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Molecular Transport Junctions: Clearing Mists**

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Recent progress in the measurement and modeling of transport in molecular junctions has been very significant. Tunnel transport in the Landauer–Imry regime is now broadly understood for several systems, although a detailed understanding of the role of contact geometry is still required. We overview some clear indications from recent research and note the quite reasonable agreement between measured and calculated conductance in metal–molecule–metal junctions. The next challenge lies in obtaining a microscopic understanding of charge transport that involves reduction or oxidation of molecules.

1. Introduction

What is the electronic conductance of a junction containing a single molecule attached at each end to metal electrodes? This simplest of questions in molecular electronics has proved surprisingly difficult to answer. In a 2003 review of the field, Salomon et al.^[1] showed that for one simple molecule, 1,8-octanedithiol attached to gold electrodes, the reported experimental values of low-bias conductance varied by over five orders of magnitude. It is difficult to discuss agreement with theory in this context. The main message of the present overview is that for 10 out of 12 molecules studied using repeated break junction methods with statistical analysis, agreement between experiment and density functional theory (DFT) calculations is within an order of magnitude (Table 1). In the worst case (1,4-phenyldithiol), it is within a factor of 50. Furthermore, some of these measurements were recently extended to include temperature effects.^[2,3] Overall, there is broad agreement between the data and calculations based on

tunnel transport in the Landauer–Imry regime. The remaining disagreements may reflect interesting and important physics (discussed below), but the situation represents a sea change from what prevailed two years ago. Impressive though these achievements are, they bear on a problem of somewhat limited technological importance: In tunnel transport the molecule acts merely as a scatterer of electrons, much as any dielectric barrier would (although this molecular entity provides elastic scattering (Landauer–Imry) channels that facilitate transport compared to a vacuum gap).

Functional molecular devices require active control of the electronic properties of the molecule, for example, switching conductance through control of the geometry and/or the oxidation state of the molecule. Single-molecule measurements have made progress here too,^[4–9] but much work is needed for development of a computationally accurate first-principles theory of transport that involves charge localization on molecules (i.e., reduction and oxidation).

2. Single-Molecule Measurements with Statistics

Theoretical modeling of molecular junctions gives reasonably consistent results (see discussion below and Table 2) if the geometries, methods, and basis sets are comparable. The problem lies with the experiments. Probably the most important factor is the nature of the contacts. Molecules in van der Waals contact mediate tunneling far less efficiently than even sigma-bonded molecules over the same distance.^[10] At least as important is contamination in junctions that are not prepared in ultraclean vacuum conditions: layers of water or hydrocarbon molecules may separate the active molecules from the contacts.^[11,12] Finally, even if the molecule contacts the electrode via strong binding, variations in the microscopic

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geometry of the contact from measurement to measurement may lead to significant variations in the measured conductance.^[4,13] It is therefore easy to understand how experimental data can vary over orders of magnitude.

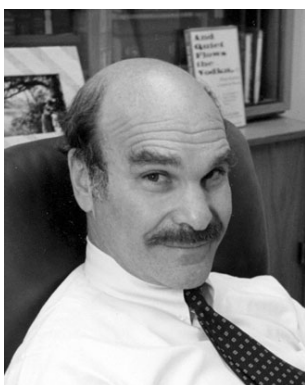
Many of these difficulties were addressed by Cui et al.,^[14] who used self-assembly to place the molecules of interest in a relatively well-defined geometry by inserting them into a self-assembled alkanethiol monolayer. The contacts were defined by using reactive thiol tethers on both ends of the inserted molecules. One end contacted the underlying Au(111) substrate while the other was attached to an Au nanoparticle. The nanoparticle was, in turn, contacted by a gold-coated atomic force microscopy (AFM) probe. Current–voltage curves obtained from junctions like these were found to be additive, that is, the current in each curve was found to be a multiple of some fundamental unit of current at a given bias. Molecule to molecule variations were characterized by making a histogram of the divisor used to minimize the variance between any one curve and the smallest family of curves. Peaks in the histogram occurred at integer multiples of a fundamental value, taken to correspond to the number of molecules (1, 2, 3, etc.) in the gap. For the 1,8-octanedithiol (inserted into 1-octanethiol) the peaks were sharp and well defined. The approach was validated by comparing the current–voltage curves to a first-principles density-functional computation of the conductance with no adjustable parameters. This comparison showed that the measured low-bias conductance was within an order of magnitude of the theoretical

