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Implications and Applications of Current-Induced Dynamics in Molecular Junctions

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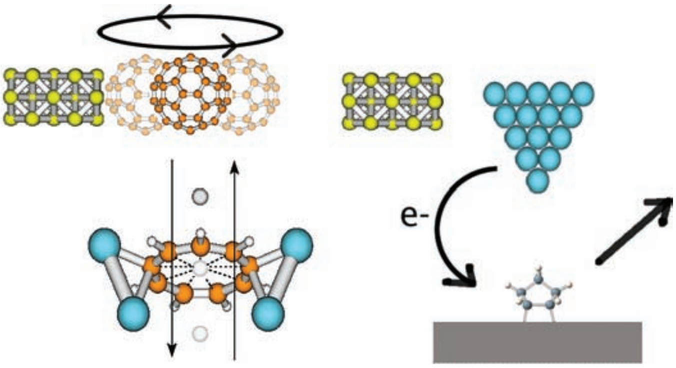

Instances of strongly nonadiabatic electronic–vibrational energy transfer have been studied since the early days of quantum mechanics and remain a topic of fundamental interest. Often such transfers are associated with electronic resonances, temporary states where transient localization of charge on the molecule provides a mechanism for channeling electronic energy into vibrational excitation. Extensively studied in the gas phase, electron resonance scattering also occurs with surface adsorbed molecules, where it manifests itself in broadened cross sections and desorption of adsorbates from metal surfaces. In this Account, we focus on a related topic: the implications of nonadiabatic, resonance-mediated scattering to the exciting field of molecular electronics. In this context, researchers can induce directed nuclear dynamics and control these processes in single molecules in contact with metallic and semiconducting electrodes.

We discuss a variety of consequences and applications of current-driven nuclear excitation in molecular devices, ranging from the design of new forms of molecular machines to surface chemistry at the single-molecule level and atom-resolved lithography. We highlight two specific examples of molecular nanomachines. In the first, a Au–C_{60}–Au transistor, the current induces the oscillatory motion of the center-of-mass coordinate of the C_{60}. The second, a zwitterion-based rattle, demonstrates excitation of intramolecular motion as the positively charged moiety is threaded back and forth through the negatively charged carbon ring. Finally, we discuss the current-induced desorption of organic molecules from Si(100) both to suggest the potential for controlled surface nanochemistry and to develop guidelines for the design of stable molecular junctions.

Modeling the exchange of energy between tunneling electrons and the vibrational degrees of freedom of a target molecule subject to bias voltage, open boundary conditions in the electronic subspace, and the dissipative effects of the electrodes poses a fascinating challenge to contemporary theories of inelastic electron transport. A scattering theory of density matrices is motivated by the need to address large amplitude, chemically relevant dynamics in tandem with an appropriate treatment of the electronic scattering problem. We provide a qualitative discussion of the theory and note the limits in which it reduces to well-known approaches.

I. Introduction

Whereas studies of electron scattering from atoms and molecules in the gas phase date back to the formative years of quantum mechanics,[1] they provide useful insight in a relatively new context: current-driven processes in molecular-scale devices. In both cases, temporary molecular states, that is, electronic resonances, mediate the charge scattering event and give rise to energy transfer to the nuclear degrees of freedom of the molecule. In the case of a molecular junction, the current initiates dynamics ranging from vibrational excitation to chemical reaction as the electrons tunnel from one contact to the other under an applied bias voltage.[2] The excitation imparted to the nuclei can result in directed coherent motion, cre-

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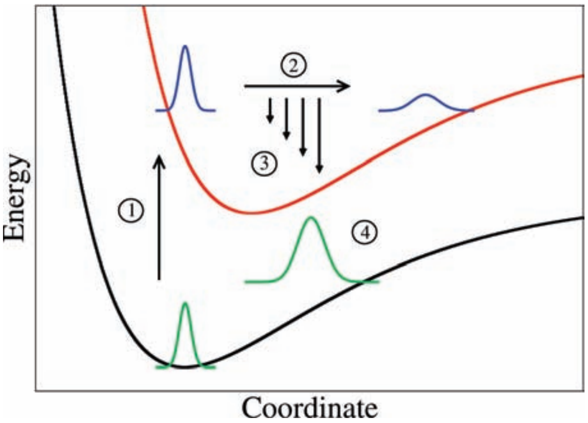

FIGURE 1. Schematic illustration of a current-driven, resonance-mediated event. Upon carrier attachment, the nuclear system is rapidly promoted to the resonance state (1) and subsequently evolves toward the resonance-state equilibrium configuration (2). As the nuclear wave function evolves, it decays back to the neutral state (3). The electronically relaxed nuclear system carries internal excitation, and dynamical events may ensue (4).

