

Nuclear Coupling and Polarization in Molecular Transport Junctions: Beyond Tunneling to Function

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Much current experimental research on transport in molecular junctions focuses on finite voltages, where substantial polarization-induced nonlinearities may result in technologically relevant device-type responses. Because molecules have strong polarization responses to changing charge state or external field, molecules isolated between electrodes can show strongly nonlinear current-voltage responses. For small applied voltages (up to ~ 0.3 volt), weak interaction between transporting electrons and molecular vibrations provides the basis for inelastic electron tunneling spectroscopy. At higher voltages and for certain time scale regimes, strong coupling effects occur, including Coulomb blockade, negative differential resistance, dynamical switching and switching noise, current hysteresis, heating, and chemical reactions. We discuss a general picture for such phenomena that arise from charging, strong correlation, and polarization (electronic and vibrational) effects in the molecule and at the interface.

Electronic conduction in the single-particle or single-molecule limit can lead to more complex behavior than can be seen in bulk transport systems. Some effects arise from the small number of electrons passing through the molecules; for example, the charging of a molecule by a single electron can give rise to a steplike Coulomb blockade behavior in the current, I , measured as a function of source/drain voltage, V_{sd} . Molecular transport junctions (MJ), in which electrons move through molecules under voltage bias, can show striking nonlinear effects, such as negative differential resistance (drops in I with increasing V) and single-molecule switching accompanied by hysteresis. Many of the most interesting experiments in molecular electronics (ME) require understanding beyond the simplest picture of MJ transport, the limit of coherent tunneling [recently overviewed by two of us (*1*)]. This is the limit of very weak coupling between the transporting charge and the polarization caused by the molecular and environmental vibrational and electronic degrees of freedom that can interact with the moving charge. In this regime, the electron does not charge the molecule (that is, the energy levels do not reorganize) but uses unoccupied energy levels to assist the tunneling process.

In this overview, we explore the more complex, exciting work in MJ's focused on the energy regime in which the molecular internal degrees of freedom become involved. This strong vibrational or electronic coupling regime is accessed at higher driving voltage. We can think about these two regimes in terms of how much interaction

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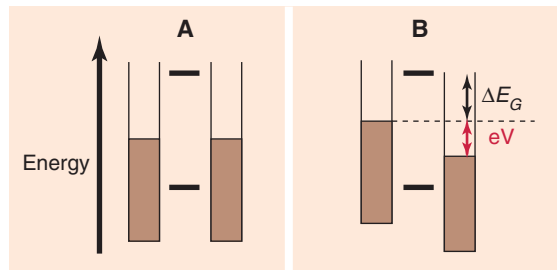


Fig. 1. (A) Energy diagram for an unbiased junction, with occupied electronic states in the electrodes in brown and molecular levels as sharp lines. (B) A voltage V is applied across the source-drain, but still the molecular levels are not in electronic resonance, because ΔE_G is still large.

the tunneling electron is allowed to have with the molecular and environmental vibrations and electronic polarization, that is, the extent of coupling.

Almost 2 decades ago, Yablonoich (*2*) pointed out that, when electron transport changes the charge state of a molecule, the vibration coupling caused by the new potential could be so strong that it could lead to bond breaking, thus obviating any applications in electronic devices. In fact, harnessing electronic changes to access vibrational motion enriches the palette of possible transport behaviors, including unusual switching and memory regimes, and provides an intrinsic scientific challenge as well as possible single-molecule device function. Indeed, MJ science might be seen as now finishing chapter 1 (devoted to establishing methods and investigating the simplest situation of coherent tunneling transport) and entering chapter 2 (examining richer phenomena involving nonlinear transport, charging, vibronic effects, switching, and spectroscopy).

Early theoretical speculations considering the use of single molecules as circuit elements (*3*) and even as extended architectures (*4*), and pio-

neering work by Kuhn and co-workers (*5*) that measured currents through adsorbed molecular layers on metals and semiconductors, introduced the idea of molecular conduction. New assembly techniques for preparing controlled molecular adlayers allowed fabrication of structures on which conductance could be measured (*6–8*). Development of scanning probe microscopy turned ME, and conductance spectroscopy in particular, into scientifically legitimate fields. A major early breakthrough was the invention of scanning tunneling microscopy (STM) (*9*) to examine conductance characteristics of single adsorbed molecules (*10, 11*). Later developments include mechanical (*12–15*) and electrochemical (*16, 17*) break junctions, allowing the inclusion of a gate electrode.