prediction.^[14] While this was a major step forward, the remaining discrepancy with theory was puzzling, particularly because the shape of the measured current–voltage curve was subtly different from the predictions of tunneling theory (and better calculations increased the quantitative discrepancy to a factor near twenty^[15]). These problems were compounded by a series of measurements on alkanedithiols of different lengths.^[16] These yielded a value for the electronic decay coefficient, β , that was too small. The problem appears to lie with the contact between the gold-coated AFM probe and the gold nanoparticle. Although the intrinsic conductance of the bulk contact was probably much higher than that of the molecule, it was probably not large enough to prevent charging of the nanoparticle, with consequent distortion of the current–voltage characteristic.^[17]

These discrepancies disappeared with the introduction of a new measurement technique.^[18] Xu and Tao formed repeated break junctions by pushing a gold probe into a gold surface so as to make a metallic contact. The probe was pulled away from the surface in a solution containing molecules with reactive groups (thiols or pyridines) at each end. The freshly broken metal junction was frequently bridged by molecules. This resulted in a plot of current versus time that shows discrete steps corresponding to an integer number of molecules bridging the gap. Figure 1 shows data for 1,8-octanedithiol in a gold break junction taken with a logarithmic current converter so that a large range of currents can be measured.^[19] Figure 1a shows the quantized conductance steps owing to the pulling of



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Table 1. Comparison of measured and calculated conductances (G) for three alkanedithiols (**1**, **2**, **3**; measurement;^[18] theory^[15]), 1,4-phenyldithiol (**4**) (measurement;^[60] theory^[15]), four carotenoid polyenes,^[61] an optically switched photochromic molecule in open (**9**) and closed (**10**) forms,^[23] oligo(phenylene ethynylene) (**11**) (measurement;^[62] theory^[15]), and an oligoaniline (**12**) (measurement;^[56] theory—O. F. Sankey, personal communication). All experimental data were obtained with the break junction method of Xu and Tao^[18] and all calculations used the DFT approach of Tomfohr and Sankey.^[15]

Molecule	G (measured) [nS]	G (theoretical) [nS]	Ratio
	95 ± 6	185	0.51
	19.6 ± 2	25	0.78
	1.6 ± 0.1	3.4	0.47
	833 ± 90	47 000	0.02
	2.6 ± 0.05	7.9	0.33
	0.96 ± 0.07	2.6	0.36
	0.28 ± 0.02	0.88	0.31
	0.11 ± 0.07	0.3	0.36
	1.9 ± 3	0.8	2.4
	250 ± 50	143	1.74
	~13	190	0.07
	0.32 ± 0.03	0.043	7.4

Table 2. Comparison of calculated low-bias conductance for 1,4-phenyldithiol connected to gold electrodes.

