

## MOLECULAR RECTIFIERS

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The construction of a very simple electronic device, a rectifier, based on the use of a single organic molecule is discussed. The molecular rectifier consists of a donor  $\pi$  system and an acceptor  $\pi$  system, separated by a sigma-bonded (methylene) tunnelling bridge. The response of such a molecule to an applied field is calculated, and rectifier properties indeed appear.

### 1. Introduction

The tremendous improvements in reliability, compactness, versatility and range of electronic circuitry due to the widespread manufacture and use of solid-state devices constitutes perhaps the major technological advance of the past quarter century. Within biological systems, however, some tasks performed by solid-state devices in electronic applications are performed, instead, by organic molecules; such tasks include storage and transfer both of energy and of electrons. It has been suggested occasionally [1] that the development of synthetic electronic devices based on organics be attempted. Particular interest has been evinced recently in the use of organic crystals both as semiconductors [2] and as possible superconductors [3]. It seems to us reasonable to examine the potential use of molecules as components of electronic circuitry by looking, as a start, at the current-voltage characteristics of a single molecule acting as a rectifier.

In this article we present semiquantitative calculations that are intended to demonstrate the feasibility of such a molecular device.

### 2. Architecture of the rectifier circuit

Common solid-state rectifiers are based on the use of  $p-n$  junctions. An organic molecule, to show rectifier properties, should have roughly the properties of a  $p-n$  junction. By the use of substituent groups on aromatic systems, it is possible to increase or decrease the  $\pi$  electron density within the organic, and therefore to create relatively electron-poor ( $p$ -type) or electron-rich ( $n$ -type) molecular subunits. Those substituents classified as electron withdrawing (that is, showing positive Hammett constants) [4] will cause their aromatic subunit to become relatively poor in  $\pi$  electron density, thus raising the electron affinity and making the subunit a good electron acceptor. Conversely, electron-releasing substituents will increase the  $\pi$ -electron density, thereby lowering the ionization potential and rendering the subunit a good electron donor [5-7].

Certain solids, the so-called charge-transfer crystals, show high electronic conductivity and spin susceptibility due to the donor-acceptor transfer of electrons [8]. This electron motion suggests that a rectifier could be built in which electrons would be allowed to pass from a cathode to an acceptor site or from a

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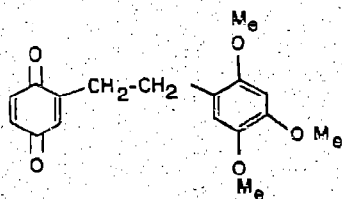


Fig. 1. An example of a hemiquinone.

donor site to an anode, but not in the other sense. If, however, the electronic systems of the donor and acceptor molecular subunits are allowed to interact strongly with one another, a single donor level will exist on the time-scale of any laboratory experiment [9]. Therefore, the donor and acceptor sites should be effectively insulated from one another in order for the device to function. This can be accomplished by the use of a sigma-electron system between the donor and acceptor pi subunits\*. Such a molecule, illustrated in fig. 1, might then be expected to show rectifier properties; electron current would be expected to pass only from left to right in the figure, along the system cathode  $\rightarrow$  acceptor  $\rightarrow$  donor  $\rightarrow$  anode. The hemiquinone molecule shown in fig. 1 may be used as a prototype for understanding rectifier behavior. The quino ( $=O$ ) groups on the left decrease the pi density and raise the electron affinity, whereas the methoxy ( $-OCH_3$ ) groups on the right increase pi density and lower ionization potential. Fig. 2 shows a similar molecule based on the extremely popular acceptor tetracyanoquinodimethane (TCNQ) and the donor tetrathiofulvalene (TTF). In this case, we have indicated a triple, rather than single, methylene ( $-CH_2-$ ) bridge; this will help ensure molecular rigidity. We will refer to the methylene bridge as a  $\Sigma$  bridge henceforth. Its purpose is to cause the pi levels of the donor and acceptor sites to be essentially non-interacting on the time-scale of electronic motion to or from the electrodes.