ating an opportunity for construction of a new generation of molecular machines as well as for performing surface chemistry at the single molecule level.[3]

Electronic resonances are temporary electronic states that arise from either transient trapping of the electron in its interaction potential with the molecule or attachment to a core excited electronic state.[4] In molecular junctions, these states typically correspond to the former category and provide the dominant channel for the inelastic current when they overlap with the electrode Fermi levels.[5] Attachment of an electron, or a hole, to the molecule allows for an extended interaction time between the charges and the nuclear degrees of freedom and hence an opportunity for energy transfer. Promotion of the initial nuclear wave function to the resonance state in general introduces new forces on the nuclei as they respond to the modified electronic distribution. The impetus for nuclear motion is evident from the differences in topology between the initial ground-state potential energy curve and that of the resonance state. If the equilibria of the two potentials are significantly displaced, the nuclei evolve away from their neutral state geometry, while the wave function continually decays back to the neutral state as a result of interaction with electrode phonons and excitation of electron−hole pairs. Figure 1 highlights the key role of both the duration of the time spent in the resonance state, that is, the resonance lifetime (τ), and the degree to which the two potentials differ for inducing nuclear dynamics in a simple one-dimensional model. Once the resonance has fully decayed, that is, the electron has tunneled off of the molecule, the nuclear wave function is significantly distorted from the initial equilibrium structure, and dynamics ensue.

The extent of the induced dynamics is correlated with the degree of charge localization across the molecule-plus-contacts system.[6] When the additional charge is highly delocalized, the equilibrium displacements in Figure 1 are small, resulting typically in weak coupling between the electronic and nuclear motions. An example is the classic junction where a highly conjugated molecule is contacted to gold electrodes via sulfur atoms.[7] At the other extreme, where the coupling of the molecule to the electrodes is weak, the orbitals are generally spatially localized, giving rise to large equilibrium displacements and consequently strong interaction between the charge and the nuclei. An increasingly popular example is the case of a fullerene in contact with gold electrodes, where weak dispersion forces connect the fullerene with one electrode and interaction with the second contact occurs through the charge tunneling process.[8]

One of the interesting potential applications of current-driven dynamics in junctions is individually driven molecular machines.[3,6,9] A molecular machine is defined as a molecule or an assembly of molecular components that is designed to perform mechanical motion in response to an external stimulus.[10] To date efforts to construct systems that respond to stimuli by directed motion have focused largely on using electrochemical charging, photochemical excitation, or chemical reactions to produce dynamic events.[10,11] Although traditional molecular machines have been driven in the solution phase, there has been growing effort to constructs such devices in the dry state on a solid support.

The molecular junction offers an inviting complement to the supramolecule-based, solution-phase traditional molecular machines. In addition to a dry environment, the molecular junction introduces the possibility of driving molecular machines individually (or coherently), on a single device level, rather than as an ensemble. It promises also the possibility to design machines that perform sustained unidirectional motion rather than stepwise evolution.[3,6,9] Finally, the dissipative nature of the environment in a molecular scale device could provide adequate relaxation such that additional chemical and light-driven stimuli would be unnecessary to reset the machine to its initial state.

A second potential application of current-driven dynamics in junctions is surface nanochemistry induced by a scanning tunneling microscope (STM). By supplying the energy required for reaction through a resonance-mediated charge transfer event, the STM is able to induce surface reactions that do not take place spontaneously and study them on a site-specific, single-molecule level. Furthermore, mode-selective chemistry may be naturally induced by the STM. Electron energy deposited into a given molecular mode via a scattering event may undergo rapid energy transfer into a second, strongly coupled mode. It will not, however, spread among the many modes of the molecule, since rapid relaxation due to electron−hole pairs and phonon excitation in the electrodes will typically take place on a faster time scale. To date STM-driven, resonance-mediated surface nanochemistry has focused on desorption reactions,[12,13] but surface exchange reactions can be readily envisioned.[14]

Another potential application of current-driven dynamics in the STM environment is new approaches to nanolithography. One of the successful methods of nanolithography on silicon surfaces is current-driven desorption of H atoms from a hydrogen-passivated surface,[15] where multiple electronic transitions into a resonant state lead to heating of the H−Si bond and eventually result in desorption. The mechanism is very similar to that discussed in general terms above but involves multiple electronic transitions and is thus conducted at high current densities. Organic molecules may offer complementary lithography routes, for instance, ones that exhibit induced desorption at lower current densities or ones that allow selective desorption of one molecule leaving another intact. Clearly, the study of current-driven dynamics in molecular-scale electronics and an understanding of the system properties that encourage or suppress them are pertinent also for the design of stable nanodevices that are immune to current-driven events.

