

# Cotunneling Model for Current-Induced Events in Molecular Wires

Thorsten Hansen,<sup>\*,†</sup> Vladimiro Mujica,<sup>†,‡</sup> and Mark A. Ratner<sup>†</sup>

*Department of Chemistry and International Institute for Nanotechnology, Northwestern University, 2145 Sheridan Road, Evanston, Illinois 60208-3113, and Argonne National Laboratory, Center for Nanoscale Materials, Argonne, Illinois 60439-4831*

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## ABSTRACT

Many phenomena in molecular transport junctions involve transitions between electronic states of the molecular wire, and, therefore, cannot be described adequately using the Landauer picture. We present a model for cotunneling processes in molecular wires. These are coherent second-order processes that can be observed at low temperatures. As an example, we consider the STM-induced dissociation of acetylene. The large voltage threshold for dissociation observed experimentally is naturally accounted for within the cotunneling model.

Most theoretical descriptions of electrons tunneling through molecules, such as the generalization of the Landauer equation used in molecular electronics,<sup>1</sup> share a common feature. They are effective one-electron descriptions that treat the electronic structure either uncorrelated, at the Hartree–Fock or tight-binding level, or correlated, using DFT. Transport in the elastic regime is then assumed to occur through molecular orbitals on a single electronic potential energy surface.

Regardless of the inclusion of correlation, effective one-electron descriptions have one major drawback: They consider one electronic state at the time, usually the ground state of either the neutral molecule or an ionic species. This is in sharp contrast to numerous experiments in recent years that demonstrate various effects, for example, switching in molecular wires, that clearly involve several molecular states.<sup>2,3</sup> We present a model for the description of coherent electron current in molecular junctions that include both an elastic tunneling and an inelastic cotunneling component. The many-electron states of the molecule form the basis for our description; thus, multiple states are naturally accounted.

Electronic cotunneling events are taken here to mean coherent second-order processes that are electronically inelastic; that is, the molecule makes a transition from one potential energy surface to another. This is in contrast to vibrationally inelastic events that transfer energy to the molecular vibrations yet leave the molecule on the same potential energy surface. Cotunneling processes are significant when incoherent first-order hopping processes are suppressed. The ionic states are assumed to be energetically

out of reach and will only appear as virtual intermediate states in the cotunneling processes. The concept of cotunneling was originally invoked to describe leakage currents through quantum dots in the Coulomb blockade regime.<sup>4–6</sup>

The theory is a scattering theory, where the current,  $I = -ew_{fi}$ , is described in terms of a transition rate,  $w_{fi}$ , obtained from a generalized Fermi's golden rule. The initial and final states,  $i$  and  $f$ , involve both the electrodes and the molecular bridge. We show that the description of cotunneling processes amounts to approximating the transition matrix by the self-energy,  $\Sigma_{fi}^{ret}$ , introduced by the molecule–electrode coupling. The self-energy therefore plays the role of an effective perturbation:

$$w_{fi} = \frac{2\pi}{\hbar} |\Sigma_{fi}^{ret}|^2 \delta(E_i - E_f) \quad (1)$$

This is the key element of our theoretical work, since it represents the link between the electron transport and the mixing of electronic states in the molecular bridge that can lead to chemical reactions and other processes involving energy transfer between the tunneling electron and the molecule. This is an important generalization of simpler one-electron models that consider only elastic tunneling, where the role of the interaction with the continua of levels in the electrodes is limited to broaden and shift the molecular levels.

A preliminary discussion of our model was presented in ref 7, where we speculated that the cotunneling mechanism provides a qualitative explanation for the most conspicuous features of STM-induced unimolecular reactions as reported for the dissociation of acetylene in ref 8. In this contribution, we formulate our model in a more general way and analyze in detail the experimental information to provide a quantitative estimate of the parameters of the theory. In this way the voltage threshold, the different time scales, and the

\* Corresponding author. E-mail: thorsten@chem.northwestern.edu.

<sup>†</sup> Northwestern University.

<sup>‡</sup> Argonne National Laboratory.

isotope effect observed in the experiment are interpreted in a consistent way.

Using the STM-induced dissociation of acetylene on a copper surface, as reported in ref 8, as a case study, we show how the large voltage threshold of several electronvolts is naturally related to the excitation energy between the ground state of the molecule and a doorway state. The energy for this transition is provided by the cotunneling process. Following the excitation, the dissociation proceeds via the coupling between the doorway state and a radical electronic state, which is strongly stabilized by the metal surface. A simple kinetic model is then used to discuss the timescales of the dissociation process. The unusually large isotope effect observed in the experiment is also explained as primarily due to the difference in geometries and dipole moments of the molecular states of the H- and D-substituted species on the surface.