To describe simply the response of such a molecular rectifier circuit to an ac signal, we will employ an independent-particle picture for the pi electrons. The empty orbital which accepts electrons from the cathode will be called the affinity state. In the free

donor acceptor molecules of the type shown in figs. 1 and 2, the electron affinity of the acceptor will be of order 1–2.5 volt, while the ionization potential of the donor will be of order 6–9 volt. These values are considerably modified in crystals [3], as we might expect them to be in our rectifier circuit, due to interaction with other (in our case metallic electrode) electronic states. For proper rectifier behavior we require the affinity level of the acceptor to be either totally or partially empty, and lie at or slightly above the Fermi level of the electrode (and of course above the ionizing level C of the donor) as shown in fig. 3.

Figs. 4 and 6 demonstrate the passage of electron current from cathode to anode and the non-conduction of current on reversal of polarity; that is, they show the rectifier property of the molecule. As soon as the applied field becomes large enough for the cathode levels to overlap the acceptor levels in fig. 4, electron transfer onto the acceptor becomes possible. The threshold for this process will depend on several factors, principally the affinity perturbed level energy  $E_B$  and the work function  $\phi$ . A similar process occurs at the donor end, where electron transfer from the donor orbital C to anode becomes possible when the applied voltage  $V > IP - \phi$ , where IP is the donor ionization potential. Motion of electrons from acceptor to donor will occur under the action of the field. The (now occupied) affinity level and the hole left on the ionized donor are sufficiently close in energy that an electron tunneling process will occur: the tunneling width can be of the order of  $10-5000 \text{ cm}^{-1}$ . This tunneling is generally inelastic as can be observed by glancing at fig. 5. The charged acceptor contains an electron in orbital B, in the ground vibrational state, that tunnels with conservation of energy to the empty orbital C at the donor site. Except in cases of resonant transfer, the level B will lie above C, so that C will be prepared in an excited Franck-Condon state, which will then decay radiationlessly [11]. This process is clearly irreversible so long as B lies above C.

We thus think of current passage through our rectifier molecule as a three-step equivalent-resistance Kirchhoff net, with the three steps being cathode to acceptor, acceptor to donor and donor to anode transfers. Thus when polarity is reversed as shown in fig. 6 level D would have to be lowered to the Fermi level of the metal on the right and the Fermi level of the metal on the left would have to be lowered below

\* Compare, e.g., the beautiful experimental work on photoelectron spectra of methylene-bridged aromatics by Berkowitz et al. [10], and related papers.

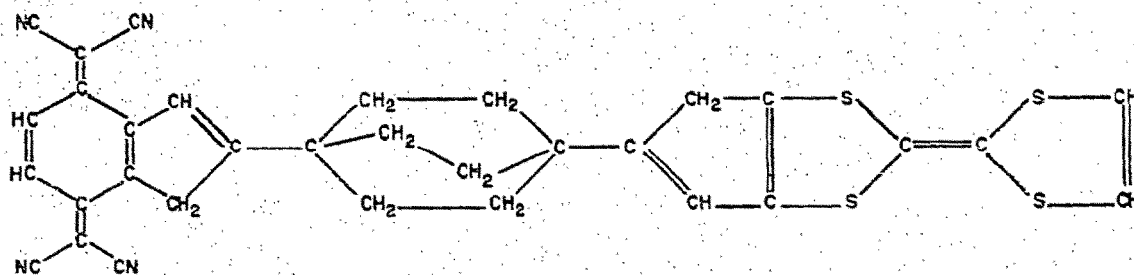


Fig. 2. An example of a rectifier molecule.

