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Molecular Signatures in the Transport Properties of Molecular Wire Junctions: What Makes a Junction "Molecular"?

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The simplest component of molecular electronics consists of a single-molecule transport junction: a molecule sandwiched between source and drain electrodes, with or without a third gate electrode. In this Concept article, we focus on how molecules control transport in metal-electrode molecular junctions, and where the molecular signatures are to be found. In the situation where the molecule is relatively short and the gap between injection energy and molecular eigenstates is large, transport occurs largely by elastic tunneling, stochastic switching is common, and the vibronic signature can be found using inelastic electron tunneling spectroscopy (IETS). As the energy gaps for injection become smaller, one begins to see stronger molecular signatures – these include Franck–Condon-like structures in the current/voltage characteristic and strong vibronic interactions, which can lead to hopping behavior at the polaron limit. Conformational changes induced by the strong electric field lead to another strong manifestation of the molecular nature of the junction. We overview some of this mechanistic landscape, focusing on significant effects of switching (both stochastic and controlled by the electric field) and of molecular vibronic coupling.

Keywords:
- break junctions
- molecular electronics
- self-assembled monolayers
- single-molecule studies
- tunneling

1. Introduction

The intense current research effort in molecular electronics is justified both by the fundamental challenge posed by non-equilibrium quantum dynamics for transport in these mesoscale structures and by the expectation that the electronic transport properties of a molecular-scale device can be tailored with the tools of synthetic chemistry and surface science to make possible a technology at the nanometer scale.[1–3] The field was greatly stimulated by the first pioneering experiments,[4–8] focused on fabrication methodology and proving that the current passing through a single molecule was a measurable quantity. However, these experiments immediately revealed that the current/voltage (I/V) characteristic of a molecular junction did not necessarily say much about the particular molecule employed. The nature of the metal–molecule contact and the specific geometry were the least controllable aspects of the experiment and the ones that ultimately determined the measured current. The reproducibility of electrical measurements in single-molecule junctions has greatly improved, but often the role of the molecule in the junction is passive – it acts mostly as a tunneling barrier between the electrodes, and the I/V curve does not show any feature that is specifically molecular.

Some of the intriguing observations made on molecular-scale devices were proved not to have a truly molecular origin. Recently Lau et al.[9] showed that a Pt/stearic acid/Ti

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junction can be switched reversibly to higher or lower conductance states by applying a large negative or positive potential pulse to the titanium electrodes. The authors used a scanning probe technique to provide strong evidence that the switching is due to the formation and dissolution of metal filaments through the molecular layers, a mechanism that is probably at work also in many other reported switches that behave similarly.[10–12] The negative differential resistance (NDR) and memory effects observed in self-assembled-monolayer (SAM) containing species with low reduction potential[13] was initially attributed to some conformational or electronic change in the molecule; it may actually originate from the *lateral hopping* of the charge residing in the monolayer,[14,15] or from charge trapping due to vibronic coupling on the molecule or at the interface.[16]

In these two examples, interfacial or metallic effects could be confused with purely molecular mechanisms. It is therefore interesting to ask to what extent current molecular junctions exploit the molecules as an active element of the circuit and what characteristics of the I/V curve reveal features that are truly molecule dependent. Finding *molecular signatures* in the measured I/V curve makes it possible to discriminate between molecular and other interfacial phenomena, avoiding improper interpretation of the measurements.

In this paper, we touch on three classes of recent experiments characterized by the emergence of unequivocally molecular features in the I/V curve. Molecules can reveal their presence in the junction due to the coupling of the electron transport with the nuclear motions. The coupling with high-frequency modes ($>100\,\mathrm{cm}^{-1}$) only weakly affects the total current in the tunneling regime, but gives rise to the important effect of inelastic electron tunneling (IET) measurable through IET spectroscopy, as described in the next section. We discuss a simplified rationalization of the possible transport regimes in Section 3, focusing on conditions under which one can observe switching in I/V curves due to the charging of the junction. Large geometry changes (due to low-frequency modes) may be driven by the inter-electrode electric field without requiring the oxidation or reduction of the molecule. When the conformational changes are accompanied by large conductance changes, a different kind of switching takes place, a few examples of which are given in Section 4. In Section 5 we discuss the amount of fine-tuning of the I/V curve that can be achieved by chemical modifications and the ways this can be probed.