Diagrams like those in Fig. 1 are often used to discuss MJ transport qualitatively (*18, 19*). In these one-electron energy-level diagrams, the single-electron energies shown should not be confused with molecular state energies. Molecules have a finite number of electrons and show substantial charge interaction effects both in the purely electronic states and in the vibrational-

electronic (vibronic) manifolds. Energies of the frontier molecular orbitals, the highest occupied and the lowest unoccupied molecular orbital (HOMO and LUMO, respectively), can change by more than 1 eV upon charging, even without notable geometry changes (unlike the simpler tunneling case). Such changes arise from electron interactions within the molecule. Coulomb interactions make these one-electron energies dependent on total electron count n , thus,

$$\epsilon_i = \epsilon_i(n) \quad (1)$$

and Fig. 1 must be interpreted quite carefully, because the energies will change upon charging.

Early work on MJ's focused on the regime (*1, 20*) where the two levels corresponding to the HOMO and LUMO in Fig. 1 remain far above and below the relevant Fermi energies of the electrodes. In that case, molecular charging does not take place, transport occurs in a coherent tunneling regime assisted by the molecular levels, and the molecule just acts as a tunneling barrier. This is the Landauer-Imry (L-I) regime (*21*). Although the measurements discussed here are steady-state type, relative time scales, associated with important energy parameters, play a decisive role in characterizing transport regimes. The injection gap, ΔE_G , determines the tunneling traversal time, $\tau_c \sim \hbar/\Delta E_G$, in off-resonance situations (*22*), whereas the spectral density, Γ , is related to the molecule-metal coupling and determines, in the absence of nuclear distortions, the time, \hbar/T , spent by an electron on the molecule before escaping into the metal leads.

Vibronic coupling effects are strong when the time spent by the electron on the bridge is long

enough for the charge to interact with the nuclear dynamics. A criterion for the weak coupling limit is given by $M/\sqrt{\Delta E_G^2 + (\Gamma/2)^2} \ll 1$, where M is the vibronic coupling. Then the electron is transported too rapidly for it to interact significantly with vibrations, and inelastic tunneling can be treated as a weak perturbation. In the opposite limit of strong coupling, such perturbative treatment breaks down. As applied voltage increases, the effective ΔE_G decreases, so an entirely new experimental regime, involving important vibronic effects, becomes available.

A General Model

Conductance spectroscopy (current/voltage measurement) depends on geometry, energy levels and interaction strengths, and effects of the external thermal bath. Molecular levels have discrete MO energies, whereas the electrodes are macroscopic, with continuous densities of states. An appropriate understanding of transport behavior requires treating the (nonequilibrium) dynamics of the molecule between electrodes with different chemical potentials.

To fully describe transport in MJs, we must understand the electrodes, the molecular vibronic structure and response, possible optical excitations, geometric changes, and thermal effects. To clarify where these arise, we use a crude phenomenological model Hamiltonian to describe the molecule, the leads, and their interaction:

$$H = H_{\text{MOL}} + H_{\text{LEAD}} + V \quad (2)$$

The molecular Hamiltonian, H_{MOL} , describes the molecular electrons (H_{el}), vibrations (H_{vib}), and their interaction, $H_{\text{el-vib}}$:

$$H_{\text{MOL}} = H_{\text{el}} + H_{\text{vib}} + H_{\text{el-vib}} \quad (3)$$

The electronic part is a sum of free electron and electronic correlation terms:

$$H_{\text{el}} = \sum_i \epsilon_i n_i + (\text{correlations}) \quad (4)$$

with n_i the number of electrons in energy level i . The Hamiltonian H_{vib} describes harmonic vibrations on the molecule, and the vibronic mixing ($H_{\text{el-vib}}$) term can be written

$$H_{\text{el-vib}} = \sum_{\ell} M_{\ell}^{\alpha} Q_{\alpha} n_{\ell} \quad (5)$$

with M_{ℓ}^{α} as the vibronic coupling strength, n_{ℓ} as the number of electrons in the level, and Q_{α} as the dimensionless normal coordinate displacement. The form of Eq. 5 assumes that the most important vibronic interaction arises from a shift in the oscillator equilibrium point that is proportional to the level occupation.