Low bias conductance [μ S]	Method	Reference
1	DFT-Jellium	[63]
5	Bias-dependent DFT	[64]
35	TransSIESTA	[13]
47	DFT + bulk states	[15]
5.5	NEGF	[65]

the gold quantum wire itself and Figure 1b shows steps caused by molecules in the gap. The molecules are relatively stiffer than the gold nanowires^[20] so they remain in place as the gold is extended on each side of the molecule. During this time, the gap conductance remains relatively constant (because it is dominated by the molecule) causing a plateau in a plot of conductance versus time. Integer number of molecules may bridge the gap, resulting in a series of plateaus. These are seen as peaks in a histogram of the measured currents (Fig. 1c). The single-molecule conductance determined here (ca. 13 nS) is somewhat smaller than that reported by Xu and Tao^[18] (ca. 19 nS) owing to the problems in calibrating the logarithmic amplifier over a wide range of currents (the value reported by Xu and Tao has been replicated with a linear converter,

though not the high current plateaus because the gold saturates the amplifier in this arrangement). This method yields the commonly accepted value for β , and the measured conductance values are close to the calculated values for alkanedithiols^[18] There is still, however, uncertainty about the contact geometry.

3. Calculated versus Observed Results

In the interest of uniformity, we have chosen a set of calculations reported by Sankey's group to compare with appropriate measurements. Sankey uses the Landauer approach of Equations 1–4 below, within a DFT context. There are some special features of his approach: it builds a periodic lattice of slabs and molecular layers, it uses the zero-voltage electronic structure without modification from the effect of higher bias, and it uses a basis of confined pseudo-atomic orbitals. It also assumes that the voltage drop is symmetric—that is, if an energy $e\Phi$ is dropped across the molecule, the

assumption is that the left electrode and right electrode go up and down in chemical potential by $e\Phi/2$, respectively.

Other DFT-based electronic structure calculations differ in detail,^[21,22] particularly in the assumed geometry, in the band alignment approach, and in the basis set. Nevertheless, most of the calculations are semiquantitatively in agreement with Sankey's, so we adopted this set for our discussion here.

Published results for several molecules obtained by two laboratories are summarized in Table 1. These are molecules for which first-principles DFT calculations have been carried out by the Sankey group, and calculated values of the low-bias conductance are listed alongside the experimental values. Different theoretical approaches are compared in the next section.

The first thing to notice is that in the context of historical disagreements of five orders of magnitude or more, the general agreement between theory and experiment is remarkably good. Entries 9 and 10 are for a photochromic molecule that was optically switched between open and closed states in the same series of experiments.^[23] The absolute measured conductances of the two forms are about twice the calculated values. The measured closed/open conductance ratio is 131:1 while the theoretical ratio is 178:1, a remarkable degree of agreement. In general, the agreement between theory and experi-

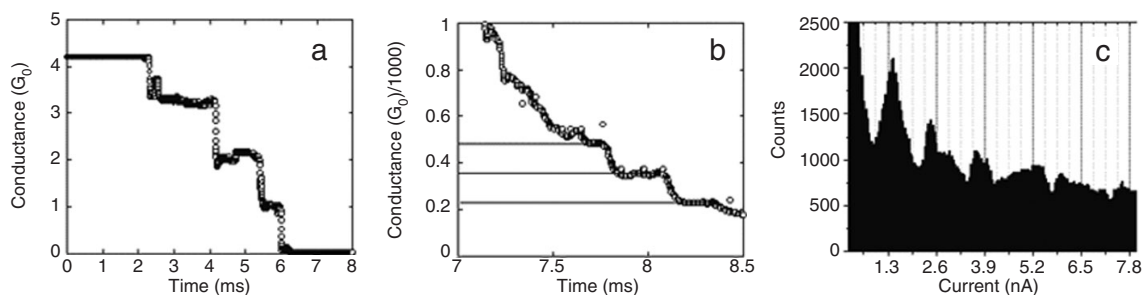


Figure 1. a) Conductance versus time in the high-current regime where the signal corresponds to breaking of the gold–gold contact itself. The conductance drops in units of G_0 (quantum of conductance; $77 \mu\text{S}$) as the quantum wire is narrowed. The wire breaks at about 6 ms. b) Data taken at a later time in another pull, showing much smaller steps (ca. $1.5 \times 10^{-4} G_0$) only seen in the presence of 1,8-octanedithiol molecules. c) A histogram of the number of broken junctions at different currents at an applied bias of 0.1 V in the presence of 1,8-octanedithiol.

ment is within a factor of two or three. It is a little worse for the oligoaniline molecule (12 in Table 1) and the oligo(phenylene ethynylene) (11 in Table 1). The worst-case result is observed for perhaps the most studied of molecules; for 1,4-phenyldithiol (entry 4 in Table 1), the experimental conductance is about 1/50 th of the calculated value.