In this Account, we present an overview of the theory underlying inelastic events in the vibronic space of molecular junctions and discuss avenues for harnessing this mechanism to create useful electronic devices. In the following section, we begin by briefly highlighting approaches to model inelastic current, with the goal of achieving a formalism in which large amplitude chemical dynamics can be described as well as mechanical motions. We focus on a general scattering theory approach within the density matrix formalism and discuss a specific limit that connects our method to the often implemented master equation approach for vibrational dynamics. The discussion of the theory can be skipped without detriment to the subsequent sections, where we explore the concept of molecular machines and device design. To exemplify the former, we highlight two illustrative systems: a fullerene-based oscillator and a zwitterion-based rattle. The problem of surface nanochemistry and the development of stable (current-immune) devices are addressed in section V, and the final section concludes with a discussion of future directions.

II. Approaches to Inelastic Current

The work of Landauer[16] has been foundational to molecular electronics in connecting the conductance of a molecule, a property familiar on the macroscopic scale, with its probability of transmitting an electron, an inherently quantum mechanical entity. Subsequent efforts have focused on developing scattering theory-based approaches for elastic current[16] and on understanding how the structure of the molecule effects transmission.[17] Only more recently the question has been addressed of how the presence of the nuclear degrees of freedom of the molecule not only effects the current[18] but could also result in useful motion.[3] The need for accurate methodologies is emphasized by the fact that nuclear vibrations may effect not only the quantitative current but also the qualitative mechanism by which it is transmitted.[18]

While space limitation does not allow a complete account of the efforts to describe tunneling current through molecular devices, we mention two approaches that are widely used to include the inelastic portion. Continuing with the conceptual picture developed by Landauer, multichannel scattering techniques have been proposed,[19] which account for all orders of electronic interaction, and perturbative treatments of the coupling between the electron and the molecular vibrations. For a single harmonic vibration linearly coupled to the scattering charge, Wingreen et al. have shown that both the transmission probability and the current can be obtained analytically.[20] For the instance where the coupling between the electron and the nuclei is weak, perturbative methods can be applied within Fermi's Golden rule,[21] as well as adaptations of the Landauer-type expression for current.[22]

Two limitations of the above methods were noted in the previous literature, namely, their restriction to thermal distributions in the vibrational manifold and failure to incorporate the appropriate Fermi statistics for the scattering electrons.[18] If the rate of energy deposition exceeds the rate of energy relaxation to the environment, a net heating will excite the vibrations of the molecule and a nonequilibrium distribution will arise, which has not been addressed in these scattering approaches and likewise cannot be ruled out *a priori*. Regarding the treatment of the quantum statistics for the transmitted electrons, scattering approaches often rely on *ad hoc* inclusion of the Fermi distributions in the electrodes, which produces deviations from self-consistent methods.[18] It has been shown that such errors can affect not only the quantitative currents reported but also the qualitative physics observed in the phonon bands of the transmission curve with respect to a gate voltage.[23]

Calculations based on the many-body theory of nonequilibrium Green functions (NEGF) address these restrictions and allow for proper treatment of the Fermi statistics. A recent overview of the NEGF methodology has demonstrated its ability to investigate vibrational heating in molecular junctions and to probe the consequent non-Boltzmann nuclear distributions.[18,23] While the method is powerful in its handling of the bias voltage, the nonequilibrium electronic distribution, and the open system boundary conditions in the electronic subspace, its common application carries restrictions on the description of the nuclear motion. Developed to handle small amplitude vibrations, most applications of this method describe the nuclear degrees of freedom as harmonic oscillators interacting with the electrons via a simple functional form. For the purpose of describing general chemical dynamics, the use of a harmonic approximation is questionable and in the instance of chemical reactivity, it fails to produce the correct physics.

III. Scattering Theory of Density Operators: A Formalism for Current-Induced Dynamics

Recently, an alternative approach has been developed, which builds on scattering theory to describe the nuclear modes. Only a brief overview of the method is presented here; the interested reader is referred to ref 26 for details.