Both the term H_{LEAD} and the molecule-electrode interaction V are represented simply, ignoring interelectronic repulsion and retaining only site energy and neighbor tunneling terms (Hückel-type or tight-binding model).

This minimal description can be supplemented by the interactions between molecular vibrations and the thermal environment, the vibrational anharmonicity, the possible role of photons or excitons, and the electron-electron interactions. Different behavior regimes determined by these parameters can be accessed by changing junction conditions, including applied voltage bias, gate potential, and structural patterns of the molecule.

Most electron transfer (ET) theories for molecular systems, and much MJ modeling, ignore the effect of electronic correlations except in a mean-field approximation. Even within the latter, different molecular charge states will have different energy levels. Ignoring electron correlations can lead to confusion and inaccuracies because they can cause important energy shifts upon charging (see below). The electron-vibration interaction (Eq. 5) gives rise to correlation between electron and nuclear dynamics. These two interactions provide the broad spectrum of behaviors discussed here.

The most powerful description of transport in MJs is given by the nonequilibrium Greens function (NEGF) formalism (23, 24) (although simpler descriptions such as scattering theory may be useful close to equilibrium). In this formalism, terms known as “self-energies” are used to describe the effects on a particular system, in this case the molecule, of interactions (both internal, such as anharmonicities and electron-electron interactions, and external, interactions with the environment in which the molecule is found) that are not included in the system description. These self-energies have direct spectroscopic manifestations, appearing as a shift (real part of the self-energy) and broadening (imaginary part, sometimes called spectral den-

Coulomb blockade regime (14, 25–27), in which coherence between the charge motion from the left electrode to the molecule and that from the molecule to the right electrode is lost, rate equation approaches are useful [if we think of the molecule as a quantum dot, this is the Coulomb blockade (27) limit in mesoscopic structures]. These are also complicated, because the entire Fock space on the molecule (that is, all the possible excitations and populations) may be accessed (26). In the inelastic electron tunneling spectroscopy (IETS) regime, the vibronic coupling $H_{\text{el-vib}}$ is a weak perturbation on the elastic scattering picture.

Weak Polarization Effects: Inelastic Tunneling Spectroscopy

In MJs, optical spectroscopy is not yet used as a standard tool for several reasons. Injecting light into a small gap between metallic leads is difficult, and the sample can be as small as a single molecule, implying small signal-to-noise ratio. Nuclear dynamics effects are usually deduced from the vibrational structure in tunneling spectra. This structure is associated with H_{vib} and $H_{\text{el-vib}}$ in Eq. 3; the former represents the molecular vibrations, whereas the latter refers to the charge-state dependence of the equilibrium molecular geometry. IETS appears as a small correction to the transmittance in the L-I regime, arising from small modifications to the transmittance associated with molecular vibrations when the tunneling occurs far from an electronic resonance: Essentially, the moving charge has no time to interact with the nuclear polarization (but it uses a new, inelastic, channel imparting energy to the vibrations).

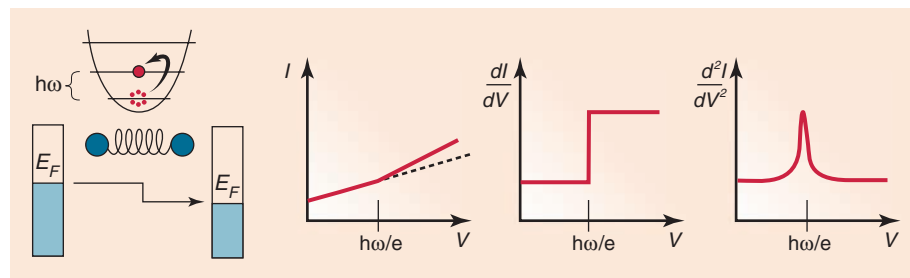


Fig. 2. The expected IETS behavior as the voltage V_{sd} is increased through a vibrational resonance.

sity) of molecular energy levels. In addition, the environmental self-energies determine fluxes of energy and particles into and out of the system. The need to evaluate these self-energies leads to difficult theoretical problems, best analyzed in model systems and generally not yet numerically approachable for realistic junctions.