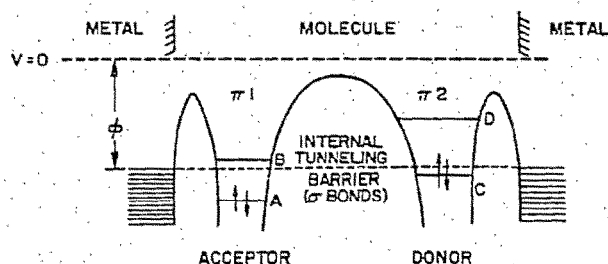


Fig. 3. Energy versus distance of the device (schematic). B and D are the affinity levels and A and C the highest occupied levels, of acceptor and donor, respectively.

level A in order to obtain assisted tunneling through these levels. As can be seen from the figure, the threshold voltage for this process should be relatively high. There may be an additional mechanism for conduction in this direction that has to be taken into account. The first step of this mechanism involves an internal tunneling from level C of the donor to level B of the acceptor. This would lead to a hole at the right side and an electron on the left side. Following this initial step, tunneling would proceed from charged  $\pi$  levels to and from the metals. This mechanism also in-

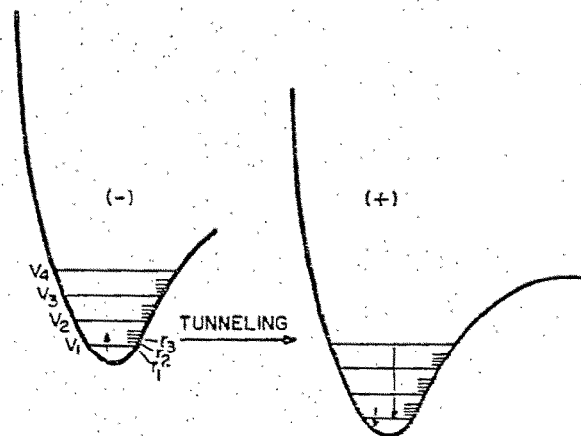


Fig. 5. Internal tunneling.

volves a threshold voltage, since it is imperative that the donor highest occupied molecular orbital C, on the right, be energetically at or above the acceptor  $\pi$  affinity orbital B, before tunneling would occur. It is the nonreversibility of the internal tunneling (for small applied fields) that yields the rectification properties of these molecules. It is thus possible to

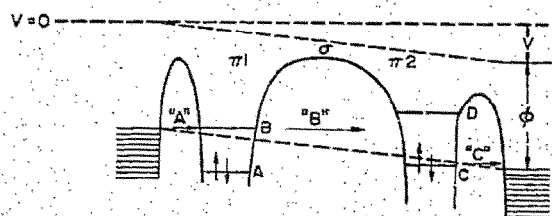


Fig. 4. Energy levels shift with applied voltage. "A", "B", and "C" are three tunneling processes.

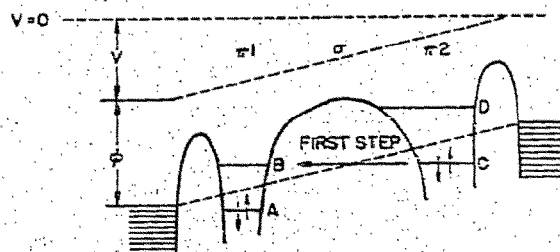


Fig. 6. Reverse applied voltage.

design materials that would have a larger threshold voltage for conduction in one direction than for the other direction; that is, rectifiers.

