$$G = \frac{G_0}{2} \left[ \varepsilon_0 \left( \frac{f_s t_s^2}{f_t^2} - \frac{\Delta \Phi t_s}{\Gamma_s} \right) - \frac{f_s t_s^2}{f_t^2} \Delta \Phi \right] + \frac{\varepsilon_0 \left( \frac{f_s t_s^2}{f_t^2} - \frac{\Delta \Phi t_s}{\Gamma_s} \right) + \frac{f_s t_s^2}{f_t^2} \Delta \Phi \right]^2 \tag{18}$$

where $G_0 \equiv 2e^2/h = 77.48$ mS is the conductance quantum. For $\Gamma_t \rightarrow t_t$, it reduces to the well known form $G/G_0 = \Gamma_s \Gamma_t/\{t_s^2 + (\Gamma_s + \Gamma_t)^2/4\}$.[4,14,70]

Numerical results of simulations using parameters characteristic for Au/OPT3-Au and Au/Anth-S-Au junctions are presented in Figures 5b and 6b, respectively. Concerning the parameter values employed there, we note the following. Physically, one can expect $T_s \leq t_s$. If the opposite were true, the charge transfer within the bulk electrode would be less efficient than the charge transfer to the metallic layer at the metal-SAM interface, see Equation (2). Furthermore, in view of the fact that $\Delta \Phi \approx 0$ in the real junctions envisaged possessing one end physisorbed on the tip, we assumed $T_t = t_t$.

Inspection of Figures 5b and 6b reveal that unequal values $T_s \neq t_s$ cannot explain current rectification in the Au/OPT3-Au and Au/Anth-S-Au junctions. The smaller $T_s$ than $t_s$ is, the smaller then unity is also the value of RR. This behavior of RR is at odds with rectification direction observed experimentally (namely RR $> 1$, see the red curves in Figures 5a and 6a).

To be sure, while the foregoing analysis rules out significant effects tracing back to unequal $T_s$ and $t$-values in the specific (Au/OPT3-Au and Au/Anth-S-Au) junctions considered, it still indicates that non-equal $T_s \neq t_s$ may give rise to an observable (albeit presumably not spectacular) rectification for other types of junctions. Efforts to improve unimolecular rectifiers via interface engineering may be rewarding from this perspective.

5. Conclusion

In the present paper, we examined SAM-induced asymmetries inherently present in molecular junctions as potential sources of current rectification RR. In our analysis, we particularly insisted on the excellent agreement with experiment for real CP-AFM molecular junctions because this is a sound prerequisite to quantify the impact of the SAM-induced changes in the metal work function $\Delta \Phi$ on rectification. This framework allowed us to reliably state that an observable impact on the RR-value of real junctions cannot be arise merely because of highly unequal values $\Delta \Phi \neq \Delta \Phi_t$. To avoid misunderstandings, one should emphasize here that the aforementioned apply to current rectification. Unequal values $\Delta \Phi_s \neq \Delta \Phi_t$ can affect other properties. Notice, for example, that, to leading order, no $\Delta \Phi_t$’s enter the right hand side of Equation (16), while the contrary is the case in Equations (17) and (18).

The present finding on the impact on RR adds further evidence to support a rather counter-intuitive conclusion formulated recently[46] an effect that breaks the forward–backward in-
the possibility that $\Delta \Phi$'s make the transfer integrals $T_{s,t}$ between metal interfaces and bulk electrodes different from the bulk values $t_{s,t}$. While the presently reported results exclude this possibility for the specific benchmark Au/OPT3-Au and Au/Anth-S-Au junctions investigated, they suggest that unequal $T_{s,t}$ and $t_{s,t}$ values can be of interest for other molecular rectifiers.

From this perspective, employing intervening narrow-band monoatomic metal adlayers between SAMs and traditional bulk metals may be an appealing route for interface engineering on the path towards improved molecular rectifiers.

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Conflict of Interest

The author declares no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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charge transport, current rectification, electron tunneling, molecular junctions

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