
Electron exchange between two electrodes mediated by two electroactive adsorbates

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Experimental data for electron exchange between two electrodes covered by electroactive films are presented and discussed in terms of the Gerischer model. A model Hamiltonian is proposed for such indirect electron exchange involving two intermediate species. Explicit model calculations are performed for the case in which the coupling between the two adsorbates is weak and determines the overall rate. The calculations agree well with the experimental data, and can be used to determine the energy of reorganization associated with the electron transfer.

1 Introduction

At present, much research is focused on the development of nanotechnology in general and of molecular-sized transistors in particular.^{1,2} As early as 1974 Aviram and Rattner³ had pointed out that electron transfer through donor–acceptor systems may exhibit current rectification, an effect which could be used in nanoscale electronic devices. A good view over the current activities in this field can be obtained from the collection of papers in ref. 4 and the theory is well summarized in the recent review by Nitzan.⁵

The construction of molecular electronic devices requires a source and a drain, and one or more localized electronic levels. The roles of source and drain can be taken by two electrodes, which may take the form of tips of scanning tunneling microscopes. Working in an electrochemical environment has the advantage, that two potential differences can be controlled individually: the bias voltage between the two electrodes, and the potential drop between one electrode and the solution, in practice between one working and one reference electrode. Functionalized adsorbates attached to the electrodes can provide the electronic levels required to construct molecular devices on a nanotechnological scale.

In this work we treat a particular system of interest to nanotechnological applications: two metal electrodes covered by films of adsorbates containing electroactive centers, and consider electron exchange mediated by these centers. We have realized this process in a system consisting of two mercury electrodes covered by electroactive films and obtained unusual current-potential characteristics. Various possibilities for electron exchange under such circumstances have recently been discussed by Kuznetsov and Ulstrup,⁷ and a model for both elastic and inelastic transitions has

been proposed by one of us.⁸ The experimental situation corresponds to the case in which the coupling between the two adsorbed states is weaker than that of the adsorbates to their substrates.

The rest of this paper is organized as follows: First we present our experimental results and discuss them qualitatively within the Gerischer model of electrochemical electron transfer.⁹ Then we propose a model Hamiltonian for the indirect exchange *via* two adsorbates and present explicit model calculations for the experimental situation.

2 Experiments and qualitative discussions

Full details of the experiments will be given elsewhere;¹⁰ here we merely summarize those facts that are needed for understanding the electron transfer aspects. The system consisted of two hanging mercury electrodes, whose relative position could be controlled by micrometers. Monolayers of $[\text{Ru}(\text{NH}_3)_5(\text{NC}_5\text{H}_4\text{CH}_2\text{NHCO}(\text{CH}_2)_{10}\text{SH})][\text{PF}_6]$ were deposited onto the electrodes by self-assembly (see Fig. 1). Hg–SAM//SAM–Hg junctions were formed by bringing the two electrodes into intimate contact. The Ru-complexes served as intermediate states for electron exchange between the two electrodes.

Two kinds of experiments were performed: In the first experiment both electrodes were initially held at the same potential in the reduction region for the redox species. The potential of the first electrode was kept fixed, while that of the other was scanned into the oxidation region (see Fig. 2). When the potential of the second electrode approached the equilibrium potential ϕ_0 for the $\text{Ru}^{2+/3+}$ couple, the current began to rise and reached a constant value when the potential was well beyond ϕ_0 . Thus, the whole current–potential curve has a sigmoidal shape.

In the second experiment initially both electrodes were again held at a potential in the reduction region, but a bias of 100 mV was applied between them. Then, both potentials were swept at constant bias in the positive direction (see Fig. 3). This resulted in current potential-curves of a roughly Gaussian shape with a peak near the equilibrium potential ϕ_0 .

Qualitatively these results can be understood within the Gerischer model for electrochemical electron transfer.⁹ Here, an electroactive species is characterized by densities $D_{\text{red}}(\varepsilon)$ of reduced and $D_{\text{ox}}(\varepsilon)$ oxidized states, which have the Gaussian form familiar from Marcus theory. Each Gaussian has a width of $(4\lambda k_{\text{B}}T)^{1/2}$, where λ is the energy of reorganization. At equilibrium, $D_{\text{red}}(\varepsilon)$ is centered at an energy of $-\lambda$ below the Fermi level of the electrode, while $D_{\text{ox}}(\varepsilon)$ is centered at $\varepsilon = \lambda$. For the relation of this model to the Marcus theory, see 11.