### 3. Calculations

The passage of electric current through a molecular system can generally be considered simply from the viewpoint of perturbation theory, with the total molecular wavefunction perturbed by the applied field. In the case of our A- $\Sigma$ -D system, however, the  $\Sigma$  bridge effectively separates the pi units, and the concept of a total molecule wavefunction to describe the response to an external field is no longer necessarily the most convenient starting point. Instead, we now choose to consider the three steps of cathode  $\rightarrow$  A, A  $\rightarrow$   $\Sigma \rightarrow$  D, and D  $\rightarrow$  anode as processes in an equivalent resistance network; arguments for the use of this method have been given by Mott and Twose, Kirkpatrick and others [12]. The essential reason for the use of this model is really based on time-scales; the electrode and bridge processes occur on such different time-scales that each one is really not dynamically coupled to the others. We will also choose to ignore, in our present crude independent-particle description, any direct excitonic interactions of the donor hole with the acceptor electron. The electronic eigenenergies (donor acceptor levels) as well as the effective tunneling matrix-elements can be roughly estimated using self-consistent field molecular orbital calculations. Alternatively, and preferably, these levels can be found from photoelectron spectra of the molecule. Our SCF calculations, which were carried out for the molecule of fig. 1 using the INDO semi-empirical method [13], give rough one-electron energies for the molecule alone; interaction shifts and broadening must then be added.

#### 3.1. The cathode $\rightarrow$ acceptor step

To estimate the rate of this transition in an applied field, we have employed a variant of the transfer-hamiltonian method originally proposed by Oppenheimer [14] to treat field ionization. In this method, the expression for the transition probability per unit time is simply

$$P = \frac{2\pi}{\hbar} \sum_f |\langle f | -Fz | 0 \rangle|^2 \delta(E_f - E_0). \quad (1)$$

Here  $|f\rangle$  is the final eigenstate (in our case, the vibronic state on the A site),  $|0\rangle$  is the initial eigenstate (the metallic wavefunction), and the electric field of strength  $F$  is directed along the  $z$  axis. Duke [15] has shown the equivalence of (1) to Bardeen's calculation of junction tunneling [16]. The only difference between (1) and the usual golden-rule result is that  $|f\rangle$  is associated with the unperturbed hamiltonian on the final site, rather than with the original unperturbed hamiltonian of which  $|0\rangle$  should be an eigenstate. The state  $|0\rangle$  has simply been taken as a plane-wave state (Bloch states within the electrode would of course be more correct, but we do not expect this to make much difference in our final result).

For the states  $|f\rangle$ , however, the unperturbed states of the pi system of the acceptor are not good enough. As studies of molecular adsorption have shown, the molecular eigenstates undergo both shift and broadening due to interaction with the electrodes. Gadzuk [17] presented an early treatment of these effects for the case of an atom interacting with a metallic surface. He showed that the concept of image charges could be taken over from classical electrostatics, and that an estimate of both the shift and the broadening could be obtained from perturbation theory. For the case of an alkali atom adsorbed on a metal, he showed that correct semiquantitative results could be obtained using as an unperturbed basis set the bare atom  $s$ -function and the free-electron states within the metal. The level shift is then simply

$$\Delta E = \langle s | H_{a-\text{met}} | s \rangle / \langle s | s \rangle, \quad (2a)$$

where  $|s\rangle$  is the atomic function and  $H_{a-\text{met}}$  is the  $s$ -electron interaction with the image charges in the metal. For the adsorption of K on Pt, he finds that  $\Delta E$  drops off slowly with distance, from 0.3 volt at 3 Å separation to 0.1 volt at 15 Å\*. Similar values had been previously suggested by Rasor [18] and by Levine [19], while Gomer [20] had proposed the essential shape of the  $\Delta E$  curve as a function of distance.

For our molecule-metal interaction, we first compute the shift for each atomic basis function. The

\* For slightly smaller distances, the shift goes up dramatically: for distances of order 2.5 Å, values of 1.5–2 volt seem reasonable.

total shift of the molecular orbitals on the rectifier donor and acceptor ends will then be given by linear combinations of these basis-function shifts. That is, if we say, for a particular molecular orbital  $\varphi_i$

$$\varphi_i = \sum_{\alpha} C_{i\alpha} u_{\alpha}, \quad (2b)$$

where  $u_{\alpha}$  are the atomic basis functions, then, denoting by  $H_{m-met}$  the molecule-metal interaction, we have

$$\langle \varphi_i | H_{m-met} | \varphi_i \rangle = \sum C_{i\alpha} C_{i\beta} \langle u_{\alpha} | H_{m-met} | u_{\beta} \rangle. \quad (3)$$

We find the coefficients  $C_{i\alpha}$  using the INDO procedure, while the final matrix elements in (3) are evaluated using the image-charge procedure of Gadzuk\*.