2. Inelastic Tunneling

Electrons are said to cross the junction via inelastic tunneling if, during the coherent tunneling transport process,[17] they exchange energy with one or more vibrational levels of the junction. At very low temperature (<10 K) all the vibrational modes are in their ground state and the electron can only lose vibrational quanta of energy $\hbar\omega_\alpha$ (ω_α is the frequency of the molecular vibrational mode α). The inelastic channel that causes the excitation of mode α is opened only when the bias V is such that $|V|>\hbar\omega_\alpha/e$ (Figure 1). The sharp but small increase in conductance ($\mathrm{d}I/\mathrm{d}V$) each time a new inelastic channel in opened is seen as a peak in a plot of $\mathrm{d}^2I/\mathrm{d}V^2$ at $|V|=\hbar\omega_\alpha/e$. The measurement of $\mathrm{d}^2I/\mathrm{d}V^2$ therefore constitutes an *inelastic electron tunneling spectroscopy* (IETS) providing information on the vibrational levels of the junction. Only a minority ($<2\,\%$) of electrons cross the junction inelastically and only the vibrations that modulate the tunneling probability are active in IETS, providing an active inelastic channel.

The IETS technique has been long used in surface science,[18–21] but it was applied to single-molecule STM measurements only a few years ago.[22–24] In the past year several groups proved independently that this technique could be applied to metal–molecule–metal junctions. These groups used different experimental test beds (a nanopore device,[25] a cross-bar arrangement,[26,27] a metal/SAM/Au-nanoparticle junction,[28] and in wire junctions and break junctions[29])

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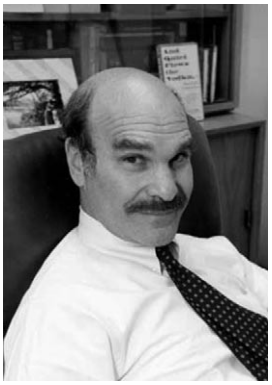

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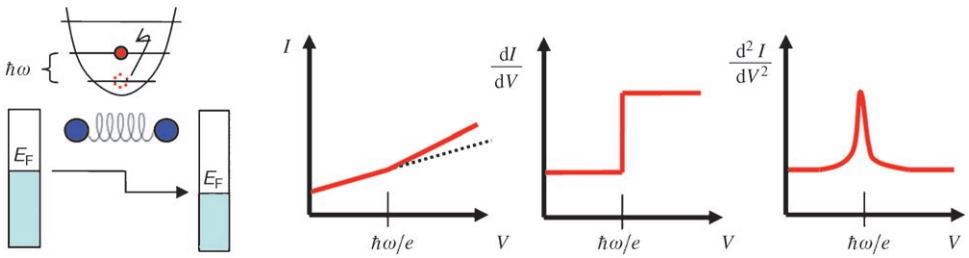

Figure 1. Illustration of the principle of inelastic electron tunneling spectroscopy (IETS): If the difference in chemical potential between the two electrodes is larger than the vibrational energy of one molecular mode, the electron can cross the junction losing one quantum of vibrational energy. This additional inelastic channel causes a small increase in conductance at $V=\hbar\omega/e$, better evaluated as a peak in a plot of d^2I/dV^2 versus V.

and carried out the measurement adding an ac modulation to the dc bias and collecting the second-harmonic signal, proportional to d^2I/dV^2, with a lock-in amplifier. Molecular vibrational features show up in all reported spectra, including (so far) dihydrogen, alkane thiolates and dithiolates, oligo-phenylene-ethynylene, and oligo-phenylene-vinylene.

The most obvious reason for the impact of IETS in molecular electronics is its applicability to virtually any junction, showing unmistakably that a molecule is actually bridging the two electrodes. Less trivial is the detailed assignment of all the features in IETS spectra to specific molecular vibrations, since the selection rules are not known and the comparison with the infrared or Raman spectra of related compounds does not provide a complete picture. A fully assigned IETS can be used to characterize the junction geometry and to understand how the electrodes modify the electronic structure of the molecule. A vibrational transition induced by a tunneling electron can be used as a *probe* of the local environment since its energy can be affected by partial charging of the molecule. The richness of information from IETS can be exploited best in conjunction with a predictive/interpretative tool provided by the theory.

Analysis of inelastic transport in model systems[30–48] reveals a complex phenomenology that can be captured by the non-equilibrium Green's Function formalism.[49,50] However, to interpret the features in any given spectrum, several approximations are appropriate for both the Hamiltonian used to describe the system and the transport models. The vibrations involving the interfacial atoms are very difficult to predict, so it was suggested to use few interfacial metal atoms with infinite mass[51] or just to remove the metal atoms for the vibrational analysis. Since in most cases the electron–phonon coupling[52] is small (IETS is a small change in overall current) and the bias is low (<0.2 V), a simple perturbative approach may provide a fast and reliable method to interpret IETS measurement.[43,44] This approach assumes that the main effect of the molecular vibration is to modulate slightly the tunneling matrix elements, and the intensity of the inelastic tunneling peaks can be related to the derivative of the tunneling matrix element with respect to the molecular normal coordinates. The simulated spectra obtained with the perturbative method are often in very good agreement with experiment, as exemplified in Figure 2. Although the numerical approach does not allow the formulation of selection rules, it naturally leads to propensity rules that can guide intuition. "Longitudinal" vibrations that involve the carbon backbone of the molecule seem to be the most active modes in IETS. Further joint experimental and computational investigations[53] are needed to clarify other aspects of these measurements, but the initial agreement seems very promising. One of the crucial aspects for which the comparison of experiment and theory seems useful is the discrimination between adsorbates laying flat on the surface and bridging the two electrodes.

