Electron Transfer Dynamics of Bistable Single-Molecule Junctions

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Received May 28, 2006; Revised Manuscript Received August 18, 2006

ABSTRACT

We present transport measurements of single-molecule junctions bridged by a molecule with three benzene rings connected by two double bonds and with thiol end-groups that allow chemical binding to gold electrodes. The I−V curves show switching behavior between two distinct states. By statistical analysis of the switching events, we show that a 300 meV mode mediates the transition between the two states. We propose that breaking and reformation of a S−H bond in the contact zone between molecule and electrode explains the observed bistability.

Single-molecule transistors and tunnel devices have been a very active research field over the past few years.1−15 However, there are still a large number of unresolved experimental questions relating to the geometry of these devices. Diagnosis in terms of vibrational states has been an important recent tool in molecular electronic transistors and inelastic tunneling spectroscopy measurements1,4,11,15−19 in verifying the structure of the junctions. Because of intrinsic instabilities, many of the single-molecule devices also show switching behavior between two distinct chemical configurations. The statistics and mechanisms of the switching dynamics in single-molecule devices have not been understood in detail. In this paper, we present experiments on single-molecule devices exhibiting switching behavior and we show how the statistics of the bistability can be used to deduce information about the processes that give rise to this phenomenon.

We have fabricated nanogap devices and measured low-temperature current—voltage characteristics using the method detailed in refs 6 and 20. The electrodes were prepared by deposition of gold onto an Al2O3 covered gate electrode through a lithographically defined mask. By using an oblique evaporation angle, we fine-tune the gap between the source and drain electrodes to a few nanometers. Both the substrate and the evaporator were mounted in a vacuum chamber immersed in liquid helium. Subsequently, in the same vacuum cycle, the molecules were evaporated onto the surface in a submonolayer concentration. Then the substrate temperature was raised to 30 K to activate a surface diffusion of molecules, while measuring the nanogap conductance, as described in ref 7. After a single jump in nanogap conductance (corresponding to the first molecule being captured in the gap) the sample was cooled back to 4 K and transport measurements were performed at this temperature.

Here we report on junctions bridged by molecules, which are similar to the previous work by some of us,6 but shorter (three instead of five benzene rings). The molecule is an oligophenylenevinylene derivative, which has been end-capped by acetyl-protected thiol groups, which is also different from the end cap used in ref 6. The molecule is denoted OPV3 below, see Figure 1. The synthesis of this class of molecules has been reported elsewhere.21 The acetyl protecting group allows direct chemical bonding between sulfur and gold at room temperature. For our low-temperature deposition, we find consistently large conductances (see Figure 1) on the order of one tenth of the conductance quantum indicating that chemical binding also takes place at cryogenic temperatures, possibly mediated by current-induced local heating in the contacts (cf. bottom of Figure 7). The devices show no or only very weak gate effects consistent with good electrical contact with the electrodes. This is in contrast to previous measurements reported in ref 6, where the chemical binding between gold and the thiol end cap was inhibited by a stable protective group. This most likely explains the much larger transmittance between electrode and molecule and, hence, that the present experiments are not in the Coulomb blockade regime and show little or no gate effect.
The $I-V$ curves are slightly nonlinear and show switching behavior between two distinct current curves. Here we show that the binding to the contact is not fully relaxed and that this is the cause of the instability.

We have investigated more than 10 nanogap samples bridged by OPV3 molecules. Many of the samples show switching behavior, indicative of two-level instabilities. Typically, the samples have several switching transitions at different critical biases. Here we focus on the samples that have clearly separated switching points in the bias voltage window in order for a quantitative analysis to be possible. For these devices, we have identified two types of switching phenomena.

**Type I.** Examples of the first type are shown in Figures 2 and 3. For these samples, the switching between states with different conductance values occurs only once within the bias window studied. The transition happens for increasing bias sweeps. This means that at some critical bias values transitions to other states are possible, but once escaped from the initial (metastable) state the system cannot make transitions back to the original state. For large biases of opposite sign the switch can, however, be reset (cf. Figure 3).

**Type II.** An example of this type is shown in Figure 4. For these types of switching phenomena, the transitions between the two states occur in both directions. For example, when sweeping the voltage in the negative direction in Figure 4 the system switches several times between the two current branches and ends up in one of them with some probability.