Table 2 lists calculated values for the low-bias conductance of 1,4-phenyldithiol as calculated with a number of different approaches. The work of Tomfohr and Sankey^[15] yields values that are relatively high, but with the exception of the results of the Jellium model^[24] the other values are within an order of magnitude of Sankey's.

Thus, over a range of greater than a factor of one thousand in measured conductances, the agreement between theory and experiment is generally within about a factor of 10. This is a strong indication that theory and experiment are on the right track.

4. Theoretical Overview

The theory of transport in metal–molecules–metal junctions distinguishes several different regimes.^[25–27] These regimes are defined by a series of parameters that include the applied voltage $e\Phi$, the thermal energy $k_B T$, the energy of repulsion between two electrons on the molecule, normally denoted U , the so-called spectral density Γ (essentially the inverse lifetime of the electron on the molecule because of leakage into the electrode), and the molecular orbitals and the electronic spectra of the molecules and the electrodes.

The coherent tunneling regime occurs when Γ is larger than all of the others. For a very simple molecule coupled to a metal, the matrix of Γ is labeled by the different atomic orbitals of the molecule. For the given atomic orbital i , the matrix elements of Γ depend on the energy, as given by

$$\Gamma_{ij}(E) = \sum_k \delta_{ij} t_{ik} g_{kk}(E) t_{ki} \quad (1)$$

where t_{ik} is the tunneling matrix element that mixes the i^{th} atomic orbital on the molecule with the k^{th} band state orbital

on the metal electrode, $g_{kk}(E)$ is the Green's function element of the k^{th} electrode band state. Generally, one assumes that only one terminal atomic orbital in the molecule will touch these electrodes so that all the elements of Γ are zero except for two: one touching the left and one touching the right electrode.

When Γ_{ij} exceeds U , $k_B T$, and the spacing of the molecular orbitals, the system is in the coherent (Landauer–Imry) regime.^[26,27] Here, for a given geometric structure, the current can be calculated by

$$I(\Phi) = \int dE [f_L(E, \Phi) - f_R(E, \Phi)] T(E, \Phi) \quad (2)$$

where f is the Fermi distribution function for the electrode states (L: left, R: right) and G is the so-called Green's function or propagator, and is given by^[28]

$$G^{-1}(z) = zS - H_m - \Sigma_L - \Sigma_R \quad (3)$$

and (in an approximate molecular orbital scheme) by

$$G_{ij}(E) \approx \sum_{\mu} \frac{c_{j\mu} c_{i\mu}}{E - \epsilon_{\mu} - \Sigma_{\mu}(E)} \quad (4)$$

where z , S , H_m , Σ_L , Σ_R , are the complex energy variable, the overlap matrix, the Hamiltonian of the (extended) molecule, and the self-energy terms on the left and right electrodes, respectively. The Σ terms are related to Γ by

$$\Gamma_A = i[\Sigma_A - \Sigma_A^+] \quad (5)$$

where $A=L$ or R . The sum runs over the molecular orbital states μ ; the coefficients in the numerator are the molecular orbital expansion coefficients; and the self energy Σ_{μ} has both real and imaginary parts—the imaginary part is proportional to Γ , and the real part is often small.

The calculations in Tables 1 and 2 were performed using this form within the coherent tunneling regime. Here inelastic tunneling is very weak, and so the elastic, coherent tunneling process dominates transport. This is expected to hold for

nearly all cases where very small molecules are used, simply because the tunneling time through the molecule is sufficiently fast that there is no opportunity for the vibronic coupling to lead to either dephasing or relaxation of the molecule.