Consideration of a related scenario, where an electron scatters off a gas-phase molecule, is helpful in forming intuition. In the gas phase, the initial state of the system is described by an incoming asymptotic state corresponding to a freely evolving electron and target molecule. As the electron starts to interact with the molecule, the two entities are no longer described by a single eigenstate of H_0, but rather by an eigenstate of the full Hamiltonian, $H = H_0 + V$, where V is the interaction between the charge and the molecule. The relationship between the freely evolving initial state, where the potential is taken as zero, and the full scattering state of the system is given formally by the Lippman–Schwinger equation of scattering theory,

$$|\Psi^+\rangle = |\psi_0\rangle + GV|\psi_0\rangle = \Omega|\psi_0\rangle \tag{1}$$

where $|\Psi^+\rangle$ is a complete scattering state of the system, $|\psi_0\rangle$ is an incoming eigenstate of H_0, G is the Green's operator corresponding to the complete Hamiltonian, and the second equality defines the Møller operator, Ω. The index "+" in $|\Psi^+\rangle$ denotes the incoming wave boundary conditions. Equation 1 describes the operation of the Møller operator as a mapping between the initial state and the full scattering state of the system, as discussed in several texts.[24]

The description of charge scattering in a molecular device borrows from the above concepts, which link the freely propagating states of the system with the fully interacting representation. In the device case, the extension to ensemble scattering theory is necessary to properly account for the interaction with the electrodes. Using density matrix theory, one can describe the scattering in terms of initial distributions across the asymptotic states in both nuclear and electronic subspaces. In the remote past, the system is described by the free Hamiltonian density matrix,

$$W_0(t) = \sum_{\substack{l \\ \mu\nu}} P_l^{\text{elec}} \rho_{\mu\nu}(t) |l, \mu\rangle\langle l, \nu| \tag{2}$$

where $|l, \mu\rangle$ is an eigenstate of H_0, namely, a product state of an electron in the electrode state $|l\rangle$ and the molecule in a vibrational state of its neutral ground-state potential energy surface, $|\mu\rangle$. The P_l^{elec} correspond to the probabilities of filling each asymptotic electrode state and are chosen to represent electrodes whose electronic levels are filled up to their respective Fermi energy levels. The molecule is described by a generalized vibrational density matrix, $\rho_{\mu\nu}(t)$. Within the electronic subspace, $W_0(t)$ describes the incoherent population of the electronic levels, but the nuclear subspace retains all of the coherent dynamics. The form of eq 2 connects this method to the familiar model of two thermal reservoirs of charge carriers coupled to a scattering region. The asymptotic distribution of eq 2 can be mapped onto the fully interacting density matrix via application of the Møller operators introduced above,

$$W(t) = \Omega W_0(t) \Omega^\dagger \tag{3}$$

where $W(t)$ is the fully interacting molecule-plus-electrodes density matrix.

The Liouville–Von Neumann equation describes the time evolution of the scattering density operator through

$$\frac{\mathrm{d}}{\mathrm{d}t} W(t) = \frac{-i}{\hbar} [H, W(t)] \tag{4}$$

where H is the full system Hamiltonian. Starting with the density operator defined over both the electronic and nuclear coordinates, an equation of motion can be derived for the reduced nuclear density under the influence of the current,

$$\frac{\mathrm{d}}{\mathrm{d}t}\rho_{\alpha\beta}(t) = \frac{-i}{\hbar \mathrm{Tr}\{\rho(t)\}}\sum_{l\in L,R}\langle l,\alpha|[H,W(t)]|l,\beta\rangle \qquad (5)$$

Equation 5 is entirely general in describing the nuclear dynamics and as a result retains all of the coherence effects in the nuclear subsystem. Although the examples in the next section are based on eq 5, it is instructive to consider a familiar limit of this relation, which lends itself to intuitive interpretation and is also numerically convenient. Such an approximation is obtained by restricting attention to the evolution of vibrational populations, the diagonal terms of the nuclear density matrix, where $\alpha = \beta$. Within this limit, an approximation known as the secular approximation in dissipative dynamics,[25] the equation of motion for the nuclear subspace is simplified to the form,

$$\frac{\mathrm{d}}{\mathrm{d}t}P_\mu(t) = -\sum_\mu w_{\mu\to\alpha}P_\mu(t) + \sum_\alpha w_{\alpha\to\mu}P_\alpha(t) \qquad (6)$$

where P_μ is the probability of finding the system in the vibrational state $|\mu\rangle$ and $w_{\mu\to\alpha}$ is the rate of transfer of probability from vibrational state $|\mu\rangle$ to $|\alpha\rangle$ accompanied by the transport of an electron from the initial to the final electrode. Equation 6 describes the rate of change of the population in a given vibrational state $|\mu\rangle$ as the rate of influx from all other vibrational levels minus the rate of out flux to the other vibrational states and is referred to as a master equation.[25] Similarly it can be shown that eq 5 reduces in an appropriate limit to the successful Landauer equation.[26]

At the heart of the theory are matrix elements of the transition operator between an initial and a final vibrational–electronic state of the asymptotic Hamiltonian. Within the formulation of ref 28, these elements are computed by evolving an initial vibrational state subject to a non-Hermitian Hamiltonian, whose imaginary part is the resonance decay rate, $\Gamma = \hbar/\tau$. The latter is obtained from a nonequilibrium Green function calculation, as discussed in ref 28. For our present purpose, it suffices to note a simple and intuitive limit of the theory of ref 28, where it reduces to the insightful instantaneous transitions model, developed by Gadzuk for description of photochemistry on metal surfaces.[27] Within this model (see Figure 1), the initial vibrational eigenfunction is instantaneously projected into the resonance state through the rapid electron attachment event, allowed to evolve in the resonance state for a period τ_R, and instantaneously projected back to the ground electronic state. The continuum nature of the relaxation may be accounted for within this limit by averaging the observables over τ_R with a weight function $1/\tau \exp(-\tau_R/\tau)$.