Next, we describe the basics of the model that we are going to use to understand the statistics of the switching events and the underlying mechanisms. The two states are denoted by 1 and h for low and high conducting states, and the corresponding probabilities to be in one of the two are denoted $P_1$ and $P_h$. These can be determined from a simple rate equation expressing the rate of change from each of them. For $P_1$, we have

$$\frac{dP_1}{dt} = -\Gamma_{1\rightarrow h}(V(t))P_1 + \Gamma_{h\rightarrow 1}(V(t))P_h$$

with a similar equation for the low state, but because $P_1 + P_h = 1$ we need only solve a single differential equation. Here $\Gamma_{1\rightarrow h}$ (and $\Gamma_{h\rightarrow 1}$) are the rates for going from state l(h) to state h(l). The $I-V$ characteristics are recorded by scanning the bias voltage at a certain velocity so that $V(t) = ut$, and the rates $\Gamma_{1\rightarrow h}$ also depend on time. We can therefore use voltage instead of time as the variable.
in order for the thermal activation scenario to explain the behavior.

The voltage dependence appears in eq 1, and we obtain

$$\frac{dP_l(V)}{dV} = -\Gamma P_l(V) + \Gamma_{h\rightarrow l}(V), \quad \Gamma = (\Gamma_{h\rightarrow l} + \Gamma_{l\rightarrow h}) \quad (2)$$

This equation has a formal solution in terms of the initial voltage

$$P_l(V) = p(V)\left\{ \int_{V_l}^{V} \frac{dV'}{\mu} \int_{V}^{V'} p(V') \Gamma_{h\rightarrow l}(V') + P_l(V') \right\} \quad (3a)$$

$$p(V) = \exp\left( - \int_{V_l}^{V} \frac{dV'}{\mu} \Gamma(V') \right) \quad (3b)$$

For the actual rate appearing in eq 3, we will consider two types of transitions. (a) The transition from one state to the other is thermally activated. The voltage dependence appears because the potential landscape is a function of voltage and, in particular, at a critical voltage the ground state changes from one configuration to another. (b) The transitions are current-induced because of excitations of the molecular vibrations by the incident current. The excited vibrational states have a larger overlap with the other state, which enhances the switching.

For situation a, the rate for making transitions from one state to the other is taken to be of the form

$$\Gamma_{\text{thermal}}(V) = \omega_0 \exp[ (W - qV)/k_B T] \quad (4)$$

due to the bias voltage, and $\omega_0$ is the attempt frequency in the metastable well.

For situation b with vibrational-assisted transitions, the rate for making transitions due to emission of a single vibron is of the form

$$\Gamma_{\text{cur-ind}}(V) = \frac{\gamma G(|V| - \Omega/e)}{e} \Theta(|V| - \Omega/e) \quad (5)$$

when assuming a constant density of electronic states. Here $G$ is the conductance, $\Omega$ is the frequency of the vibration, and $\gamma$ is an effective electron–vibron coupling. For other models such as the one discussed by Gao, Persson, and Lundqvist, it is necessary to have strong nonequilibrium distribution of the phonon to induce transitions. If the oscillator state where transitions become possible is given by $n$, then the transition rate will acquire the approximate form (when $\Omega \ll eV$)

$$\Gamma_{\text{cur-ind,n}}(V) = \frac{GV/|V|^n}{e} \quad (6)$$

where $V_c$ is a parameter that depends on the ratio of the damping rate to the current level. More detailed studies of the nonequilibrium vibron distribution function has been done. With these ingredients, we now attempt to understand the observed switching behaviors.

First, we discuss the device with Type I switching in Figure 2. Because there is only one transition for each bias voltage sweep, we need only consider the rate of transitions from the 1 to h states. Once we find the distribution function $P_l(V)$, we can also find the probability for a transition at a given voltage and compare with the observed data. The probability is found by setting $\Gamma_{h\rightarrow l} = 0$, $V_l = 0$, and $P(l)(V) = 1$ in eq 3. The probability distribution for switching at the bias voltage $V$ then becomes $\Gamma_{1\rightarrow l} P_l(V)$. Assuming a simple thermal transition rate as in eq 4, we get for the switching distribution

$$\left( \frac{dP_l}{dt} \right)_{\text{thermal}} \propto \exp(-W - qV/k_B T) \quad (7)$$

where

$$P_l(V) = \exp\left( \frac{k_B T}{\Lambda} \left[ 1 - e^{qV/k_B T} \right] \right) \quad (8)$$