Current-induced events in molecular transport junctions is an actively studied topic both experimentally<sup>8–20</sup> and theoretically.<sup>21–30</sup> For example, Seideman and co-workers discuss how the current can trigger nuclear dynamics via the electron–phonon coupling, thus inducing rotations, conformational changes, or unimolecular chemical reactions in the molecular junction.<sup>21–25</sup>

Cotunneling provides a complementary mechanism for dynamic events that, so far, has not been discussed in the context of molecular transport junctions. The transfer of kinetic energy of the tunneling electron to the molecule is analogous to the vertical excitation invoked in photon-induced gas phase reactions, but it is mediated by the electrode via the self-energy. Physically, our model combines electron transport and energy transfer in a way that is suitable for the description of surface chemical reactions. This kind of description may have important implications for nano-electrochemistry and nanocatalysis.

**Cotunneling Model.** We shall consider a molecular wire that in the relevant regimes of voltage, gate voltage, temperature, and so forth can be found in a number of neutral quantum states. In the following, we shall work with two molecular states,  $|a\rangle$  and  $|b\rangle$ , for simplicity, but generalization to more states is straightforward.

If the charged states of the molecule are energetically accessible, redox processes will occur and the junction can conduct by incoherent hopping processes. This is the regime of nanoelectrochemistry. At sufficiently low bias, or if the charged states are higher in energy, the incoherent hopping of electrons will be suppressed. This is analogous to the low-bias situation in the Coulomb blockade regime of metallic quantum dots.<sup>31</sup>

Any current in this regime is the result of coherent processes that are higher order in the, presumably weak, metal–molecule coupling. We shall consider only the lowest order processes, being second order in the metal–molecule coupling. First, there are elastic processes that leave the molecule in the same state, also known as superexchange processes. Second, there are inelastic processes that induce transitions between the molecular states. These are the cotunneling processes. This choice of words implicitly

assumes that the states  $|a\rangle$  and  $|b\rangle$  differ in energy. This, of course, need not be the case; they could be degenerate and differ in some other quantum number. This case is also naturally accounted for in our model.

We think of the Hamiltonian for the entire system as a sum of three parts,

$$H = H^{\text{lead}} + H^{\text{mol}} + V \quad (2)$$

corresponding to the leads, the molecule, and the electrode–molecule coupling, respectively.

The electrons in the leads are described in the conventional way, using operators  $c_k^\dagger$  and  $c_k$  that create or annihilate electrons in single-electron states indexed by  $k$ . The lead Hamiltonian reads

$$H^{\text{lead}} = \sum_{k \in L} (\epsilon_k - \mu_L) c_k^\dagger c_k + \sum_{k \in R} (\epsilon_k - \mu_R) c_k^\dagger c_k \quad (3)$$

where  $\mu_L$  and  $\mu_R$  denote the chemical potentials in the left and right leads, respectively.

In the molecular Hamiltonian we include not only the two molecular states of interest,  $|a\rangle$  and  $|b\rangle$ , but also the two charged states, a cationic state  $|n - 1\rangle$  and an anionic state  $|n + 1\rangle$ , where  $n$  is the number of electrons in states  $|a\rangle$  and  $|b\rangle$ . The two charged states will appear as virtual intermediate states during superexchange and cotunneling processes. The molecular part of the Hamiltonian is expressed as

$$H^{\text{mol}} = \sum_{j=a,b,n+1,n-1} E_j |j\rangle \langle j| \quad (4)$$

This Hamiltonian is defined in Fock space, in that it includes states that differ in the number of electrons. In general, we could write each many-particle state as a superposition of Slater determinants,  $|\varphi_i\rangle = c_{i_1}^\dagger c_{i_2}^\dagger \dots c_{i_m}^\dagger |0\rangle$ , where  $c_{i_j}^\dagger$  creates an electron in the  $j$ th molecular orbital used in the construction of the  $i$ th Slater determinant, for example,

$$|a\rangle = \sum_i a_i |\varphi_i\rangle = \sum_i a_i c_{i_1}^\dagger c_{i_2}^\dagger \dots c_{i_m}^\dagger |0\rangle \quad (5)$$

where  $a_i$  is a coefficient, but we use the projection, or Hubbard, operators because the results derived below do not rely on the details of the electronic structure and are therefore valid for the exact many-particle states or approximate states at any given level of electronic-structure theory.