In the L-I limit, the inequality $\Delta E_G > \Gamma \gg k_B T$ (where k_B is Boltzmann’s constant and T is temperature) holds, and the effect of vibronic coupling is small. The Landauer formula (Eq. 6 below) is then useful if electronic correlations can be disregarded. For smaller Γ and/or faster thermal relaxation, we approach the so-called

Initial observations of IETS in MJ were obtained in STM structures (28). Other testbeds, involving molecular adlayers, were then studied, and true single-molecule junctions have been investigated by using IETS (29–31). As Fig. 2 demonstrates, for bias energy eV_{sd} less than the vibrational energy $\hbar\omega$, the tunneling is elastic. Above a threshold where $\hbar\omega = eV_{\text{sd}}$, the transporting electron can deposit $\hbar\omega$ on the molecule. A second inelastic channel could then open, in addition to the elastic one. The cross section for such an excitation is very small because the electron traversal time ($\sim \hbar/\Delta E_G$) is much smaller than the oscillator period. One expects such a

threshold for each normal coordinate of the molecule, unless propensity rules limit such excitation (see below).

The expectation for what one would see on the basis of a simple channel addition model is shown in Fig. 2. The change caused by the opening of the vibrational resonance channel at $eV_{sd} = \hbar\omega$ are usually not visible because the cross section is so small. Such changes can, however, be observed as reproducible features in the second derivative d^2I/dV_{sd}^2 plotted against V_{sd} . These features are usually peaks, indicating increase in transmission upon opening of a vibrational channel, but dips, that is, negative peaks, resulting from interference between the elastic and inelastic transmission are sometimes observed as well. A plot of d^2I/dV_{sd}^2 versus V_{sd} is referred to as the IETS spectrum. Experimental measurements made in a crosswire junction at 9 K are shown in Fig. 3.

Elegant theoretical approaches to IETS (32–37) include some that deal with a correct analysis of the line shapes (38, 39) rather than simply assuming that the elastic and inelastic channels are additive (the basis for Fig. 2). The weakness of the spectrum suggests use of perturbation theory, which has reproduced experiments well (40), and allows data interpretation. The L-I coherent conductance, g , is

$$g = 2e^2/h \text{Tr}[\Gamma^R G \Gamma^L G^+] \quad (6)$$

$$(G)^{-1} = E - H + (i/2)\Gamma \quad (7)$$

where Γ^R and Γ^L are spectral densities in the right and left electrodes, respectively, whereas G is the (retarded) Green's function, with H the system Hamiltonian. Using a normal-coordinate expansion and standard DFT calculations, we can compute the conductance of the inelastic channel (and the IETS spectrum). Propensity rules for IETS can be also be derived, but unlike selection rules for Raman or infrared spectroscopy these rules do not arise from the symmetry properties of the light-matter interaction. Rather, the rules follow from invariance properties of the Green's function matrix, and some arguments about intensities are expected along particular pathways (41–43). They are helpful in assigning spectra, discerning chemical reactions in the junction, obtaining a pathway description for tunneling, and finding the geometry in MJs.

Because IETS measurements are sensitive to molecular geometry and charge (42, 43), they might help understand processes outside the L-I regime, in particular when charge on the molecule changes with applied voltage (where strong electron-vibration coupling can also lead to new functional properties).

Strong Polarization Effects

IETS is the most useful, reliable characterization tool available today for MJs. Other important

phenomena are associated (44) with polarization interactions in junctions:

1) Resonance inelastic electron tunneling spectroscopy (RIETS) is related to the standard IETS just as resonance Raman scattering is related to Raman scattering. Whereas the normal, weak coupling processes provide information about the ground molecular state, their resonance counterparts are sensitive to vibrational structure and motion in the excited state (for Raman scattering) or the intermediate molecular ion (in MJs).

2) Strong vibronic and polarization interactions are implicated in charging phenomena. Charging coupled to nuclear motion can lead to nonlinear phenomena, such as bistability, hysteresis, switching, and negative differential resistance (NDR), that pertain to junction functionality. The coupling of change in electronic charge distribution with response of the nuclear configura-