The manifestations of electron–phonon coupling can be more complicated than in IETS. Qiu et al.[54] used a scanning tunneling microscope (STM) to image an individual copper phthalocyanine molecule adsorbed on a thin insulating layer of Al_2O_3 deposited on the surface of NiAl (a conductor). The electrons from the STM tip tunnel into the molecule where they reside for a finite amount of time before further tunneling to the NiAl surface; effectively, this is a double-barrier tunnel junction. This two-step incoherent mechanism was investigated theoretically by Sumi,[55] who predicted the occurrence of equally spaced peaks in the dI/dV spectra (not d^2I/dV^2) due to the resonance of the molecular vibronic levels with the Fermi energy of one electrode, essentially a Franck–Condon manifold.[45] Experiment seems to agree with the prediction although quantitative theoretical analysis is not yet available.

Features attributed to molecular vibrations were observed early on in three-terminal devices (or single-molecule transistors, SMTs)[56] but their detailed assignment was made problematic by the poor control of device geometry and molecular orientation. Two recent reports provided a statistical analysis of the vibration-related features appear-

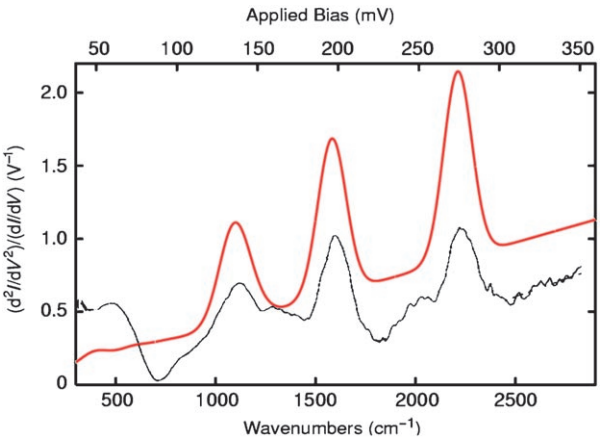

Figure 2. Experimental (data from Ref. [27]) and computed (Ref. [44]) IETS spectrum of the oligo-phenylene-ethynylene molecule.

ing in SMT measurements, allowing some insight into the mechanism of coupling between nuclear motion and tunneling. Yu et al.[57] observed peaks in the d^2I_D/dV_{SD}^2 plot of a SMT based on a Co^{II} complex that correlated well with the Raman spectra of the same molecule (V_{SD} is the potential between source and drain). The features observed did not depend on the gate voltage (V_G) and seem to occur via the same mechanism underlying IETS. Pasupathy et al.[58] in a SMT based on the C_{140} molecule observed vibronic features as peaks in the dI_D/dV_{SD} map whose position depends linearly on the gate voltage. This phenomenon seems analogous to that observed in a two-terminal device,[54] where a two-step tunneling takes place and the rate of the first tunneling event is enhanced by the resonance of one electrode's Fermi energy with a vibronic level of the molecule in the junction.

3. Regimes of Transport and Emergence of Bistability

Like the more general mesoscopic transport problem, of which it is a special case, molecular junction transport can occur in many different transport regimes. These can be distinguished by many energy scales including the injection gap E_G between the frontier molecular orbitals and the injection energy from the electrode, the spectral density Γ characterizing the mixing at the molecule–electrode interface, the vibronic coupling strength (measuring the energy associated with the nuclear reorganization when the molecule is reduced or oxidized), the on-molecule Coulomb repulsion (quantifying the energy required to put an extra electron on the molecule), and the thermal energy. Figure 3 presents a crude characterization of how transport regimes vary with E_G and Γ.

The molecule–electrode electronic coupling is characterized by Γ, which is essentially the inverse lifetime of the electronic states on the molecule. For large Γ, the transmission peaks are broadened and off-resonance injection is easy (Regions II, IV), while small Γ gives sharper textures but significantly reduced off-resonant injection (Region III). Vibronic coupling can change the transport mechanism in both Γ regimes.