Because of the differing choices of representation above, the electrode–molecule coupling Hamiltonian is an unconventional mixture of two types of operators. We write it as a sum of two terms,  $V = V^{\text{cat}} + V^{\text{an}}$ , which are given by

$$V^{\text{cat}} = \sum_{j=a,b} \sum_{k \in L,R} \{ V_{kn-1,j} c_k^\dagger |n-1\rangle \langle j| + V_{kn-1,j}^* |n-1\rangle \langle k| \} \quad (6)$$

$$V^{\text{an}} = \sum_{j=a,b} \sum_{k \in L,R} \{ V_{kj,n+1} c_k^\dagger |n+1\rangle \langle j| + V_{kj,n+1}^* |n+1\rangle \langle k| \} \quad (7)$$

The two terms, eq 6 and eq 7, correspond to the coupling of the neutral molecular states,  $|a\rangle$  and  $|b\rangle$ , to the cationic,  $|n - 1\rangle$ , and anionic state,  $|n + 1\rangle$ , respectively. Each individual term describes a virtual charge transfer process to or from the molecule. The term  $V_{kn-1, a} c_k^\dagger |n - 1\rangle \langle a|$ , for instance, describes the virtual oxidation of state  $|a\rangle$  to the cation  $|n - 1\rangle$  accompanied by the creation of an electron in the electrode. The Hamiltonian, eq 2, with coupling terms as in eq 6 and eq 7 is also known as the ionic model.<sup>32</sup>

*Current.* In a molecular transport junction, we can think of the current as the net result of individual scattering events that take electrons across the junction. We shall construct system wide scattering states and calculate the transition rates among them using a generalized Fermi's golden rule,

$$w_{fi} = \frac{2\pi}{\hbar} |T_{fi}|^2 \delta(E_i - E_f) \quad (8)$$

Here,  $T$  is the transition matrix and the indices  $i$  and  $f$  indicate the initial and final state of a particular scattering event. The contribution of this transition to the current is then simply given by

$$I = -ew_{fi} \quad (9)$$

The scattering states are constructed as direct products of many-particle states describing each part of the junction. As an example, we can write

$$|i\rangle = |L\rangle |a\rangle |R\rangle \quad (10)$$

$$|f\rangle = c_l |L\rangle |b\rangle c_r^\dagger |R\rangle \quad (11)$$

where  $|L\rangle$  and  $|R\rangle$  represent the Fermi sea of electrons in the respective electrode. This choice of initial and final states corresponds to a situation where an electron is transferred from a state  $l$  in the left electrode to a state  $r$  in the right. If the bias is reversed or at higher temperatures, different or additional types of initial and final states must be considered.

The transition rate,  $w_{fi} \equiv w_{ba}^{lr}$ , from  $|i\rangle$  to  $|f\rangle$  depends on the electrode indices  $l, r$ . To obtain the full transition rate of the molecule from state  $|a\rangle$  to  $|b\rangle$ , we must sum over all available electron states,

$$w_{ba} = \sum_{lr} w_{ba}^{lr} \quad (12)$$

*Transition Matrix.* The transition matrix,  $T(E)$ , for a scattering process can be defined as

$$T(E) = V + VG^{ret}(E)V \quad (13)$$

Here,  $G^{ret}$  is the retarded Green's function with respect to the full Hamiltonian,

$$G^{ret}(E) = \frac{1}{E - H + i\eta} \quad (14)$$

where  $\eta = 0+$  is a positive infinitesimal. Likewise,  $G_0^{ret}(E)$  is the retarded Green's function with respect to the uncoupled Hamiltonian,  $H_0 = H^{lead} + H^{mol}$ .

For a coupling  $V$  as in eq 6 and eq 7, the retarded Green's function with respect to the full Hamiltonian,  $G^{ret}(E)$ , can be expanded as

$$G = G_0 + G_0VG_0 + G_0VG_0VG_0 + \dots \quad (15)$$

Here, however, we consider tunneling through a molecule in a situation where the charging energy is large. Thus, both the initial and the final states are neutral, and the charged states appear only virtually. And since the perturbation  $V$  changes the charge on the molecule, only terms of even order in  $V$  will appear the expansion of the Green's function.

$$G = G_0 + G_0VG_0VG_0 + G_0VG_0VG_0VG_0 + \dots \quad (16)$$

Defining the retarded self-energy,  $\Sigma^{ret}(E) = VG_0^{ret}(E)V$ , we

can rewrite eq 16 as a Dyson's equation,

$$G = G_0 + G_0\Sigma G \quad (17)$$

Introducing the expansion 16 into expression 13 for the transition matrix and disregarding the first term,  $V$ , lead to

$$T = VGV = VG_0V + VG_0VG_0VG_0V + \dots \quad (18)$$

When we consider cotunneling processes, meaning including only the first term of the expansion 18, we have  $T(E) = \Sigma^{ret}(E)$ . And the generalized Fermi's golden rule now reads

$$w_{fi} = \frac{2\pi}{\hbar} |\Sigma_{fi}^{ret}|^2 \delta(E_i - E_f) \quad (19)$$

Equation 19 is an important result because it represents the link between electron transport and energy transfer that can generate the driving force for a chemical reaction.