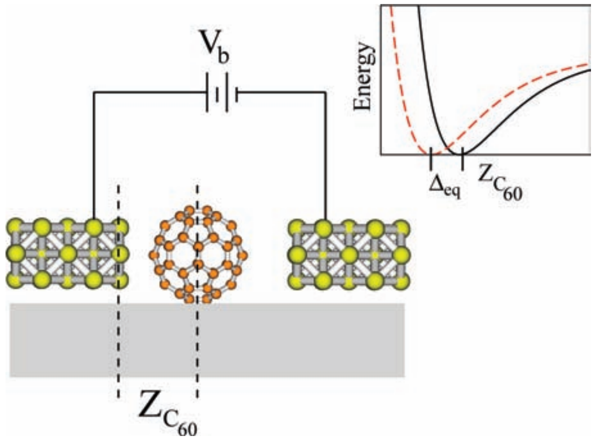

FIGURE 2. Schematic illustration of a fullerene junction, where the molecule is weakly connected to two gold electrodes as in the experiment of Park et al.[8] The inset shows the potential energy curves for the interaction of the C_{60} with the nearest gold electrode in the neutral (solid-black) and charged (dashed-red) states. The displacement between the equilibria of the two states is denoted Δ_{eq}.

IV. Current-Driven Molecular Machines

Having briefly outlined the formalism underlying the scattering process, we proceed to present two examples of molecular machines driven by the current. The first example is the fullerene-based molecular junction shown in Figure 2. Fullerene junctions have drawn extensive interest in recent years,[9,28,29] fueled in part by the experiments of Park et al.,[8] where measurements of the conductance through a Au–C_{60}–Au junction found an interesting staircase-like structure. Such features may be the result of oscillations of the center-of-mass coordinate, denoted $Z_{C_{60}}$ in Figure 2. Nuclear dynamics are induced by transient attachment of an electron to the fullerene, which leads to attraction between the localized charge and its image in the gold electrode. The additional attraction in the charged state compared with the neutral molecule pulls the C_{60} closer to the electrode. As the nuclei move toward the surface, the wave function continuously decays back to the neutral state, as shown in Figure 1, concomitant with the electron tunneling off the molecule. Subsequent to complete relaxation of the charged resonance, the nuclear wave function is back in the neutral state but is displaced from the equilibrium configuration, and oscillations ensue.

Before applying the complete theory of section III to explore the possibility of inducing machine-like motion in this junction, it is instructive to apply the simple instantaneous transitions model introduced at the end of section III, to appreciate the essential physics at a qualitative level. This is the subject of Figure 3, which provides the expectation value of the C_{60} center-of-mass vs time and illustrates the role played by

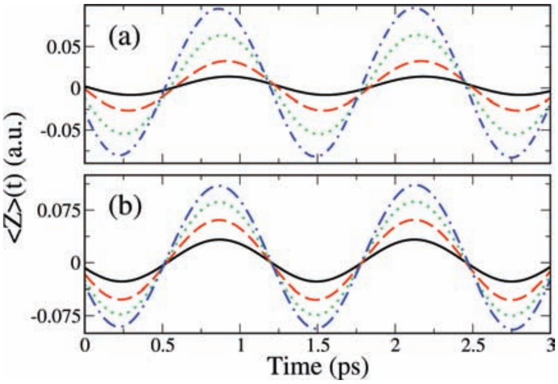

FIGURE 3. Current-driven oscillations in a Au−C_{60}−Au junction, computed within the instantaneous transitions model, demonstrating the role of the resonance lifetime, τ (a), and the equilibrium displacement, Δ_{eq} (b), in Figure 2. In panel a, comparison is made between $\tau = 10$ fs (solid, black), 25 fs (dashed, red), 50 fs (dotted, green), and 75 fs (dotted−dashed, blue) for $\Delta_{eq} = 16$ pm. In panel b, comparison is made between $\Delta_{eq} = 5$ pm (solid, black), 10 pm (dashed, red), 15 pm (dotted, green), and 20 pm (dotted−dashed, blue) for a lifetime of $\tau = 71.5$ fs.

the two parameters discussed in section I, namely, the resonance lifetime and the equilibrium displacement. As the lifetimes and equilibrium displacements are increased, the resulting amplitude for nuclear motion is enhanced, in agreement with the intuitive picture of Figure 1. In all cases, the period of oscillation is about 1.2 ps, which corresponds to the vibrational frequency of the center-of-mass vibration of the C_{60} with respect to the gold surface,[8] and the molecule is initially in the ground vibrational state.