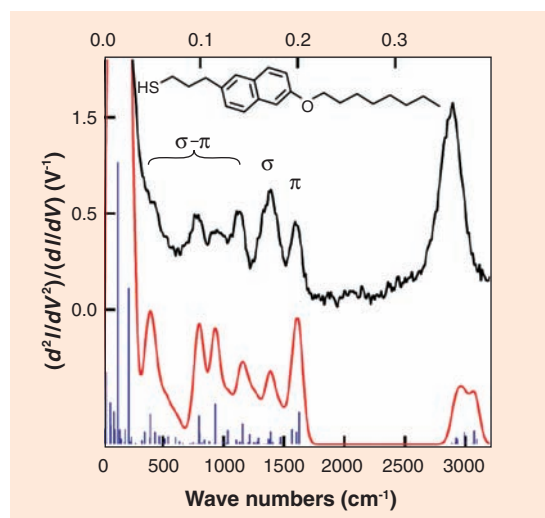


Fig. 3. Experimental (black) and computed (red) IETS spectra for the molecule in the inset, with modes specified as coupled to σ or π type tunneling. Blue lines indicate the computed frequency and IETS intensity of the individual modes [from (43)].

tion dominates molecular ET. The difference in MJs is that the initial and final charging states are nonequilibrium aspects of the current-carrying junction.

3) Strong vibronic interactions can lead to strong junction heating. Generated heat can be carried away by both phonons and electrons. Heat generation and dissipation on the molecular scale are therefore important aspects of overall junction operation.

4) Affecting molecular configuration changes and reactivity, by the combined effects of strong field and electronic current in a MJ, is another potentially important application of such junctions.

Such issues constitute some of the frontline problems in studies of MJs. Here, we briefly overview their present status.

RIETS. Under electronic resonance tunneling conditions, the injection energy measured rela-

tive to vacuum is similar to the molecular ionization energy (for hole injection) or electron affinity (for electron injection), often expressed in simplified discussions as HOMO and LUMO energies. A transient intermediate molecular ion forms and may be stabilized by electronic or nuclear polarization of the environment (image or polaron formation). The vibrational structure of the transient polaron may then appear in the inelastic signal as satellite peaks (sidebands) in the conductance-voltage plot near the conduction threshold. For this structure to be resolved, another inequality, $\omega_0 > \Gamma/2$ (where ω_0 is the relevant vibrational frequency), must be satisfied between the system time and energy scales. These satellite peaks are expected (and seen) in the conduction spectrum rather than in d^2I/dV_{SD}^2 (as in IETS).

Vibronic interactions and charging phenomena.

Interest in MJs stems partly from functionalities such as rectification, switching, and addressable memory. Change of redox state has been offered as an underlying cause for such behaviors, supported by experimental observations (45–49). Mechanisms and dynamics of such transitions are still under discussion. It is clear that nuclear motion and electron-phonon coupling are strongly involved. As in ET reactions, nuclear motion is not merely a consequence of redox state change. Rather, this transition is a cooperative vibronic process. In a mean field model (50), such multistability results from positive feedback: Formation of the transient molecular ion polarizes the electronic and the nuclear environments and further drives and stabilizes ion formation. The resulting steady state in the junction leads to a self-consistency condition in which the population of the MO and its energy are interdependent: The orbital energy is shifted by polaron formation by an amount that depends on its electronic population n . The self-consistency condition allows for multistability properties.

Whether this multistability can lead to hysteresis behavior and memory effects as suggested in (50) or to intermittent noise associated with transitions between two locally stable states as discussed in (51, 52) is an issue of relative time scales: the observation time versus the rate of transitions between locally stable states, as is evident in the experimental results (53) displayed in Fig. 4. This polarization mechanism may also cause NDR phenomena (48–50), again depending on relative time scales (54, 55). Experimental observations have not yet fully converged. For example, the predicted dependence on gate potential (50) is a central observation in (48, 49) but is far less evident in (56). The model of (50) suggests a vibronic and electronic polarization origin (57) of observed