In Region II of Figure 3, the effect of electron/vibration coupling may become strong for large vibronic couplings. This can result in trapping of charge on the molecule, due to the reorganization energy corresponding to geometric evolution in the charged state. This is the mechanism of the Marcus model of electron transfer, but in molecular junctions, it can lead to other behaviors; in particular, one can show using a simple model[16] that in the Born–Oppenheimer approximation, the dependence of the energy on the population of the molecular level can result in bistability. This bistability can manifest itself as a hysteretic current/voltage relationship (not stochastic switching, but switching between high- and low-voltage states because of populations). It can also give negative differential resistance, since at a high enough voltage charge is injected into the molecule, whose reorganization energy then takes it below the Fermi level of the downstream electrode – this sort of NDR is very different from the one observed by Hersam,[59] due to bandgaps in the silicon support.

An accurate study of bistability in a molecular wire determined by charging was presented by Blum et al.[28] They compared the I/V characteristics of two molecules, namely, bipyridyl-dinitro oligophenylene-ethynylene (BPDN) and oligophenylene-ethynylene dithiol (OPE) using several different test beds: STM measurement in a SAM with or without a gold particle attached on the top, crossed-wire junction measurement, and the so-called magnetic bead junction, which was described elsewhere.[60] Switching is displayed only by the BPDN molecule, which contains two nitro groups at its center that make it more easily reducible. All the measurements consistently show that the system with BPDN, normally in a low conductance state, switches

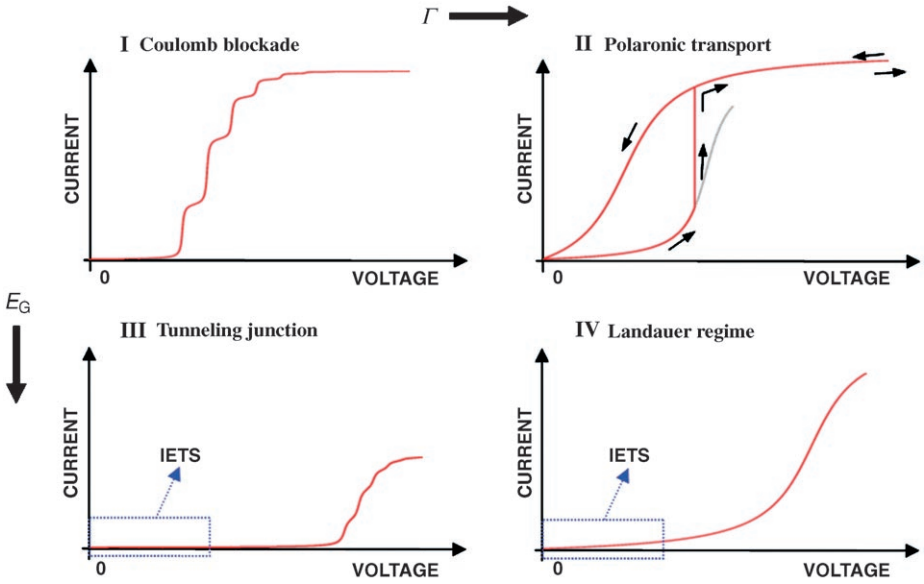

Figure 3. Different transport manifestations of the electron–phonon coupling in molecular wire junctions depending on the gap E_G between the frontier molecular orbital energy and the injection energy from the electrode and the spectral density Γ. Each plot is representative of a typical I/V plot in a different regime. The individual vibronic levels can be resolved for small Γ (i.e., small coupling between molecule and electrodes). When the vibronic levels go into resonance with one of the electrode chemical potentials (Region I), peaks in the dI/dV plot are observed[54,58] at voltages dependent on the gate bias, if present. For larger molecule–electrode coupling (Region II) the individual vibronic levels are not resolved but the electron–phonon coupling may cause polaron-type transport, which can give hysteresis and NDR.[16,28] For large E_G (Regions III and IV) the vibronic levels are accessible by the tunneling electrons only at high voltages and the effect on the I/V curve is less dramatic than in Regions I and II. However, the molecular vibrations modulate the tunneling matrix elements between the electrodes and their signatures can be seen in a plot of d^2I/dV^2 versus V at low bias (see Ref. [57] and IETS measurements in Figure 2).

to a high conductance state at a bias of $\approx$1.5 V and stays in this state until the voltage is dropped to about 0 V. The presence of similar features in all considered test beds is convincing proof that the switching mechanism has a truly molecular origin and, as a model study shows,[16] it can be explained through the polaronic transport model (Region II of Figure 3).