With the essential physics illustrated via the simple instantaneous transitions model, we proceed to explore the effect and nature of vibrational relaxation by implementing the formalism outlined in the previous section starting with the molecule in its ground vibrational state (i.e., zero temperature). The interaction between the molecule and both the substrate phonons and electron−hole (e−h) pairs is included. Interestingly, the phonon-induced dissipation in the fullerene junction is seen to be much more effective than the excitation of e−h pairs. Conventional wisdom suggests that on metallic surfaces the rate of the latter process would far exceed that of the former. The reason for this counterintuitive result is the large reduced mass associated with the vibrating mode, resulting in the vibrational frequency, $\omega \propto \mu^{-1/2}$, being below the phonon band edge of the gold electrode.

The phonon-induced damping of energy and phase from the molecular vibrational system results in rapid quenching of the oscillatory motion, as shown in Figure 4. We find, however, that even under the conditions of Figure 4, which encourage efficient phonon-induced damping, the machine exhibits several oscillations before relaxing. To observe long-time steady-state oscillations, it is required that the driving rate would match the relaxation rate. There is ample motivation to prolong the motion by tailoring the electrode material and fullerene size, since current-driven vibrations of the fullerene lead to oscillations of the current transmitted and hence, potentially, a means of generating AC fields at the nanoscale.[9]

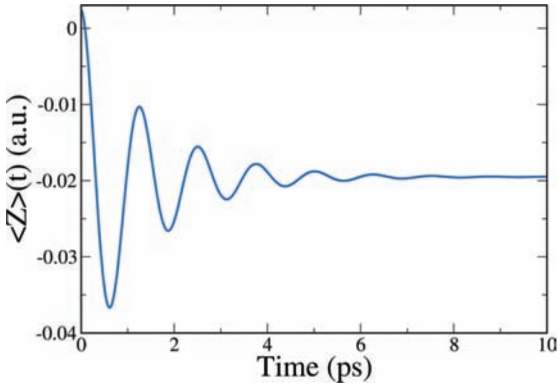

FIGURE 4. Current-driven oscillations in a Au−C_{60}−Au junction, computed within the density matrix scattering approach of eq 5 with the effects of a phonon bath included. The bias voltage is 200 mV, and the limit of zero temperature is taken.

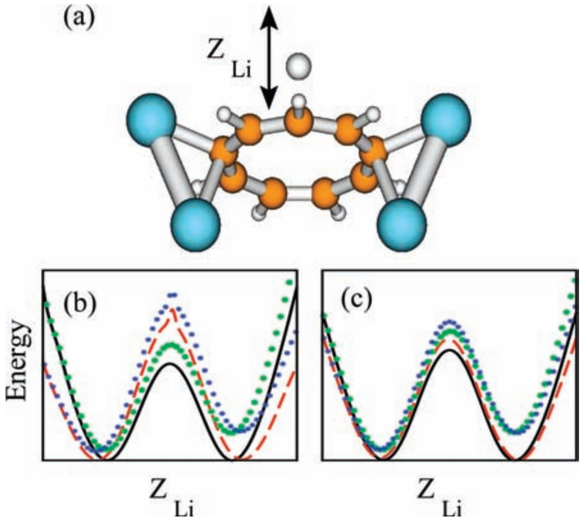

FIGURE 5. A current-driven zwitterion rattle, consisting of a lithium atom weakly bound to a carbon ring (orange) that is connected to two aluminum electrodes (blue): (a) a ball-and-stick model indicating the threading coordinate, Z_{Li}; (b) potential energy curves along Z_{Li} with the electrodes consisting of only one explicit aluminum atom, for the neutral and ionic states in the absence (solid, black and dashed, red lines, respectively) and in the presence (green dots and blue stars, respectively) of a gate voltage; (c) as in panel b for electrodes consisting of four explicit aluminum atoms.