*Transition Rates.* To calculate the cotunneling rate, we follow the strategy laid out in refs 4–6. Since both the initial and the final states are neutral, the matrix element of the self-energy operator, to second order in the coupling, can be written as a sum of two terms.

$$\Sigma_{fi}^{ret} = \langle f | VG_0V | i \rangle = \langle f | V^{cat} G_0 V^{cat} | i \rangle + \langle f | V^{an} G_0 V^{an} | i \rangle \quad (20)$$

For now, we use specific electrode states  $l$  and  $r$  and write a bra with the final state as  $\langle f | = \langle il | a \rangle \langle bc | c_r \rangle$ . The first term in the self-energy is then calculated to be

$$\begin{aligned} \langle f | V^{cat} G_0 V^{cat} | i \rangle &= \sum_{l'r'} \langle il | a \rangle \langle bc | c_r \rangle (V_{ln-1,b}^* c_r^\dagger | n-1 \rangle \langle a | l \rangle) \times \\ &\frac{1}{E_i - H_0} (V_{r'n-1,a} c_r^\dagger | n-1 \rangle \langle a | l \rangle) \\ &= \frac{V_{ln-1,b}^* V_{rn-1,a}}{E_a - E_{n-1} - \varepsilon_r} \langle L | c_l^\dagger c_l | L \rangle \langle R | c_r c_r^\dagger | R \rangle \end{aligned} \quad (21)$$

Calculation of the second term, describing the coupling to the anion, is very similar and the self-energy amounts to

$$\Sigma_{fi}^{ret} = \langle L | c_l^\dagger c_l | L \rangle \langle R | c_r c_r^\dagger | R \rangle \left( \frac{V_{ln-1,b}^* V_{rn-1,a}}{E_a - E_{n-1} - \varepsilon_r} + \frac{V_{la,n+1}^* V_{rb,n+1}}{E_a - E_{n+1} + \varepsilon_l} \right) \quad (22)$$

We can now take the square and sum over all states in the electrodes, with indices  $l$  and  $r$ . Assume, for simplicity, that the coupling elements are constant at each electrode; that is,  $V_L \equiv V_{ln-1,b} = V_{la,n+1}$  and  $V_R \equiv V_{rn-1,a} = V_{rb,n+1}$ . We now have

$$\sum_{lr} |\Sigma_{fi}^{ret}|^2 = \sum_{lr} \langle L | c_l^\dagger c_l | L \rangle \langle R | c_r c_r^\dagger | R \rangle \left| \frac{V_L V_R}{E_a - E_{n-1} - \varepsilon_r} + \frac{V_L V_R}{E_a - E_{n+1} + \varepsilon_l} \right|^2 \quad (23)$$

Define the spectral density as  $\Gamma^L = 2\pi |V_L|^2 \rho(\varepsilon_l)$ , which is the same expression used in the single-particle formulation,<sup>1</sup> and assume a flat density of states. The summations can then be rewritten as

$$\sum_i |V_L|^2 \rightarrow \int d\varepsilon_l Q(\varepsilon_l) |V_L|^2 \approx \frac{\Gamma^L}{2\pi} \int d\varepsilon_l \quad (24)$$

The matrix element  $\langle L|c_l^\dagger c_l|L\rangle$  corresponds to the zero temperature limit of the Fermi distribution for the left lead and should be replaced with a thermal average

$$f_L(\varepsilon_l) = f(\varepsilon_l - \mu_L) = \sum_i W_i \langle L_i|c_l^\dagger c_l|L_i\rangle \quad (25)$$

where  $W_i$  represents the Boltzmann weight of the configuration  $|L_i\rangle$ .

Including thermal averaging over electrode configurations, we arrive at a general result for the inelastic scattering rate:

$$w_{ba} = \frac{\Gamma^L \Gamma^R}{2\pi\hbar} \int d\varepsilon_l \int d\varepsilon_r \left( \frac{1}{E_a - E_{n-1} - \varepsilon_r} + \frac{1}{E_a - E_{n+1} + \varepsilon_l} \right)^2 \times f_L(\varepsilon_l) (1 - f_R(\varepsilon_r)) \delta(E_a - E_b - \varepsilon_r + \varepsilon_l) \quad (26)$$

The elastic tunneling rate,  $w_{aa}$ , corresponding to electron transport involving only the ground state  $|a\rangle$  can now be obtained simply by choosing  $E_b = E_a$ ,

$$w_{aa} = \frac{\Gamma^L \Gamma^R}{2\pi\hbar} \int d\varepsilon_l \int d\varepsilon_r \left( \frac{1}{E_a - E_{n-1} - \varepsilon_r} + \frac{1}{E_a - E_{n+1} + \varepsilon_l} \right)^2 \times f_L(\varepsilon_l) (1 - f_R(\varepsilon_r)) \delta(\varepsilon_l - \varepsilon_r) \quad (27)$$

In comparing the expressions for the inelastic and elastic scattering rates, the only difference is the energy conservation condition appearing in the argument of the delta function. This condition is harder to satisfy in terms of availability of states in the inelastic case, eq 26, than in the elastic case, eq 27, and this difference will eventually translate into the appearance of a voltage offset of the inelastic contribution.