Striking bistability is shown in the *I*/*V* curve of the rotaxane molecules prepared and studied in a crossed-wire junction by Heath, Stoddart, and co-workers.[61–63] While the previous example employed simple and essentially rigid molecules, rotaxanes are complicated supramolecular systems whose structural bistability has been extensively studied in solution employing electrochemical and spectroscopic methods.[64] The great control obtained by chemical synthesis on the structure and the dynamics of these compounds has been described in several reviews and will not be covered in this article.[65,66] The switching behavior in the transport experiment is essentially electrochemical for the rotaxanes. A series of electrochemical measures proved that in solution the oxidation of the compound is associated with a displacive conformational change of the rotaxane (the macrocycle shifts from one site to another of the thread). It is probable that, at the appropriate voltage, the switching to a high conductance state is due to oxidation of the molecule and the consequent conformational changes. Computational studies suggest that the two conformations are expected to have very different conductances.[67]

4. Controlling the Molecular Switching through the External Electric Field

Since the early observation of random conductance switching,[68] a number of papers have appeared describing the random or stochastic switching of a single molecule between "on" and "off" states characterized by a high and low conductance.[65,69–72] In the original experiment, STM was used to image phenylene ethylylene-based oligomers hosted in a SAM of dodecanethiol, and the conductance switching was attributed to conformational changes or tilting fluctuations. Additional experiments[71] proved that the switching persisted also when the top of the molecule was chemically connected to a gold nanoparticle, suggesting that the switching can originate in the lability of the gold–thiol interaction. The collection of results obtained with different molecules[73,74] confirms that such random switching is a general phenomenon,[72] at least for thiol molecules on gold.[75]

Stochastic switching may teach us much about the nature of the metal–molecule geometry and disordered dynamics, but it is an undesirable aspect for technological application. Controllable rather than stochastic conductance switching is one of the fundamental aims in molecular electronics. Different ways have been proposed to control the *state* of a molecule in a circuit.[65] Very interesting proposals involve the control of the conductance through chemical[66,76] or photochemical reactions.[77,78] These ideas, often derived from the neighboring fields of supramolecular chemistry and photochemistry, have been nicely reviewed elsewhere.[65,66] The switching mechanism due to a stable polaron formation on the molecular wire (essentially a solvent-free electrochemical reduction or oxidation of the wire) was discussed at the end of the previous section. In this section we will focus on another switching mechanism, also determined by the electric potential, that does not involve charging the molecular wire.

As mentioned above, several papers reported reversible switching behavior in two-terminal metal-based junctions in which the on and off states were induced by very large ($>$10 V) positive or negative bias pulses. The switching mechanism probably involves the formation of a metal fibril between the electrodes,[10] a process both poorly understood and difficult to control. Many studies[73] indicate irreversible damage when too large a voltage ($>$2 V) is applied. It seems reasonable to believe that, under large biases, the molecule leaves the junction or is decomposed as a consequence of local heating or charging.[79,80] Reversible processes taking place on a nanometer-scale Au electrode under large voltages are likely to involve the metal rather than the molecular component of the device. The probable non-molecular origin of several switching behaviors does not diminish the potential usefulness of such devices (see, for example, the Nanocell architecture[11] and the switching phenomena characterized by Williams and co-workers[9]), but it suggests that further theoretical and experimental investigations are required to put this technology on a firmer ground. Note that a device can be based on the reversible formation of metal filaments: Terabe et al.[81] fabricated a quantized-conductance atomic switch based on the reversible formation of a Ag nano-protrusion at the surface of a Ag_2S crystal.

A purely molecular mechanism of controlled switching, proposed theoretically in different guises by several authors,[82–85] based on stereochemical changes and not involving the permanent charging of the junction molecules, has been observed experimentally.[86–88] One remarkable difference between a molecule and an inorganic semiconductor is the presence of conformational degrees of freedom, controllable by synthetic chemistry. The inter-electrode electric field can be used to switch the molecule in the junction between two stable conformations (no third gate is needed). The observation of this phenomenon requires that the two conformations are relatively close in energy (with respect to k_BT) and that the difference in the dipole moment of the two conformations (the component perpendicular to the electrodes) is of the order of few Debye.[82] If the two conformations have sufficiently different conductances, the junction behaves as a rectifier or switch. Molecular electronics devices based on conformational changes have distinct advantages, since it is easier to design stereochemical changes than to fine tune the electronic levels of an interface, and diodes are far easier to fabricate at the 1 nm scale than are transistors.