There are two equivalent sets of redox systems in these experiments. Since the self-assembled layers have a low conductivity, we may safely assume that both sets are at the same electrode potential; hence the densities $D_{\text{red}}^1(\varepsilon)$ and $D_{\text{red}}^2(\varepsilon)$ are the same, and so are the corresponding densities of oxidized states (see Fig. 4a). A change in the potential of either electrode simply shifts its Fermi level with respect to these densities of states.

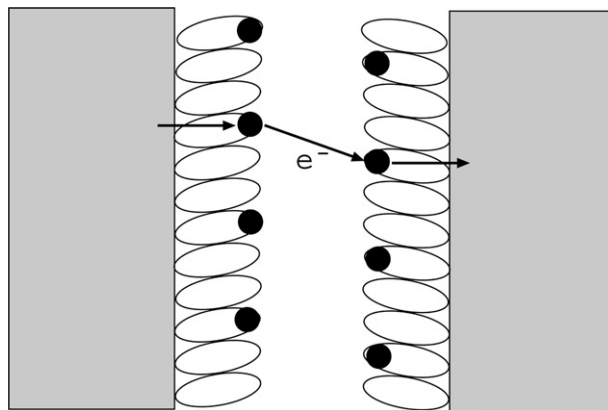


Fig. 1 Electron exchange between two metals involving two adsorbed intermediate states.

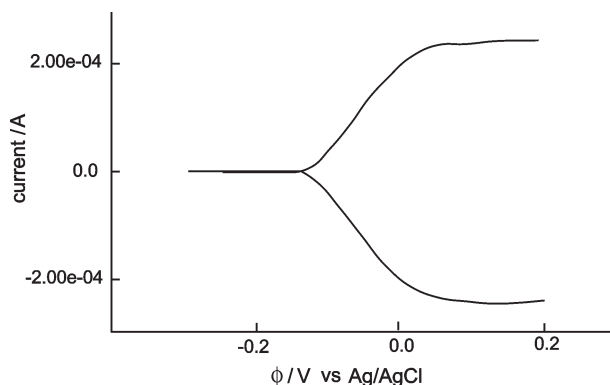


Fig. 2 Currents at both electrodes as a function of the potential of electrode 2; the potential of the first electrode was kept constant at -0.2 V.

Electron transfer occurs from the reduced levels of system 1 to the oxidized levels of system 2, or *vice versa*, and is therefore determined by the product:

$$D_p(\varepsilon) = D_{\text{red}}^2(\varepsilon)D_{\text{ox}}(\varepsilon) = \frac{1}{4\lambda k_B T} \exp\left[-\frac{\lambda^2}{2\lambda k_B T}\right] \exp\left[-\frac{\varepsilon^2}{2\lambda k_B T}\right] \quad (1)$$

where the common Fermi level of the two redox systems has been taken as the energy zero. The current passing between the two tips is then proportional to the integral taken between the Fermi levels of the two electrodes (see Fig. 4b):

$$i \propto \int_{E_1^+}^{E_2^+} D_p(\varepsilon) d\varepsilon \quad (2)$$

From these considerations the two experiments outlined above are easy to understand: In the first experiment we start with the Fermi levels of both metals well above the center of $D_p(\varepsilon)$, so there are no empty states to tunnel into, and the current is zero. As the Fermi level of the second electrode is lowered, empty states become available, and the current rises until the Fermi level has passed well below the maximum of $D_p(\varepsilon)$; all the states pertaining to system 1 are full, those belonging to system 2 are empty, and the current reaches a limiting value.

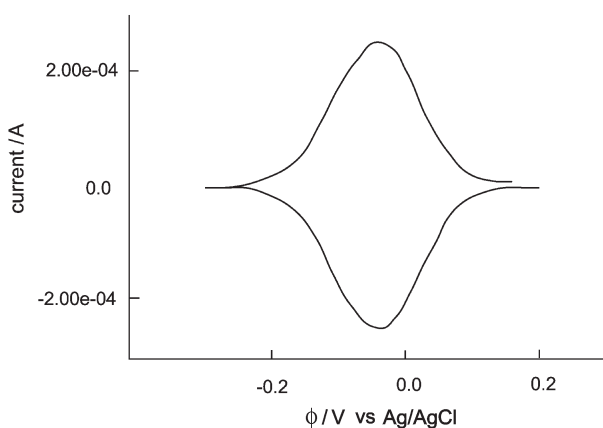


Fig. 3 Currents as a function of the potential of electrode 1; the bias between the two electrodes was kept at 0.1 V.