Expressions such as eq 26 and eq 27 could be mapped onto a single-particle theory. If we associate the electron affinity with a LUMO energy,  $E_a - E_{n+1} \sim \varepsilon^{LUMO}$ , and the ionization potential with a HOMO energy,  $E_{n-1} - E_a \sim \varepsilon^{HOMO}$ , the excitation energy,  $\Delta E = E_b - E_a$ , appearing in eq 26 would be the only reference to the many-particle states. At the Hartree–Fock level of theory, this mapping is ensured by Koopmans' theorem, but it is also often used, without a formal proof, within the Kohn–Sham approach to density functional theory.

*A Simple Case.* Consider the inelastic cotunneling process in a simple case where one intermediate state, say the virtual cation,  $|n-1\rangle$ , is dominant. In this case, eq 24 reduces to

$$w_{ba} = \frac{\Gamma^L \Gamma^R}{2\pi\hbar} \int d\varepsilon_l \int d\varepsilon_r \frac{f_L(\varepsilon_l) (1 - f_R(\varepsilon_r))}{(E_a - (E_{n-1} + \varepsilon_r))^2} \delta(E_a - E_b - \varepsilon_r + \varepsilon_l) \\ = \frac{\Gamma^L \Gamma^R}{2\pi\hbar} \int d\varepsilon_l \frac{f_L(\varepsilon_l) (1 - f_R(E_a - E_b + \varepsilon_l))}{(E_b - E_{n-1} - \varepsilon_l)^2} \quad (28)$$

In the zero temperature limit, the rate can be expressed analytically. Define the ionization potentials for the states  $|a\rangle$  and  $|b\rangle$  as  $A = E_{n-1} - E_a$  and  $B = E_{n-1} - E_b$ , respectively. Now we substitute the integration variable by  $u = B + \varepsilon_l$ , and at zero temperature, we obtain

$$w_{ba} = \frac{\Gamma^L \Gamma^R}{2\pi\hbar} \int \frac{du}{u^2} (1 - \vartheta(u - B - \mu_L)) \vartheta(u - A - \mu_R) \\ = \frac{\Gamma^L \Gamma^R}{2\pi\hbar} \int_{A+\mu_R}^{B+\mu_L} \frac{du}{u^2} \\ = \frac{\Gamma^L \Gamma^R}{2\pi\hbar} \left[ \frac{1}{A + \mu_R} - \frac{1}{B + \mu_L} \right] \quad (29)$$

For identical electrodes, the chemical potentials are given by  $\mu_L = -W + eV/2$  and  $\mu_R = -W - eV/2$ , where  $W$  is the work function of the metal, and the expression for the inelastic tunneling becomes

$$w_{ba} = \frac{\Gamma^L \Gamma^R}{2\pi\hbar} \frac{eV - \Delta E}{(A - W)(B - W) + \frac{eV}{2} \Delta E - \frac{e^2 V^2}{4}} \quad (30)$$

where  $\Delta E = E_b - E_a$ .<sup>47</sup> To obtain the corresponding elastic rate, we set  $b = a$  to obtain

$$w_{aa} = \frac{\Gamma^L \Gamma^R}{2\pi\hbar} \frac{eV}{(A - W)^2 - \frac{e^2 V^2}{4}} \quad (31)$$

Consider the numerator in eqs 30 and 31. In eq 30 for the cotunneling rate, an additional term  $\Delta E$  appears. This is the voltage threshold.

We have considered cotunneling as an excitation mechanism, using a positive  $\Delta E = E_b - E_a$ . If we want to invoke cotunneling as a deexcitation mechanism, we must redo the calculations above and arrive at a deexcitation rate of

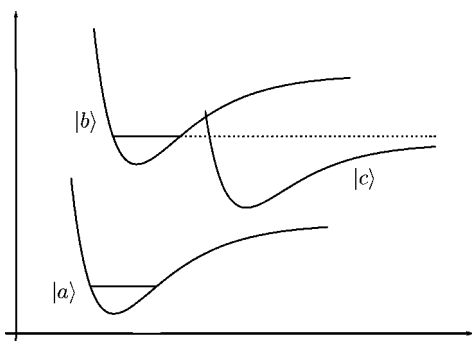
$$w_{ab} = \frac{\Gamma^L \Gamma^R}{2\pi\hbar} \frac{eV + \Delta E}{(A - W)(B - W) - \frac{eV}{2} \Delta E - \frac{e^2 V^2}{4}} \quad (32)$$

Due to a larger availability of states that can participate in deexcitation, one sees that  $w_{ab} > w_{ba}$ .