Thus far, the calculations have been based on those for either elastic electron tunneling (Oppenheimer transfer hamiltonian) or adsorption (shift and broadening of molecular levels). There is, however, one extra complication brought about by the fact that, even after broadening due to interaction with metallic electrodes has been included, there can still be important contributions from vibrationally inelastic tunneling; that is, a contribution to the electron transfer possibility can arise from transfer of an electron from the cathode to a vibrationally excited level of the acceptor. On the basis of strong-coupling theory [11] and assuming, as is generally the case for aromatics, that one particular normal mode (usually the  $1400 \text{ cm}^{-1}$  stretch) is far more strongly coupled than any other, one can evaluate the relative transition probabilities to various vibrational states. This is a standard problem in electron-transfer reactions. For our present calculations, we have taken the diagonal Frölich-type coupling constant as 1.5, the standard spectroscopic value. The contribution of the inelastic component is in fact small for the electrode process; it makes its major contribution in the internal tunneling step.

### 3.2. $A \rightarrow D$ motion

Within our equivalent-resistance scheme and one-electron model, we have effectively chosen to write

the electronic hamiltonian of the entire molecule as

$$H_{el} = H_D + H_A + V_{DA}, \quad (4)$$

$$V_{DA} = \sum_{i \in D} \sum_{j \in A} T_{ij} a_i^{\dagger} a_j + \text{c.c.} \quad (5)$$

The  $H_A$  and  $H_D$  are the subunit electronic hamiltonians for the A, D ends, and of course include two-electron terms. The  $i, j$  in (5) run over the one-electron pi states of the donor and the acceptor<sup>†</sup>, respectively;  $T_{ij}$  is an effective one-electron transfer, or tunneling matrix element, and  $a_j^{\dagger}$  is a Fermion creation operator for orbital  $j$ . Using simple molecular-orbital splitting considerations (or, more elaborately, a canonical transformation), the size of the tunneling elements  $T_{ij}$  can be estimated from separate SCF-type calculations on D, on A, and on A- $\Sigma$ -D. The element  $T_{da}$  was evaluated in this fashion for the molecule of fig. 1 using the INDO parametrization, and found to be  $360 \text{ cm}^{-1}$ . While this is certainly not quantitatively correct, it is in qualitative agreement with expectations as to the transfer probability for a  $\Sigma$  bridge, and we will use it without further correction<sup>††</sup>.

When the rectifier molecule is placed between electrodes, the one-electron levels will, as stated above, shift and broaden. The transfer probability for an electron passing from A to D will still be proportional to  $|T_{da}|^2$ , but it will also contain density-of-states factors on the final state, as well as Franck-Condon factors describing the possibility of inelastic transfer. Both the electronic changes and the vibronic factors were discussed above in connection with cathode  $\rightarrow$  acceptor motion.

### 3.3. Donor $\rightarrow$ anode motion

This is treated in a transfer-hamiltonian procedure, very similar to the cathode  $\rightarrow$  acceptor calculation.

## 4. Results

A current-voltage characteristic can be calculated along the lines described above. The true characteristic

\* Gurney [21] has pointed out that, due to tunneling, the one-electron levels will in fact become broadened. This broadening is negligible at our assumed 3 Å separation.

<sup>†</sup> We have assumed that the  $i, j$  states are approximately orthogonal, so that  $[a_k, a_l^{\dagger}]_{+} = \delta_{kl}$ .

<sup>††</sup> The  $\pi$ - $\Sigma$ - $\pi$  idea was first suggested to us by P.E. Seiden.