When electronic interactions are considered, it is necessary to self-consistently recalculate the wave functions for the molecule (or extended molecule) and the Green functions. This is usually done using a contour integral formulation that amounts to a mean-field approximation. This mean field can fail, and indeed it does fail (and badly) in the limit when U becomes comparable to, or even exceeds Γ .

Using standard molecular orbital electronic structure methodology (once again assuming a geometry), and adopting a particular basis set, model Hamiltonian, and mean-field approximation (nearly always DFT, but Hartree–Fock based methods have also been used)^[29,30] real calculations can be completed, as described above.

The major issues in such calculations are the choice of geometry, computational method, and the so-called “band lineup” problem (which essentially describes where the Fermi level of the electrodes lies compared to the electronic manifold of the molecule).^[31] In one-electron models, like the extended Hückel model, this lineup issue is simply parameterized. In the self-consistent field methods, it should emerge from the converged calculation.

Figure 2 shows the simplest picture of this problem: when the voltage is applied to the system, and assuming that the Γ s are the same on both sides of the molecule, then one electrode will go up in energy by $e\Phi/2$, the other will go down by the same amount. Then when $2e\Phi$ becomes equal to $E_{\mu} - E_{\nu}$, there will be a single electron resonance between the (shifted) Fermi level of the electrode and the molecular state. This should lead to a conductance peak, often in the wrong place compared to the experiment, essentially because band alignment issues have been incorrectly treated. There are complications here; in particular, when metallic electrodes are used, one should be concerned with image effects, which could lead to stabilization of charge states on the molecule, and the band

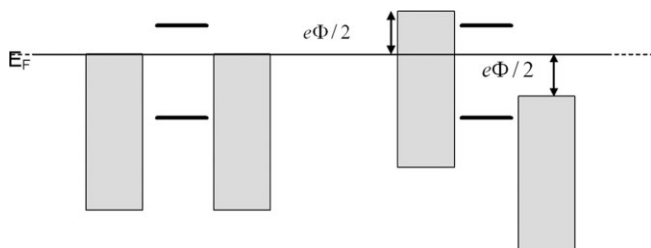


Figure 2. Schematic diagram of the frontier molecular orbitals in a simple tunneling junction. The upper and lower levels are the empty and occupied frontier orbitals of the molecule; the vertical axis is an energy axis, the image to the left is the equilibrium position, with the Fermi level (E_F) of the metals in the gap between the frontier molecular orbitals. The picture on the right shows the situation when a large applied potential $e\Phi$ is present, and the transport through the molecule can occur in a facile fashion.

lineup. This problem has not yet been satisfactorily resolved.^[32,33] Consistency of basis sets between the molecule and metal is a significant problem in finding accurate results.

Utilizing semiconductor electrodes, as has been done in a few laboratories,^[34–39] leads to different sets of issues but does avoid the image problem.

5. What About Contact Geometries?

Geometric modifications could change everything. Most calculations suggest small (factors of a few) changes in transport when the S/Au coordination environment is modified slightly. Very large geometric modifications can occur when the symmetry changes so that the σ – π mixing between the metal filament and the sulfur changes from being allowed to being symmetry forbidden. In general, one does not expect to see such large fluctuations because the true orthogonality point is extremely improbable.