A demonstration of conformational switching achieved through an external electric field was presented by Yasuda et al. (see Figure 4a).[86] The authors incorporate a diazastilbene derivative into a SAM of *n*-dodecane thiol and observe blinking in the conductance similar to that seen else-

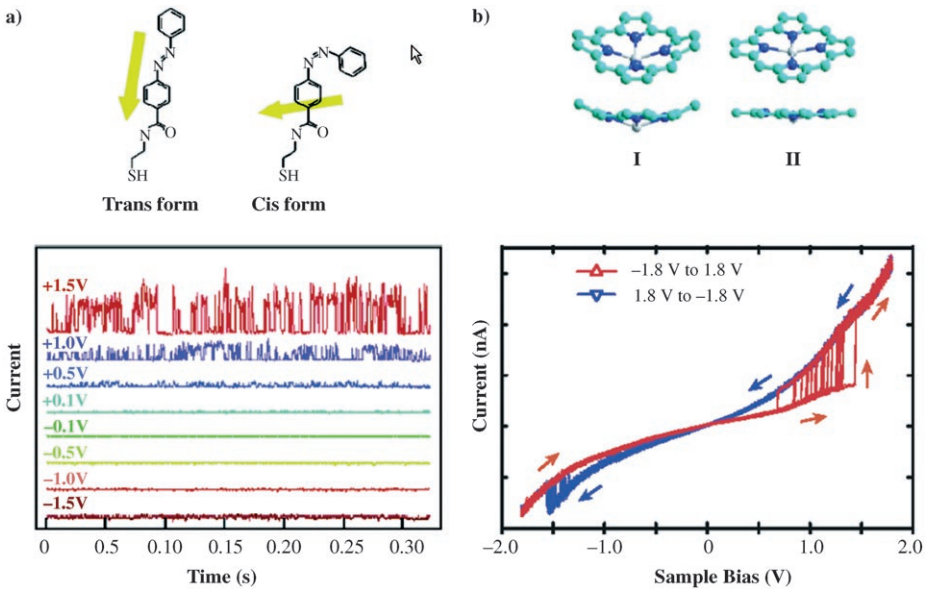

Figure 4. a) Random switching of a diazastilbene molecule between a high (trans) and low (cis) conductance state as a function of time for different values of sample bias (from Ref. [86]). b) *I*/*V* characteristic of a Zn porphyrin for repeated cyclic scans of bias: The system switches to a more highly conductive state at $V \approx +1.2$ V and switches back to the low conducting state at $V \approx -1.5$ V. Two molecular conformations that might be responsible for this behavior are shown at the top (from Ref. [88]).

where in STM measurements with a constant height mode.[68] Diazostilbene shows rich photochemistry, based on trans–cis isomerization about the N=N bond that can be triggered by optical absorption. In the system studied, some molecules do not display switching (probably the ones more constrained in their position by a tight packing with the neighbors) while a fraction start switching between the high- and low-conductance states when the applied bias is larger that 1.5 V. The low-conductance state was assigned to the cis conformation, energetically less stable and with a greater tip–molecule distance (the comparison with previous STM studies of similar compounds contributed to this interpretation). Also using STM, Lewis et al.[87] studied a similar system using an oligo-phenylethylene wire with a nitro substituent inserted in a SAM containing an amide group. The system switches between a high (on) and a low (off) conductance state. One of them is probably characterized by H-bonding between the nitro and the amino groups (a more precise hypothesis was not attempted). The external bias is able to control the state on the active molecule. Statistical analysis showed that the on state is favored at $+1.0$ V and disfavored at -1.0 V.

A significant step in the identification of electric-field-induced conformational changes was made using an isolated Zn^{II} porphyrin imaged with STM on NiAl(110).[88] The system displayed switching between two conformations, as was clear from the current jumps in many repeated *I*/*V* cycles (See Figure 4b). Two distinguishable *I*/*V* curves, belonging to two different conformers, are easily identified. The system jumped to the higher conductance state at positive bias (≈ 1.1 V) and went back to the lower conductance state at $V \approx -1.5$ V (the exact switching voltage changed slightly each time the measurement was made). If the electric field is causing the conformational change, the switching voltage should increase linearly with the tip–substrate distance. Ho and co-workers verified in this way that the electric field is responsible for the observed switching.[88]

It is probable that electric-field-induced conformational changes are more common than previously thought, and observations like the three mentioned above are likely to become more frequent. However, the observed controlled switching is still too noisy for technological application and, most importantly, none of these studies was specifically designed to control this effect tightly. After these proofs of principle, it would be desirable to investigate systematically the degree of control that can be achieved exploiting predetermined conformational molecular changes induced by the external potential. Simulations suggest that very promising switching properties should be experimentally achievable.[84]

5. Chemical Fine Tuning of the *I*/*V* Curve

The poor reproducibility of the *I*/*V* curves in the first measurements of Au-based junctions was correctly attributed to the unpredictability of the molecule–metal geometry, which was then identified as a key problem in molecular electronics. For the same reason, systematic experimental studies on the effect of small chemical changes on the *I*/*V* curve were initially carried out only theoretically. It appears that current theoretical methods describe most of the essential physics of coherent tunneling transport and that most of the (remaining, large) inaccuracies might be eliminated through an improved computational description of the junction.[41]