Whereas the previous example demonstrates motion induced in the translation of the molecular moiety of the device, our second machine involves excitation of intramolecular motion. The lithium rattle shown in Figure 5 is comprised of a single lithium atom bound to a cyclononatetraene

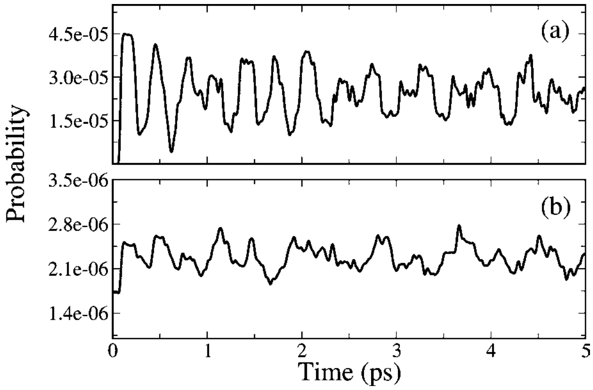

FIGURE 6. Current-driven dynamics in the zwitterion rattle of Figure 5. Probability density of the lithium atom in the upper well as a function of time for the single aluminum atom potential (a) and the four aluminum atom potential (b) at a temperature of 600 K.

molecule[30] connected to two aluminum electrodes. The difference in electronegativities between the lithium and carbon ring produces a zwitterionic ground state with the lithium positively charged and the carbon ring negatively charged. The lithium is held to the ring by the ionic interaction in a double well potential with a barrier height of 0.75 eV, which can be penetrated by tunneling of the lithium from one side of the ring to the other. As electrons traverse the system, they can localize partially on the carbon ring and weaken the interaction with the lithium atom. Thus, in the resonance state, the lithium's equilibrium position is pushed out from the ring plane, producing a distortion between the neutral and charged state equilibria. Application of a gate voltage superimposes a linear potential onto the double well and breaks its symmetry, such that the lithium atom localizes initially in the lower well of the potential. An inelastic scattering event via the resonance state channels electron energy into the vibrational mode of the molecule, populating a wavepacket of excited vibrational states wherein the Li atom tunnels through the interwell barrier. Inelastic current thus results in a controlled threading motion through the ring. The threading was monitored by calculating the probability of finding the lithium in the raised well of Figure 5 as a function of time. Clear oscillations over the first few picoseconds correspond to the lithium shuttling from one side of the ring to the other, see Figure 6.

The zwitterion junction provides a simple and convenient prototype to explore the effects of charge delocalization on current-driven dynamics. The degree of localization of the charge can be systematically varied by including a varying number of aluminum atoms in the clusters. If only a single aluminum atom is included to represent each contact, the extra charge localizes strongly onto the carbon ring and the displacements in the potential minima are enhanced, as shown in Figure 5, giving rise to large amplitude dynamics. As the number of explicit aluminum atoms included increases, the charge state delocalizes and the equilibrium displacement between the initial and resonant states decreases. As expected from the general discussion of section I (see Figure 1), the ensuing current-driven dynamics is correspondingly suppressed. This is evidenced by the order of magnitude decrease in the probability for lithium tunneling with increasing number of metal atoms in Figure 6.

V. Surface Nanochemistry

The examples considered in the preceding of "shaking" a zwitterion rattle and "bouncing" a fullerene show the potential utility of inelastic current to produce molecular motion, but what if such events are an undesirable feature? In the construction of molecular electronics, one might be more interested in generating stable junctions, in which minimal dynamics occur, such that reliable current–voltage characteristics are maintained under continual use. Can design rules be developed to guide efforts to create devices where current-induced failure is eliminated?

A synthetic paradigm in which these questions have been addressed is the development of hybrid organic–silicon technology.[31] Silicon-based molecular electronics are generally more susceptible to current-driven damage than the metal-based analogues since the Si surface tends to localize the charged resonance. At the same time, the technological potential and the fundamental interest of semiconductor-based devices enhance the interest in learning to inhibit current-driven dynamics in such systems. STM experiments performed in ultrahigh vacuum on isolated organic molecules adsorbed onto Si have shown that under application of a bias voltage, the induced current often results in desorption of the molecule from the surface.[13] Early studies[32] suggested that desorption would occur in systems where conjugation is retained in the adsorbed state but not in species where π bonding is lost upon adsorption. Conjugated systems are associated with low-energy resonances that can be readily accessed under low bias voltage conditions, leading to desorption via the resonant mechanism of section I. It was thus proposed that stability could be attained by focusing on the use of entirely σ-bonded molecules for conducting current, since such systems lack resonances near the Fermi energy level of the electrodes.