and

$$\frac{1}{\Lambda} = \frac{\omega_0 e^{-W/k_B T}}{qa} \quad (9)$$

Equation 7 can now be compared with experimental histograms directly. This is done in Figure 2, where eq 7 is normalized and plotted (red curve) using two fitting parameters $q = 0.05e$ and $\Lambda = 6.4 \times 10^{11}$ meV. The fit is seen to reproduce the data very well.
Using the alternative current-induced transition rate in eq 5, where the transition is assumed to take place due to absorption of a single quantum of a higher energy vibration, that is, a vibrational energy $\Omega$ near switching voltage, one gets a different result. Solving the equations as above, one then obtains the resulting distribution function

$$\left(\frac{dP}{dt}\right)_{\text{cur-ind}} \propto \left(V - \frac{\Omega}{e}\right) \Theta\left(|V| - \frac{\Omega}{e}\right) \exp\left(-\frac{G(|V| - (\Omega/e))^2}{2eu}\right) \quad (10)$$

The best fit using the distribution is shown in Figure 2 (green curve). The parameters are $G/(2eu) = 0.006$ (meV)$^{-2}$ and $\Omega = 200$ meV. Clearly, this model is not capable of reproducing the long tail toward smaller voltages seen in the experimental data. We have also tried to use the Gao et al. expression (eq 6) and, in fact, a good fit can be done, but for unrealistic parameters $n = 25$ (and $V_0 = 209.5$ mV). For such high value of $n$, one should instead consider a full solution of the nonequilibrium distribution, which is likely to approach a thermal-like distribution. However, because the thermal fit in eq 7 gives good agreement without an elevated temperature, we infer that the mechanism suggested by Gao et al. is not relevant here. We have, in fact, also attempted to fit the histograms in Figure 2 by using a higher temperature. A slightly increased temperature can also be made to fit the data, but not more than 10% increase in temperature could be allowed in order to fit the data. To conclude on the Type I switching, we have successfully accounted for the observed switching probabilities versus voltage using a thermal activation model. Given this agreement, it is therefore very likely that the potential landscape of the two-level systems depends on voltage as illustrated in Figure 3 in the top panel, where, at some bias voltage, the ground state changes from conformation B to A, at which point B becomes metastable.

At still higher bias voltages, the minimum corresponding to state B becomes shallow and the molecule switches to A. In ref 11, similar $I-V$ curves and switching behavior was observed, but in this work the interpretation of the switching mechanism was different for positive and negative bias. The parameters extracted above suggest that the bias-voltage-dependent energy difference between states A and B is on the order of $0.05e$ times the switching voltage, that is, 10 meV, which is a small, but not unreasonable, energy scale for atomic or molecular rearrangements.

Second, we now turn to discuss the device with Type II switching in Figure 4. As explained above, the main difference from the Type I case is that the switching happens several times, not only once. Above ~400 mV, the OPV3 is in a high conducting state. When sweeping the voltage from high to low bias voltage, the molecule switches between two configurations a number of times and eventually freezes in one of the two possible states. When sweeping the voltage in the opposite direction, the molecule always ends up in a high conducting state. As is evident from Figure 4, the switching rate increases with increasing bias voltage. It also appears that for bias voltage above ~400 mV a switching to the low conducting state is immediately followed by the switching back to high conducting state, indicating that the time spent in the low conducting state is too short for the measurement system to resolve it. Therefore, the bandwidth of our measurement setup unfortunately does not allow us to study the switching statistics, as we did above for the sample with Type I switching.

Instead, we will do a different comparison with the model, namely, compare measured current−voltage characteristics averaged over many traces with the computed distribution. The current is simply extracted as

$$\langle I(V) \rangle = P_h(V)G_hV + P_l(V)G_lV \quad (11)$$

where $G_h$ and $G_l$ are the conductances of the high and low states, respectively. When modeling the behavior for this device, we should in principle include both thermally and current-induced transitions for both switching directions. We have found that it is only possible to reproduce the observed behavior if the $l \rightarrow h$ transitions are thermally activated, whereas the $h \rightarrow l$ transitions are tunneling activated. This...
means that we use $\Gamma_{l \rightarrow h}$ of the form in eq 4 and $\Gamma_{h \rightarrow l}$ of the form given in eq 5. With this input, we calculate the average current in the positive sweep direction starting in the state $l$, by numerical integration of eq 3. This is the red curve in Figure 5. The derivative of this curve (purple curve) is used to fix the effectively four independent parameters. We find the following parameters