**Surface Reaction.** Recent experiments have shown that relatively weak tunneling currents passing through a molecular junction may induce different processes ranging from heating to desorption and even chemical reactions.<sup>8–20</sup> We are particularly interested in the remarkable experiment described in ref 8 that shows the successive breaking of the two CH bonds in an acetylene molecule adsorbed on the (001) surface of copper, under the influence of an STM tip.

Generally speaking, we can consider two different mechanisms for surface processes associated with tunneling currents: first, current-induced processes that involve excitation of vibrations via the electron–phonon coupling. These include desorption, junction heating, and mechanical vibrations of the type studied by Seideman and co-workers.<sup>21–25</sup> One can think of these as a sort of molecular Joule effect where the emission of phonons gradually heats up the junction.

Second are the processes that involve directly electronic excitations of the molecule. Such processes, like STM-induced chemical reactions, will show a large voltage threshold. Any theoretical description of such processes must involve at least two electronic states of the substrate–adsorbate system, with the coupling between them mediated by the contacts. We are



**Figure 1.** Potential energy surfaces

proposing a mechanism involving cotunneling, and in the following, we shall apply it to the dissociation of acetylene.

A different but related theoretical model was proposed by Hasegawa et al.<sup>26</sup> It implies, however, an unlikely energy reconcentration effect and assumptions about the energy parameters that we think are not adequately justified.

**Energy Diagram.** We focus on the dissociation of acetylene, as reported in ref 8, as a specific example. Consider the energy diagram in Figure 1. We treat the ground state,  $|a\rangle$ , of acetylene, and an excited state,  $|b\rangle$ , at the bottom of an excited potential energy surface. From  $|b\rangle$ , the system can tunnel through a potential energy barrier to a dissociative channel  $|c\rangle$ . To map out the diagram, we rely on energy values from the literature.

For treatments of the excited states of acetylene see refs 33–36. Theoretical calculations show that the lowest excited states of acetylene are triplet states. In optical spectroscopy such transitions would be forbidden, but the selection rules do not apply to excitation by cotunneling. The lowest excited state is the cis-bent state  $1^3B_2$ . It lies 3.81 eV above the ground state.<sup>36</sup> This is a viable candidate for the state  $|b\rangle$  in Figure 1, especially since the ground-state geometry of acetylene bound on a copper surface is cis-bent.<sup>8,37–40</sup>

An excitation energy of 3.81 eV is, of course, larger than the threshold of 2.8 eV. We mention two possible explanations for this. First, the reported excitation energies are vacuum numbers. The ground-state geometry changes upon adsorption. We assume that the main role of the surface is to stabilize the adsorbed species, but such a stabilization can be very different for polarized or charged species compared with the ground state. This could lower the excitation energy.

Second, the excitation could occur from a vibrationally excited state of the electronic ground state. This is in line with optical dissociation experiments where vibrations are excited before dissociation. Note that these are not necessarily thermal excitations. In the STM-junction, this energy would be provided via the mechanism described by Seideman and co-workers.<sup>21–25</sup>

The vibrational energies of acetylene are discussed in refs 8, 10. An average value of the CH stretch modes is 377 meV on the Cu surface. Likewise, a value of 101 meV is reported for CCH bending mode.

An increase in temperature, from 9 to 45 K, caused an increase of the voltage threshold by 0.8 V.<sup>8</sup> We speculate that the heating of the substrate could partly quench the

selective predissociation excitations of the CH stretch and CCH bending modes.

To gauge the position of state  $|c\rangle$  in Figure 1, we need to know the dissociation energy for acetylene into ethynyl ( $C_2H\bullet$ ) and hydrogen. Values for dissociation in vacuum are 5.712 eV from experiment<sup>41</sup> and 5.795 eV from theory.<sup>42</sup> This value is lowered dramatically at the Cu surface, since the stabilization of the radical is much larger than that of the neutral species. The binding energies for acetylene and ethynyl to a Cu(001) surface are reported to be 1.31 and 4.22 eV, respectively.<sup>10</sup> A similar calculation gives 1.09 and 4.36 eV.<sup>43</sup> Both references used DFT with the generalized gradient approximation (GGA). By correcting the experimental vacuum value using the calculated stabilization energies, this gives values of 2.802 and 2.442 eV for the dissociation energy.