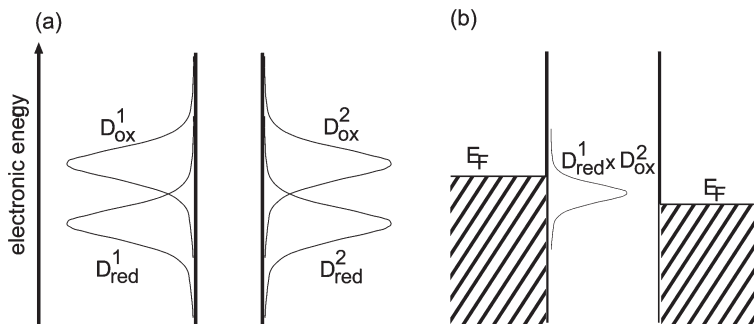


Fig. 4 Indirect electron exchange *via* two identical species in the Gerischer model.

In the second experiment the energy window between the two metal Fermi levels is kept constant and scanned across $D_p(\varepsilon)$. Hence the current practically maps $D_p(\varepsilon)$ with some distortion caused by the finite width of the window. Obviously, the second experiment is particularly suited to determine the energy of reorganization, since $D_p(\varepsilon)$ has a width of $(2\lambda k_B T)^{1/2}$.

3 Model Hamiltonian

While these qualitative considerations suffice to understand the experiments at hand it is desirable to have a quantitative formulation in terms of a model Hamiltonian. For this purpose we introduce the following terminology: We label the two adsorbates '1' and '2'; species 1 is adsorbed on a metal, whose electronic states are labeled by l , species 2 on a metal with electronic states k . Let n_i , $i = 1, 2$, l, k denote the corresponding number operators, and ε_i the associated energies; then the Hamiltonian for the non-interacting electrons is:

$$H_{\text{el}} = \varepsilon_1 n_1 + \varepsilon_2 n_2 + \sum_l \varepsilon_l n_l + \sum_k \varepsilon_k n_k \quad (3)$$

Electrons can be exchanged along the chain: $k \rightarrow 1 \rightarrow 2 \rightarrow l$ and in the reverse direction. This is effected by the transfer Hamiltonian:

$$H_{\text{T}} = \sum_k (V_{k1} c_k^* c_1 + V_{k1}^* c_1^* c_k) + (V_{12} c_1^* c_2 + V_{12}^* c_2^* c_1) + \sum_l (V_{l2} c_2^* c_l + V_{l2}^* c_l^* c_2) \quad (4)$$

where c^* and c denote creation and annihilation operators, and V an appropriate coupling strength.

Electron exchange between the adsorbates involves reorganization of the solvent, and perhaps also of a few inner sphere modes. These are represented by a phonon bath that interacts with the two electronic states on the adsorbates:

$$H_{\text{ph}} = \frac{1}{2} \sum_{\nu} \hbar \omega_{\nu} (p_{\nu}^2 + q_{\nu}^2) - n_1 \left[\sum_{\nu} \hbar \omega_{\nu} g_{\nu 1} q_{\nu} \right] - n_2 \left[\sum_{\nu} \hbar \omega_{\nu} g_{\nu 2} q_{\nu} \right] \quad (5)$$

Here, p_{ν} and q_{ν} denote the dimensionless momenta and coordinates of the phonons, and $g_{\nu 1}$, $g_{\nu 2}$ are the coupling constants for the indicated states.

The total Hamiltonian for our system is given by the sum of the terms listed above:

$$H = H_{\text{el}} + H_{\text{T}} + H_{\text{ph}} \quad (6)$$

From this Hamiltonian, a few quantities can be defined. For the two states we define reorganization energies through: $\lambda_1 = \sum_{\nu} \hbar \omega_{\nu} g_{\nu 1}^2 / 2$, $\lambda_2 = \sum_{\nu} \hbar \omega_{\nu} g_{\nu 2}^2 / 2$. In this paper we will neglect a possible overlap of the solvation spheres and assume $g_{\nu 1} g_{\nu 2} = 0$ for all ν . This assumption is in accord with the simple interpretation in terms of the Gerischer model. The effect of solvation overlap has been considered elsewhere.⁸

The interaction of the two reactive species with the metals on which they are adsorbed can be characterized by:

$$\Delta_1 = \pi \sum_k |V_{k1}|^2 \delta(\omega - \varepsilon_k) \quad \Delta_2 = \pi \sum_l |V_{l2}|^2 \delta(\omega - \varepsilon_l) \quad (7)$$

We employ the so-called wide band approximation,¹² in which Δ_1 and Δ_2 are taken as constant. This is a good approximation when these quantities are much smaller than the electronic bands in the two metals, which is generally the case.