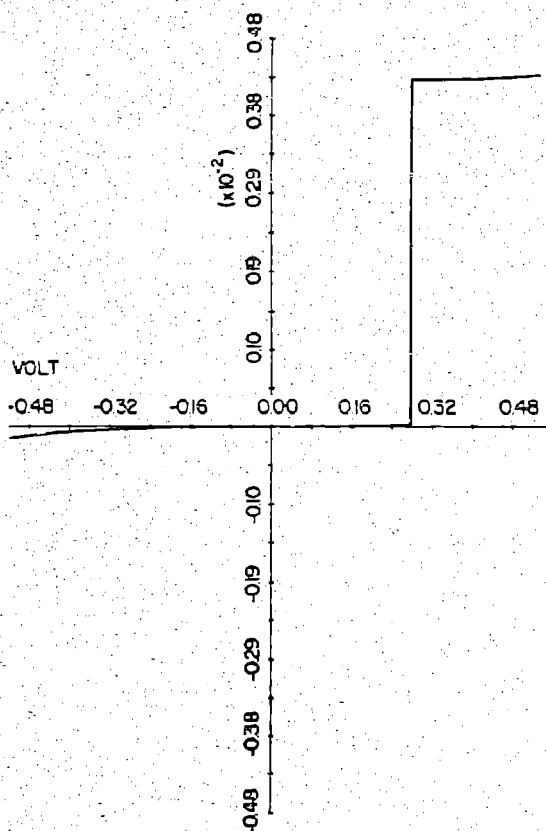


Fig. 7.  $I$ - $V$  characteristics of a molecular rectifier including direct electrode to electrode tunneling.  $I$  in  $\text{A}/\text{cm}^2$ ,  $V$  in volt, EA acceptor = 5.0 eV, IP donor = 5.3 eV,  $\phi$  = 5.1 eV.

of such a circuit, however, will contain other contributions to the current. These might include surface terms and direct passage due to inhomogeneous preparation of the molecular layer, both of which could be difficult experimental problems but will be ignored here. Another possible contributor would be direct tunneling of electrons from electrode to electrode with the sigma network as a barrier. This last contribution is rather difficult to calculate. Kuhn [22], in an elegant series of experiments, has measured the direct conductivity of molecular films of fatty acids, using a Langmuir-Blodgett film with a vapor-deposited electrode. We have compared the direct passage current with that expected by pi-electron motion in the rectifier, and it appears clear that the direct transmission contribution will be small compared to the rectifier current.

In fig. 7 we have presented the calculated  $I$ - $V$  characteristic for arbitrary choices of donor ionization potential, acceptor electron affinity, and electrode work function. More complete calculations, including a discussion of the dependence of the current on these parameters, will be published subsequently. The important observation to be made about the present result is that there is indeed a rectification evident: that is, current passes preferentially to the right in figs. 1 and 2. The threshold potential for passage of current is determined essentially by the voltage at which meaningful overlap of the broadened states  $|B\rangle$  and  $|C\rangle$  and the respective metallic states occur. In our case, the broadening has been found to be negligible, due to the large distance from the electrode, so that the  $I$ - $V$  curve is nearly discontinuous near threshold. For larger broadening, this onset of current flow will become smoother. If the reverse voltage is pushed high enough, current will indeed begin to flow through the pi system from anode to cathode; for the present choice of parameters, this occurs at an applied voltage of 0.55 volt.

A large number of materials and synthesis problems must, clearly, be overcome before such a molecular electronic device can be tested in the laboratory. Efforts towards the solution of these problems are presently under way. In addition, there are several serious drawbacks to the present semiquantitative treatment, including neglect of direct energy transfer from D to A (this can, however, be minimized if the geometry is chosen properly), possible Jahn-Teller effects, difficulties with electrode polarization, and, particularly, electron correlation effects. Some of these will be corrected in further work. The essential point to be made, however, is that these calculations seem to verify that a properly constructed single organic molecule can indeed exhibit useful device properties. In turn, such properties may aid in our further understanding of the molecular electronic structure of these molecules.

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