**Kinetic Model.** To estimate the impact of the cotunneling scheme on the rate of dissociation, we invoke a simple kinetic model. The overall dissociation process is described by three kinetic equations,

$$\frac{dP_a}{dt} = -w_{ba}P_a + w_{ab}P_b \quad (33)$$

$$\frac{dP_b}{dt} = w_{ba}P_a - (w_{ab} + w^{dis})P_b \quad (34)$$

$$\frac{dP_c}{dt} = w^{dis}P_b \quad (35)$$

where  $P_a$  and  $P_b$  describe the populations of states  $|a\rangle$  and  $|b\rangle$  of acetylene, respectively, and  $P_c = 1 - P_a - P_b$  describes the effective population of the product state. The rates  $w_{ba}$  and  $w_{ab}$  are cotunneling rates, and  $w^{dis}$  is the rate for the system to tunnel from  $|b\rangle$  to  $|c\rangle$ .

The set of kinetic equations can be solved,<sup>44</sup> for example, by Laplace transformation, and the solution is governed by the two roots,  $u_1 \leq u_2$ , of the equation

$$u^2 - (w_{ab} + w_{ba} + w^{dis})u + w_{ba}w^{dis} = 0 \quad (36)$$

For the initial conditions,  $P_a = 1$  and  $P_b = P_c = 0$ , the exact solution for  $P_c(t)$  can be expressed as

$$P_c(t) = 1 - \frac{u_2}{u_2 - u_1} e^{-u_1 t} + \frac{u_1}{u_2 - u_1} e^{-u_2 t} \quad (37)$$

As we discuss below, we assume that we are in a regime where the cotunneling processes occur at a much faster rate than the effective dissociation, thus  $w_{ab}, w_{ba} \gg w^{dis}$ . This in turn implies that  $u_1 \ll u_2$ , and the overall process will, after establishing a kinetic equilibrium between states  $|a\rangle$  and  $|b\rangle$ , be dominated by a single exponential. We have

$$P_c(t) \approx 1 - e^{-u_1 t} \quad (38)$$

where  $u_1$  to a good approximation is given by

$$u_1 \approx \frac{w_{ba}w^{dis}}{w_{ab} + w_{ba} + w^{dis}} \approx \frac{w_{ba}}{w_{ab} + w_{ba}} w^{dis} \quad (39)$$

To estimate values for the transition rates  $w_{ab}$  and  $w_{ba}$  for our case study of acetylene dissociating on copper, we assume that the overall current is well-described by  $I = -e w_{aa}$ , where  $w_{aa}$  is the elastic current from eq 31. Experimentally, a current of  $\sim 0.85$  nA is reported at a bias

of 3.0 V. This corresponds to electrons passing through the junction at a rate of  $0.53 \times 10^{10} \text{ s}^{-1}$ . We use a theoretical value of  $A = 11.5 \text{ eV}$  for the ionization potential of acetylene.<sup>45</sup> An average value for the electrode work function of  $W = 4.6 \text{ eV}$  is used since  $W_{Cu} = 4.7 \text{ eV}$  and  $W_W = 4.5 \text{ eV}$ . With these numbers, we are able to estimate an average value for the spectral density;  $\sqrt{\Gamma^L \Gamma^R} = 32 \text{ meV}$ .

Having a value for the spectral densities, we can now calculate the rate of cotunneling excitations,  $w_{ba}$ , using eq 32. We use  $\Delta E = A - B = 2.8 \text{ eV}$  and get  $w_{ba} = 1.68 \times 10^9 \text{ s}^{-1}$ . Likewise, the deexcitation rate, calculated using eq 30, is given by  $w_{ab} = 6.73 \times 10^{10} \text{ s}^{-1}$ . Other mechanisms for deexcitation, such as exciton transfer or phonon emission, are disregarded in this crude estimate of rates.

The ratio between the deexcitation and the excitation rates,  $w_{ab}$  and  $w_{ba}$ , respectively, is given by

$$\frac{w_{ab}}{w_{ba}} = \frac{eV + \Delta E}{eV - \Delta E} \times \frac{(A - W)(B - W) + \frac{eV}{2}\Delta E - \frac{e^2V^2}{4}}{(A - W)(B - W) - \frac{eV}{2}\Delta E - \frac{e^2V^2}{4}} = 40.1 \approx 40 \quad (40)$$

Now we can estimate the impact of the kinetic equilibrium between  $|a\rangle$  and  $|b\rangle$  on the overall dissociation rate. From eq 39, we now have  $u_1 = (1/41)w^{dis}$ , and since the overall experimental rate is of the order of  $u_1 \sim 1 \text{ s}^{-1}$ ,<sup>8</sup> we have  $w^{dis} = 41 \text{ s}^{-1}$ . This is much slower than the excitation and deexcitation rates, as assumed above. So, even though the excitation kinetics does constitute a bottleneck and does slow down the overall rate, in this case, by a factor of 41, the magnitude of the rate is by far dominated by the dissociating process, represented by the rate  $w^{dis}$ .