In general, the densities of reduced and oxidized states are governed both by the energy of reorganization λ and by the energy width Δ . However, in our experimental situation the active species are separated from the electrodes by the alkanethiol chains; hence $\Delta \ll \lambda$, and the exact value for Δ that is chosen in any calculation is not important as long as it is sufficiently small.

As is common in electron-transfer theory, we have neglected spin. This is permissible if the energy widths Δ_1 and Δ_2 are much smaller than the repulsive interaction energy between two electrons on the same valence orbital.

4 Model calculations

A full treatment of our model in terms of scattering theory has been given elsewhere.⁸ This includes also quantum effects such as inelastic electron transfer, which can be derived from our model Hamiltonian but will not be considered here. In the following we will limit ourselves to elastic transitions involving only classical modes, which can explain the experimental data at hand.

The total reaction comprises three electronic transitions. In accord with our qualitative discussion presented above we consider the case in which the coupling between the two adsorbates is weaker than the interaction of the two adsorbates with their respective substrates. This entails electronic equilibrium between the adsorbates and their substrates, and the two states 1 and 2, including their solvation shells, move effectively on their adiabatic free-energy surfaces, which are given by:¹³

$$U_i(q_i) = (\varepsilon_i - \lambda_i q_i) \langle n_i \rangle + \lambda_i \frac{q_i^2}{2} + \frac{A_i}{2\pi} \ln \frac{(\varepsilon_i - \lambda_i q_i)^2 + A_i^2}{\varepsilon_i^2 + A_i^2} \quad (8)$$

where the $i = 1, 2$, and q_i denotes the generalized solvent coordinate associated with the state i . From standard statistical mechanics we can calculate the probability $P_i(x_i)$ that at a particular time the system i is at a coordinate x_i .

Since the two adsorbates are chemically identical, we have $\lambda_1 = \lambda_2$, $A_1 = A_2$, $\varepsilon_1 = \varepsilon_2$, but in general $\langle n_1 \rangle \neq \langle n_2 \rangle$ since the Fermi levels of the two electrodes differ by the bias potential.

To be specific, we consider electron transfer from system 1 to system 2. The corresponding current is then given by:

$$i \propto \int P_1(x) \langle n_1 \rangle P_2(x) (1 - \langle n_2 \rangle) dx \quad (9)$$

where we have used the fact that electron transfer occurs elastically from an occupied to an empty state.

With the aid of these equations, we have performed model calculations corresponding to the experimental data. In Fig. 5 we show the effect of raising the bias while keeping the potential of electrode 1 fixed. In accord with the experiments and with the qualitative calculations, the current reaches a constant value for a large bias, and has an overall sigmoidal shape.

Of greater interest is the variation of the current with electrode potential at constant bias (see Fig. 6). The current response is roughly Gaussian, its width is the wider, the larger the energy of reorganization λ , and, of course, the larger the bias. The dependence on λ makes it possible to compare experimental and theoretical curves, and extract the energy of reorganization from the data. As shown in Fig. 7, the experimental data can be fitted quite well to a value of $\lambda \approx 0.4$ eV, which is a reasonable value for this redox system.

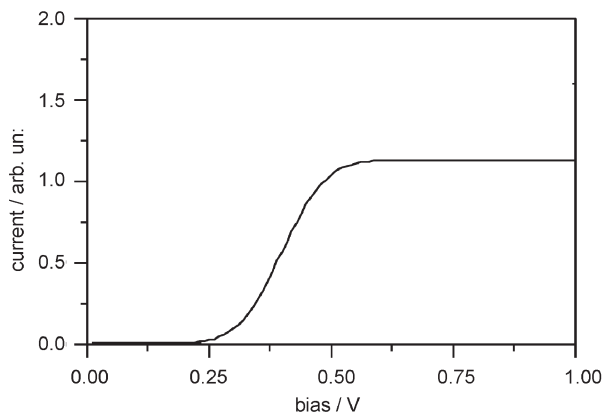


Fig. 5 Calculated current (in arbitrary units) as a function of the applied bias. At zero bias the Fermi levels of both electrodes are 0.2 eV above the Fermi level of the adsorbates. System parameters: $\Delta_1 = \Delta_2 = 0.001$ eV; $\lambda = 0.2$ eV.