Systematic computational studies have explored the role of the absorption geometry (surface site and molecular orientation), the anchoring group, the nature of the metal (including for different surfaces) and, of course, the detailed chemical nature of the molecule in the junction. Early studies of this type, based on semiempirical Hamiltonian models,[89] were followed by computationally more sophisticated investigations. For example, according to several calculations the most effective transport interface atom on Au(111) among the group VI species (O, S, Se, Te) is selenium. Both cluster computation[90–93] and extensive experimental data show that there are many stable conformations for the complex between a single thiol-capped molecule and gold,

especially if surface reconstruction is allowed. There could thus be important differences between experiments done in a SAM on a locally flat metal surface, where some order is induced by the metal–molecule *and* the molecule–molecule interactions, and experiments based on break junctions, where a single molecule is often involved but the metal surface morphology and the binding mode are not determined. Other calculations also show only small effects from adding to the molecule the usual electron withdrawing or donating substituents.[92] This is to be expected in the Landauer regime (Region IV in Figure 3), since the gap is so large that its modulation by substituents is minimal; this is just a tunneling junction. In the polaron regime (Region II in Figure 3), as in conducting polymers, this is not the case.

The *I*/*V* measurements in single-molecule junctions bear mechanistic similarities to single-molecule spectroscopy studies.[94] In single-molecule spectroscopy the effect of local environment differences can dominate the molecular-specific features. In measurements on ensembles of molecules the effect on the environment is averaged, and it contributes to the spectrum only as inhomogeneous broadening of the purely molecular spectroscopic features. Single-molecule spectroscopy sees two striking phenomena that are absent in ensemble measurements. Spectral diffusion refers to the temporal evolution of a spectral feature in the single-molecule spectrum, while the so-called blinking phenomenon refers to the spontaneous turning-on or turning-off of a spectral feature (usually the fluorescence). Precise analogues of these behaviors are seen in molecular junctions; the analogue of spectroscopic blinking was reported in 2001.[68] Current fluctuated between on and off states in the measurement of a more "conductive" guest molecule in an alkanethiol host SAM. Making this measurement less coarse, by measuring the actual currents, shows the conductance equivalent of spectral diffusion. In all these cases, the change in the geometric environment in the vicinity of the molecule is responsible for the evolution.

While in spectroscopy ensembles of molecules were studied long before single-molecule techniques were developed, in molecular electronics the inverse path has been followed. Only in the last few years, with the improvement and automatization of the measurements on nanoscale systems, is it really feasible to collect data for large ensembles of junctions, to study the relationship between local structure and charge-transport characteristics.[74,95] Tao and co-workers[95,96] developed a technique to fabricate quickly thousands of molecular junctions, measuring their conductance at fixed voltages. They moved repeatedly a gold tip of an STM into and out of contact with a gold surface in a solvent containing molecules that could bridge the two electrodes. They reported histograms giving the occurrence probability for a given value of conductance at any voltage. Upon pulling the electrode away from the surface, the conductance g decreases in steps of magnitude $g_0 = 2e^2/h$, a behavior indicating the formation of monoatomic gold filaments between the electrodes.[97] When the last such step occurs, the conductance drops well below g_0. In the region $g \ll g_0$, the residual conductance can be provided only by a molecule bridging the electrodes (with a possible small contribution from through-solvent tunneling). The conductance histogram in the region of the molecular junction shows a large but very broad peak corresponding to the average conductance of a single molecule and less-pronounced peaks at a conductance twice or three times larger the single-molecule value, which indicates the formation of multiple molecular bridges. The experiment was repeated with several different molecules and was recently extended to a three-terminal device.[98]

A different architecture but a similar philosophy characterizes work using a mechanically controlled break junction (MCB) to form two gold electrodes whose separation can be repeatedly changed between a few angstroms and a much larger distance (where no current flow is observed).[99] The system contains molecules with two thiol groups that can bind to gold, so that each time the electrodes are brought to a distance comparable with the molecular size a molecular junction may be formed and its *I*/*V* curve measured. The molecular contact can be formed many times, making possible a statistical analysis of many *I*/*V* curves. Mayor et al. proved that subtle differences in behavior due to small structural changes can be revealed by the analysis of a sufficiently large number of molecular junctions.[74] They compared the averaged *I*/*V* curve of two molecules differing in the position of the anchoring groups (see Figure 5) verifying the essential role that the anchoring geometry has on the measured *I*/*V* curve.