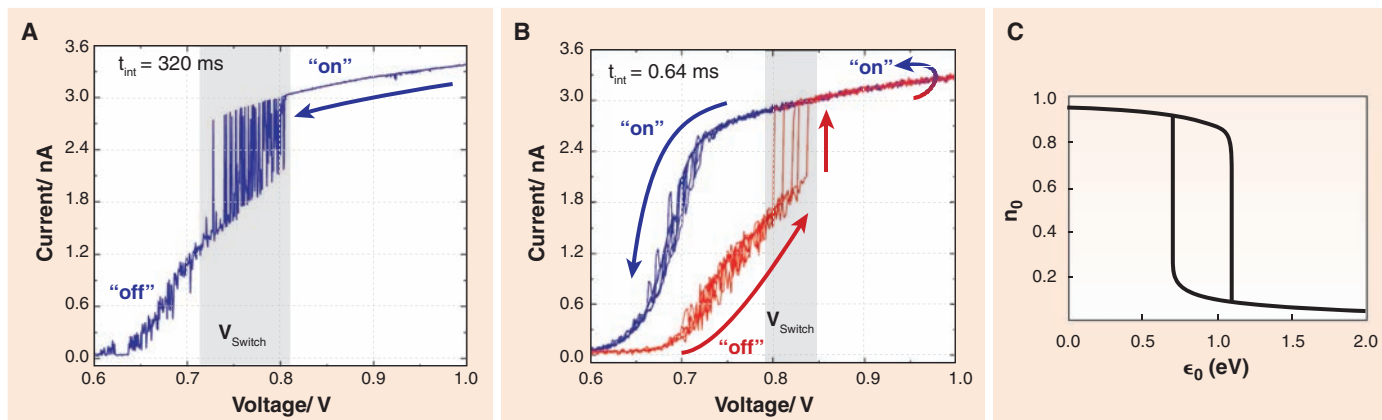


Fig. 4. Dynamics of I/V_{SD} switching response of bipyrindyl-dinitro oligophenylene ethynylene dithiol (BPDN-DT) molecules between gold contacts (53). **(A)** The voltage is changed relatively slowly, and bistability gives rise to telegraphic switching noise. When voltage changes more rapidly **(B)**, bistability is manifested by hysteretic behavior. **(C)** The locally

stable solutions of the equilibrium self-consistent relation (50) between the energy and population of the molecular level of Fig. 1. Multistability caused by polarization of the environment by the molecular charge suggests that hysteresis, switching behavior, and telegraph-type fluctuations may be observed.

charging transitions in redox MJs but is too simple to account quantitatively for the I/V behavior; a simple model comparison is shown in Fig. 5. Other mechanisms, for example, modulation of the molecule-lead bonding (56, 58), may also lead to switching and bistability phenomena. These switching mechanisms rely on molecular polarization, in sharp contrast to traditional semiconductor voltage-gated switching.

Heating and heat conduction. The combination of small molecular heat capacity and inefficient heat transfer away from the junction (2) might affect the stability and integrity of MJs operating outside the L-I regime. New work aims to assess both heat conduction and temperature rise in a current-carrying junction. When heat transport is dominated by phonons, one can derive (in the harmonic approximation) a Landauer-type equation for the heat current. Such expressions were used to analyze heat conduction properties of alkanes, predicting interesting dependence on molecular chain length (59).

The temperature rise in MJs is determined by the balance between heat dissipation and conduction rates. General theories address this balance, but application to realistic junction models is prohibitively complex. Simple models (59) show two crossover transitions. The first occurs when the bias matches the frequency ($eV_{sd} > \hbar\omega_0$) and vibrational excitation becomes possible. The second occurs when the voltage permits electronic resonance. Observations pertaining to thermal transport properties of molecular junctions have been recently published (60–63).

Current-induced reactions (64, 65). Conformational changes and chemical reactions can originate from forces exerted on the molecule, in-

cluding short-range forces exerted by a tip used to push atoms, long-range electrostatic forces from the imposed potential bias, and forces associated with the transporting current. The ultimate result of affecting chemical change depends on the balance between pumping energy into molecular bonds and dissipation of this excess energy.

New Horizons

Although IETS has been under study for nearly a decade and the above discussion may be considered a report on work in progress, we now reflect on several (unrelated) issues that we expect to become prominent in MJ research.

Understanding electronic correlations. Such phenomena as Coulomb blockade and Kondo resonances arise from strong electronic correlations that are beyond the applicability of mean-field models. Even image effects, reflecting correlations between tunneling electrons and electrons in the metal leads, are difficult to de-

scribe properly (66). Computational efforts toward improving this have been reported (67). Kondo-assisted injection might advance organic photovoltaics, and Coulomb blockade structures could lead to single-molecule memories.

Noise in molecular junctions. Noise has been extensively studied in mesoscopic conductors (68), and applications in MJs have been discussed (69–74). Noise measurements can be useful, for example, for determining the number of channels that contribute to transport and for estimating junction coupling parameters such as the electron/vibration coupling strength and the relative sizes of Γ , the inverse electron lifetime, at the two electrodes (72). Different aspects of the effect of vibronic coupling on the current noise have been studied [see (75) and references therein]. Further progress awaits a systematic experimental study of this issue.