**Time Scale.** One intriguing aspect of the experiment is the relatively long time scale of the overall dissociation process. Our simple kinetic model suggests that once the threshold has been overcome the excitation kinetics has only limited impact on the overall rate of dissociation.

Such activated processes have been discussed extensively in the literature on photochemical processes.<sup>46</sup> And also in the context of current-induced processes.<sup>21–23</sup> The main conclusion of these works is that a dissociation time  $\tau \sim \hbar/w^{dis}$  dominates the bond breaking process.

The excited state  $|b\rangle$  is playing the role of what is known as a doorway state in the literature on photochemical processes.<sup>46</sup> The coupling between the excited state and a dissociation channel of state  $|c\rangle$  is physically responsible for the breaking of the bond.

**Isotope Effect.** Another important experimental finding that can be understood within our model is the massive isotope effect in the observed dissociation threshold. The threshold for HCCH is 2.8 V, compared with 3.8 V for DCCD.<sup>8</sup>

It is well-known that isotopic substitution in a molecule leads to changes in the vibrational and rotational frequencies that are responsible for changes in the IR spectra, and in our problem this can have some bearing on the voltage threshold. For acetylene on copper, the change from C–H to C–D stretch frequency is on the order of 100 meV.<sup>8,10</sup> If

the excitation from  $|a\rangle$  to  $|b\rangle$  is indeed occurring from a vibrationally excited state of  $|a\rangle$ , this will explain some, but not all, of the change in threshold.

The electron–phonon coupling constant is another magnitude that depends on the isotope mass. However, this would be of importance mostly in modifying the efficiency of the vibrational–electronic energy transfer between the surface and the molecule, and since no significant change in the dissociation time scale was reported for the different isotopes, we can disregard this effect.

These considerations leave us with the possibility of isotope-induced geometry changes as the main explanation for the very large isotope effect observed in the experiment. In gas phase, the ground-state geometry of both HCCH and DCCD is linear, but experimental studies of normal and deuterated acetylene on a Pt surface suggests that the cis-bending of the molecule is much larger for HCCH and that DCCD is nearly linear.<sup>37</sup> This implies that the dipole moment of normal acetylene on a surface will be larger than that of the deuterated species. We expect these differences to be preserved in the excited states, hence leading to a higher stabilization of the doorway state for HCCH compared with that of DCCD. Electronic structure calculations of the excited-state potential energy surfaces of acetylene in vacuum<sup>33,36</sup> indicate that the energy is very sensitive to the bending angle. In fact, the 130° cis-bend geometry is more than 1 eV lower in energy than the linear geometry,<sup>33,36</sup> an energy difference that is well within the right order of magnitude to explain the variation in the threshold voltage associated with the isotopic substitution.

**Conclusion.** The description of charge and energy transfer processes occurring under the nonequilibrium conditions present in electrode–molecule–electrode junctions under bias is a formidable theoretical challenge. In principle, the nonequilibrium Green’s functions (NEGF) formalism affords a complete physical picture, but its complexity demands a number of approximations to extract the relevant information.

Cotunneling is an inelastic process that can be important for the description of chemical reactions because it can play an important role in providing a route for energy transfer between otherwise uncoupled electronic states. Our model identifies the self-energy with the effective coupling between the electrodes mediated by the bridge. The resulting expression for the current includes an elastic contribution, arising from superexchange processes, and an inelastic contribution, involving the transfer of energy that triggers the chemical reaction. The description of this explicit pathway connecting electron transport and the onset of a chemical reaction in a molecular junction is the main result of our work.

Using our model, we were able to rationalize in terms of excitation processes and the relative stability of the different chemical species on the surface, the main features of the STM-induced dissociation reaction of acetylene on a copper surface, a system for which detailed experimental observations are available. Although further confrontation with empirical information is required to validate our model, it is remarkable that the three main features of this system, the voltage threshold for unimolecular dissociation, the long time

scale for current variation associated with the chemical reaction, and the unusually large isotope effect, are naturally accounted within the framework of our theory.

The inclusion of several electronic states is a key element of our model. This is achieved through a generalization of the Landauer model to a Fock space description where several states with a varying number of electrons are simultaneously considered. The potential of this approach for the description of current-induced nonadiabatic processes and other effects due to electronic correlation, like Coulomb blockade and Kondo effect, is currently investigated.

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