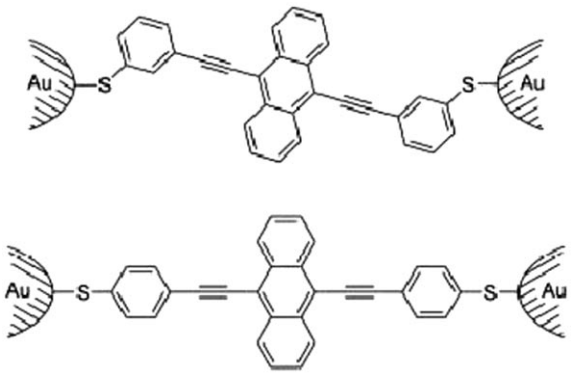

Figure 5. The molecule above forms poorer contacts with the electrodes in a break junction geometry. The automatic collection of many *I*/*V* curves for the two systems allowed assessment of the role of the binding group geometry in this case (from Ref. [74]).

The analysis of many junctions fabricated in an analogous way may help in understanding the numerous details that affect the molecular conductance and may bridge the gap between theoretical simulations (based on idealized geometries) and experimental measurements. The averaged *I*/*V* curves constitute benchmarks for the comparison of theory and experiment: Performing computations on ensembles of plausible structures might be a further step toward a meaningful comparison of results.

6. Conclusions

Our considerations in this paper have dealt with four different Regions, as indicated in Figure 3. When the energy

gap between electrochemical potential and nearby molecular energy levels is very large, the Landauer–Buttiker contact-time argument suggests that the electron is in contact with the molecule only for times very short compared to vibrational frequencies. Under those conditions, one expects coherent elastic tunneling, which can be described by the Landauer formula, as the dominant transport mechanism. The zero-voltage conductance is then proportional to the absolute square of the Green's function (describing transport through the molecule) multiplied by the product of the spectral densities of the right and left electrodes. In Region III, where the gap is large, the Green's function will be proportional to the inverse gap, so that the tunneling will be very much less than g_0, the quantum unit of conductance. Coulomb blockade (CB) behavior, arising from discrete charging states on the molecule, is expected (and seen) in Region I; at low temperatures, discrete phonon peaks are visible in the conductance. In Region III the CB requires high source/drain voltages to overcome the gap. On going from Region III to Region IV, the mechanism remains as coherent tunneling, and the magnitude of the current (proportional to the spectral density product) increases. Inelastic scattering in Region IV is expected to be very weak, and simple IETS behavior is expected to be observed.

When the gap is small, the behavior changes completely. In Region I, one has a low-voltage CB regime – here the behavior is that of a double tunneling junction because the spectral density at each side is very weak, so significant charge can only flow upon resonance injection from electrode to molecule to electrode. This regime has been explored and explained by Ho and co-workers[54] and by Crommie and co-workers,[100] and one expects to see (and indeed does see) Franck–Condon-type behavior, with different peaks in the conductance itself (not the derivative of the conductance with source/drain voltage), as the chemical potentials become resonant with the different vibronic states.

In Region II, where the spectral density becomes large and the gap is small, one can actually have resonance injection with long Landauer–Buttiker times. Then one might see vibronic transport, in particular hopping through the molecular bridge. These mechanisms are beyond the scope of this discussion, but have been presented elsewhere.[16]

The *I*/*V* characteristic is dominated by elastic tunneling in Regions III and IV, modified by a very weak IETS spectrum. In Region I, one sees low-voltage resonant injection and Franck–Condon behavior. In all regimes, however, disorder effects can induce stochastic switching. Control of molecular stereochemistry can result in stereochemical switching, along with rectification. In Region II, and perhaps in Region I, one may see charge switching and hysteresis, as molecules change geometry upon injection of charge.

The combination of vibronic and disorder effects, as discussed in this article, leads to substantial variation in transport mechanisms. As the vibronic coupling becomes stronger (in Region II), completely different, non-tunneling behaviors can occur. Thus the panoply of mechanisms available in single-molecule transport junctions is substantial, and its understanding is quite incomplete.

Technologically, most progress has actually been made not using single-molecule transport junctions, but rather using such structures as cross-bar junctions,[101] in which a number of molecules switch together. The understanding of such structures is as complex as single molecules, and exploration of that area has become a real feature of current molecular electronics research.[102]

Transport in single-molecule junctions is the simplest problem in molecular electronics. We have seen that there are regimes in which the molecule leaves almost no signature, especially Region III in Figure 3, in which weak IETS may be seen in tunneling through an insulating gap. In Regions I, II, and IV, the molecular signature can be discerned, and indeed can become dominant. Although exciting progress is being made, exploring the different mechanistic possibilities will occupy this community for some time to come.

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[102] Figure 3 includes only the dependence on E_G and Γ. As suggested in Section 3, other parameters including the thermal energy, the on-molecule coulomb repulsion, and the vibronic coupling strength will also be involved in determining the transport mechanistic regimes.

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