Illumination effects and junction spectroscopy. The slow introduction of junction spectroscopy in ME can be understood by the unfavorable ge-

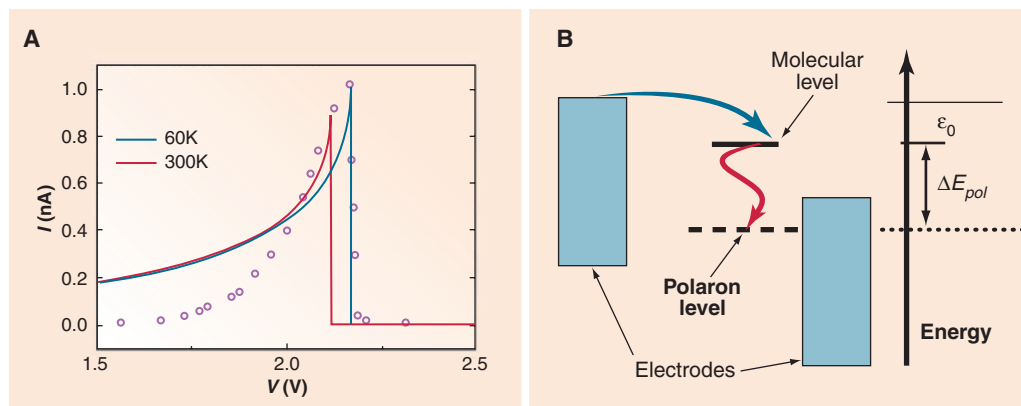


Fig. 5. **(A)** Observed (48) (dots) and calculated (in the simple polarization model, solid lines) NDR behavior. **(B)** How NDR can occur. Raising the voltage permits charging of the LUMO level, that subsequently is reduced in energy by vibronic and electronic polarization. When the total polarization energy, ΔE_{pol} , is large enough, the level energy drops below the leads chemical potentials, and (at low T) the current drops sharply. At higher T , the line broadens and shifts to lower voltage, because of thermal broadening of E_F .

ometry, where the molecule (or molecular layer) is located in a gap of molecular dimension between two essentially macroscopic leads. Recent reports using light to switch MJs (76–82) indicate that this barrier can be overcome. Indeed, light emission from biased STM junctions can be detected, and although most of the observations are associated with emission by metal plasmons there are some observations of molecular emission. Junction spectroscopy may thus become an important new avenue of research in ME, and the essential proximity of metal and/or semiconductor structures suggests a possible connection with plasmonics.

Accurate computation of transport behavior. As mentioned several times, straightforward quantitative computational methods (at the mean-field level) are available in the L-I regime of elastic tunneling and for IETS (Fig. 3). When polarization, photonic, or correlation effects are present, only model calculations are available today (such as those yielding the computational results of Figs. 4 and 5). A challenging theoretical problem is extension of these formal techniques to allow accurate numerical predictions.

The theoretical constructs and modeling discussed here suggests exciting experimental challenges, including characterizing single-molecule switching and its dynamics, noise and heating measurements, higher-order transport phenomena such as Seebeck coefficients (83) or thermopower, and spectroscopy (Raman or optical) in MJs. Many of these arise from the polarization behavior characteristic of molecules (much more than in most semiconductors). In particular, single-molecule switching (at the ~1-nm scale, well beyond current integrated circuit scaling) can occur via vibronic mechanisms that are totally different from the field-effect transistor switching. In sharp contrast to the L-I regime [in which stochastic switching arises from geometry modulations at the contacts (84, 85)], in these vibronic situations switching, charging, and polarization mechanisms provide hugely varying conductance properties among different molecules.

The vibronic and electronic polarization effects discussed quite early (2) as possible show-stoppers for ME actually can provide single-molecule switching (Fig. 4), with use of only two electrodes. This is based on polarization and oxidation state change, as opposed to the voltage modification in traditional complementary metal-oxide semiconductor circuitry [where the switching is caused by voltage on a third (gate) electrode]. The molecule switches by pulling a switch! Some of these polarization and correlation effects are only now starting to be clarified and promise to lead to answers to device applications and to important new questions.

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