\[ \frac{\mu}{\omega_0} \exp\left(\frac{W/k_B T}{k_B T}\right) = 5.7 \times 10^{-10} \text{ mV} \quad (12a) \]
\[ \Omega = 300 \text{ meV} \quad (12b) \]
\[ q = -0.021e \quad (12c) \]
\[ \gamma = 1.1 \times 10^{-12} \quad (12d) \]

using the measured value for the conductance ($G = 20 \mu S$), $T = 4.2$ K, and $u = 53$ mV/s. As above, we find that the potential of the well shifts with the bias voltage corresponding to a small fraction of an electron charge, which again is a reasonable value of the effective charge on the molecule. The extracted value of $\gamma$ implies that one out of $10^{12}$ tunneling electrons induces a switching event. This parameter describes the combined effect of Franck–Condon overlap factors and hence also the effects of dissipation. It is therefore very difficult to get a quantitative estimate of this parameter and we regard it merely as a phenomenological parameter.

Finally, the active vibrational level is found to have an energy near 300 meV, which we comment on below. When performing the fitting procedure we find that $I-V$ characteristic is very sensitive to the parameters in eq 12. In fact, we estimate the value of the onset of the current switching is accurate within 10%.

The analysis thus points at a mode around 300 meV as being responsible for the vibrational assisted switching. For the organic molecule in our experiments, only one type of vibration exists in a wide energy window around 300 meV, namely, a H–S vibration. We speculate that this remarkable result is evidence that a proton is attached to the sulfur bound to the gold electrode, creating a contact with a slightly higher contact conductance then the unprotonated sulfur contact (cf. Figure 7). Once the proton is attached to $S$, it can detach when the successive tunneling electrons emit a H–S vibron. This scenario also explains why tunneling activation is only possible in one direction. According to the model, the reattachment of the proton can only happen via thermal excitation. From the numbers in eq 12, we estimate the barrier to be $10^{-20}$ meV. A plausible mechanism for this chemistry occurring in the contact zone is discussed below (cf. Figure 7).

With the same parameters we now compute the average $I-V$ when starting in the h state (Figure 5) with reasonable good agreement with measured average curve. We also compute the average current when sweeping from high to low bias and, furthermore, compared to the derivative (the red curve in the bottom panel of Figure 5). Again, good agreement is seen. We can therefore understand the full behavior of the observed switching statistics using the simple model and the parameters in eq 12.

As a note of warning, we remark that the averaged $I-V$ characteristics have some resemblance to inelastic tunneling spectroscopic (IETS) curves. Experiments where the switching behavior is not resolved could therefore incorrectly be interpreted as showing IETS features. This
clearly shows that information about the dynamics of the switching can be of paramount importance for the understanding of the mechanisms behind the structures observed in the averaged $I-V$ curves.

We have also plotted the calculated occupations in Figure 6. For the red curve, the evolution starts from a metastable state in state $h$ can be excited by the electron-transfer reaction as described in the text, resulting in switching between states $h$ and $l$. The excitation process is activated and hence the red curve will first drop down to zero, and later will follow the green curve. For a faster sweep rate, the kink on the red curve cannot be resolved. The measurements presented in Figure 5 have been recorded at a sweep rate, where the transition region is well resolved.

In summary, we have presented experimental results for single-molecule devices showing switching behavior between two metastable states. We have analyzed the data in terms of a rate equation, using both thermally activated and current-induced transition rates. For future research in single-molecule devices, which often show this type of switching behavior, it is therefore important to make careful studies of the statistics, that is, as a function sweep rate, to gain information about the stability of the nanojunction.

We have been able to conclude which mechanisms are effective in the transitions and for the first time propose a plausible reaction scheme for the contact zone chemistry of the ubiquitous thioesters that account for the deprotection of the thiol and offer an explanation for the presence of a vibrational mode at $\sim 300$ meV. Further evidence is needed to substantiate this proposal, which we are currently planning to test through exchanging hydrogen with deuterium in the acetyl group and by calculations of the energy landscape inferred from the models presented here.

Acknowledgment. We are grateful to F. Lombardi, T. Bauch, K. Bechgaard, and L. Henriksen for inspirational discussions. The work was supported in part by the European Commission through project FP6-003673 CANEL of the IST Priority. (The views expressed in this publication do not necessarily reflect the official European Commission’s view on the subject.) Funding from the Danish Research Councils and the Danish Nanotechnology Program and Swedish SSF and VR is gratefully acknowledged.

Note Added after ASAP Publication. This paper was originally posted on the Web September 21, 2006. An author name was added to references 5 and 12. The corrected version was published ASAP September 25, 2006.

References


NL0612087