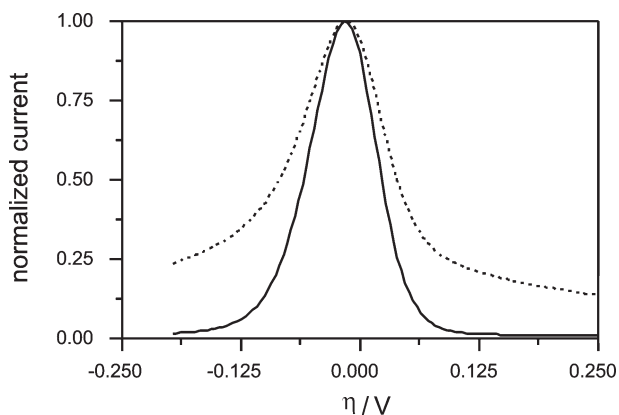


Fig. 6 Calculated current as a function of the overpotential applied to the electrode 1; the bias was set to a constant value of 0.1 eV. Full lines: $\lambda = 0.2$ eV; dotted lines: $\lambda = 0.3$ eV; other parameters as in Fig. 5.

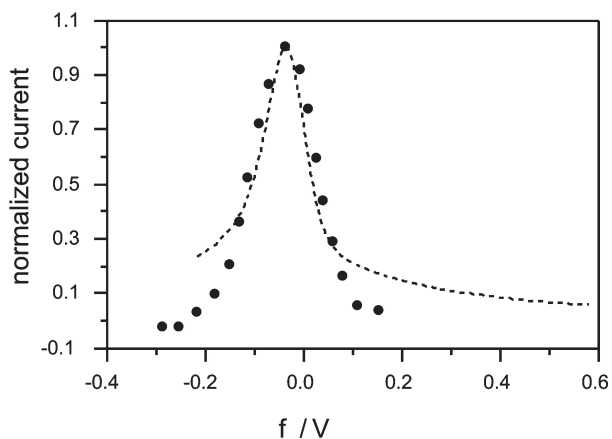


Fig. 7 Comparison between experimental and theoretical data. In the calculations, $\lambda = 0.4$ eV; other parameters as in Fig. 6.

5 Conclusion

Advances in the preparation of self-assembled monolayers and in the formation of pairs of electrode with an ultrathin gap has made it possible to study indirect electron exchange involving two intermediate species. Such system exhibit current-potential characteristics that could, in principle, be used for molecular electronics. In particular, scanning the bias can result in diode-like behavior. The presented experimental results can be understood within a semiclassical version of a theory for such processes proposed by one of us.⁸

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References

- 1 *Molecular Electronic Devices*, ed. F. L. Carter, Marcel Dekker, New York, 1982.
- 2 *Molecular Electronics: Science and Technology*, ed. A. Aviram and M. Ratner, *Ann. NY Acad. Sci.*, 1998, vol. 852.
- 3 A. Aviram and M. Rattner, *Chem. Phys. Lett.*, 1974, **29**, 277.
- 4 *Molecular Electronics II*, ed. A. Aviram, M. Rattner and V. Mujica, *Ann. NY Acad. Sci.*, 2002, vol. 960.
- 5 A. Nitzan, *Annu. Rev. Phys. Chem.*, 2001, **52**, 681.
- 6 C. Lambert, G. Nöll and J. Schelter, *Nat. Mater.*, 2002, **1**, 69.
- 7 A. M. Kuznetsov and J. Ulstrup, *J. Chem. Phys.*, 2002, **116**, 2149.
- 8 W. Schmickler, *Chem. Phys.*, in press.
- 9 H. Gerischer, *Z. Phys. Chem. (Munich)*, 1969, **26**, 21.
- 10 E. Tran, A. E. Cohen, M. A. Rampi, W. Schmickler and G. M. Whitesides, manuscript in preparation.
- 11 W. Schmickler, *Interfacial Electrochemistry*, Oxford University Press, New York, 1996.
- 12 R. Brako and D. M. Newns, *Rep. Prog. Phys.*, 1989, **2**, 655.
- 13 W. Schmickler, *J. Electroanal. Chem.*, 1986, **204**, 31.