Recent experimental results on cyclopentene adsorbed onto Si(100) challenged this conclusion (Figure 7). It was found that desorption takes place at both bias polarities, however, with very low probability.[13] Extensive calculations of the trans-

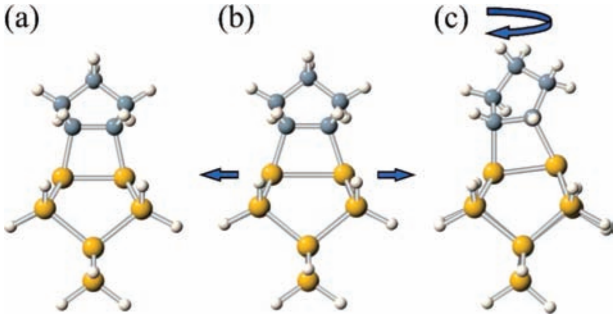

FIGURE 7. Equilibrium geometries of the neutral and charged states of cyclopentene adsorbed onto a Si(100) surface, where the surface is represented as a cluster of silicon atoms (orange) saturated by hydrogens to mimic bonding in the bulk. The neutral (a), positive ion (b), and negative ion (c) states of the system are shown, and the arrows indicate their distortions from the neutral geometry. Reprinted with permission from ref 13, *Phys. Rev. Lett.* **2006**, *97*, 187601. Copyright 2006 American Physical Society.

port and electronic structure of the cyclopentene-based junction, have shown that the strong hybridization with the surface leads to a drastic decrease of the σ orbital energies, bringing both the HOMO and the LUMO into the vicinity of the Fermi level.[13] It was found also, however, that the resonance lifetimes of both resonances are surprisingly long, much longer than what conventional wisdom, based on systems such as adsorbates on metal surfaces and the well-studied benzene/Si(100), suggests. Furthermore, these numerical studies[13] found unexpectedly large equilibrium displacements of both resonances compared with the neutral ground state. Thus, while answering one question, namely, providing the reason for which desorption is unexpectedly observed, the numerical studies opened another question, that is, why is the observed desorption rate so low? Whereas the discussion of section I suggests that long lifetimes and large equilibrium displacements would lead to efficient desorption, the cyclopentene/Si system exhibits longer lifetimes and larger equilibrium displacements than the benzene/Si analog, yet orders of magnitude lower desorption yields.

Further dynamical and structural studies, designed to address this question and to draw more general conclusions, point to the role played by *mode coupling* in current-driven dynamics. Often the mode into which the electron energy is deposited is not the molecule—surface vibrational mode but rather an internal mode. This is the case in both the benzene/Si(100) and the cyclopentene/Si system. In the former, however, efficient mode coupling allows rapid energy transfer into the reaction coordinate whereas in the latter the initially excited mode does not couple efficiently with the desorption mode. We recall that current-driven dynamics, here and more generally, has to compete with relaxation of the vibrational excitation and that the latter can be efficient, in particular when the reduced mass associated with the initially excited mode is large.

The results of this section carry interesting implications to the prospect of silicon-based molecular electronics, a subject of increasing fundamental and technological interest.[33] They suggest that organic molecules, with their typical strong binding to silicon, may hybridize sufficiently with Si(100) to bring the σ orbitals to STM accessible energies and cause current-driven phenomena in systems that lack π bonding. Our results illustrate also the role played by system details, such as the extent of mode coupling and of vibrational dissipation. On the one hand, these conclusions suggest routes to interesting surface nanochemistry. On the other, they suggest means of suppressing undesired current-induced failure.

VI. Future Directions

The previous sections reviewed the topic of current-driven dynamics in molecular junctions, an emerging subdiscipline of molecular electronics with potential applications ranging from new forms of molecular machines to STM-driven nanochemistry and the design of stable molecular electronics.

From a fundamental perspective, current-driven dynamics in junctions is a lovely example of strongly nonadiabatic surface chemistry and a phenomenon that distinguishes molecular-scale from macroscopic molecular electronics. On the theoretical level, current-driven dynamics is an interesting challenge, involving a strongly coupled multidimensional system subject to nonequilibrium and open boundary conditions in the electronic subspace, which interacts with both electron—hole pairs and phonons in the electrodes. Experimentally one faces the rewarding challenge of observing signals from single systems. From a technological perspective, the increasing interest in nanoscale, individually driven molecular machines on the one hand, and the concern of current-induced failure on the other, make current-driven dynamics a problem of growing relevance. It is thus expected that future experimental and theoretical research will continue to enhance our understanding of the fundamental principles and potential applications of current-driven dynamics in molecular scale electronics.

Note Added after ASAP. This paper was posted to the web on May 13, 2010 with a missing reference. The revised version was posted on July 1, 2010.

BIOGRAPHICAL INFORMATION

Ryan Jorn was born in 1981 in Elmhurst, IL. He received a B.A. in physics and chemistry at Ripon College in 2003 and his Ph. D. at Northwestern University in 2009. His thesis research focused on the study of vibrational excitation and decoherence in molecular junctions.

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