Geometric modifications will, as is clear from Equation 1, change Γ and could change the regime. For example, when Γ gets really small ($\Gamma/\bar{U} \ll 1$, where \bar{U} is the effective charging energy that is in the order of one volt), one enters the so-called Coulomb blockade regime. Even for molecules that strongly delocalize, and therefore might be expected to “conduct” quite well, this regime can be (and has been) encountered.^[8,9]

The contact structure can dominate transmission by changing both the value of Γ and the extent of charge transfer. This complication leads to both the greatest strength and greatest weakness of the repeated break-junction method as currently implemented.^[18] The precise nature of the contact is unknown and probably varies from pull to pull, as evidenced by the width of the peaks in the histogram. In fact, a careful re-examination of data for 1,8-octanedithiol found three distinct sets of conductance values.^[2,19] The dominant data set corresponded to ca. 20 nS (as listed in Table 1) but features were also found at ca. 4 nS and ca. 1 nS. Theoretical simulations show that, for the particular case of 1,8-octanedithiol, connections to an on-top site or a hollow site on Au(111) give rather similar conductances (ca. 20 nS) if the electrode surface is basically planar.^[19] In contrast, a conical arrangement of atoms (as might be present at the end of a pulled wire) can result in a much reduced current.^[4] Both the 20 nS and the 4 nS features give current–voltage curves that fit simple tunneling models well, have the expected value for β (ca. 1 per methylene unit when the lower-current datasets are compared for different molecular lengths), and the measured currents were found to be independent of temperature.^[2] Thus, it is tempting to associate them with tunnel transport between either somewhat planar or somewhat pointed contacts. The 1 nS feature, on the other hand, is both temperature dependent and has a value of β that is too small (ca. 0.6 per methylene group) when similar features are compared across a series of molecules.^[3] Since the value of conductance (1 nS) and value of β exactly coincide with the results of earlier work with self-assembled

metal–molecule–metal junctions^[14,16] it is tempting to assign these results to geometries in which an attached gold cluster is poorly contacted to the main electrode.^[17]

Subsidiary conductance peaks were also found in an aniline trimer^[40] (cf. the aniline heptamer, entry 12 in Table 1). The main series had a peak conductance that was four times that of the subsidiary series, similar to the ratio found for the two main alkanedithiol series. It is interesting to note that *no evidence was found for a subsidiary series in the longer oligomer (N=7)*. This suggests that the effects of contact geometry become more obvious as the molecule gets shorter. Indeed, the problem with 1,4-phenyldithiol may lie with the possibility of a plethora of conductance peaks, depending in detail upon how the experiment is carried out. Thus the conductance value listed in Table 1 for 1,4-phenyldithiol has proved difficult to replicate (Latha Venkataraman, personal communication). This is a problem that can be addressed using different conjugation methods in certain circumstances.^[41]

It is interesting to note that Venkataraman et al.^[41] were unable to reproduce the distinct peaks in conductance histograms even with simple alkanes containing thiol attachments, and consequently question the validity of the approach. This discrepancy can not be a consequence of differences in the experimental method (a fixed break junction^[41] versus a scanning probe^[18]) because Gonzalez et al. have found robust conductance peaks in alkanedithiol conductance measurements made with a break junction.^[42] Importantly, they demonstrate that the peaks can be observed without any data selection while most prior work has involved some kind of data selection.^[2]

6. Vibronic Effects

In the Landauer–Imry coherent tunneling regime, there is still a possibility that the electrons can scatter inelastically from the molecule and deposit energy into a normal mode. When the second derivative of the current is plotted with respect to voltage at very low temperatures, bumps corresponding to this inelasticity are expected—the bumps should occur at voltage $V = \hbar \omega / e$, where ω is the frequency of a normal mode and \hbar is Planck's constant. The intensity of such peaks depends on the mechanism of transport, and the shape of such peaks is in fact quite complicated, reflecting the different vibronic and electronic couplings that the molecule undergoes in the junction. Recording this spectrum, called the inelastic electron tunneling spectrum (IETS) has become very popular because it gives important information, not only demonstrating that the molecule is present in the junction, but also providing useful information in connection with propensity rules for which peaks can appear, as well as density functional calculations for actual assignment. Figure 3 shows an example and this very important topic is discussed extensively elsewhere.^[12,43–51]

Vibronic coupling dominates standard molecular electron-transfer reactions and is the basis for the analysis of electron

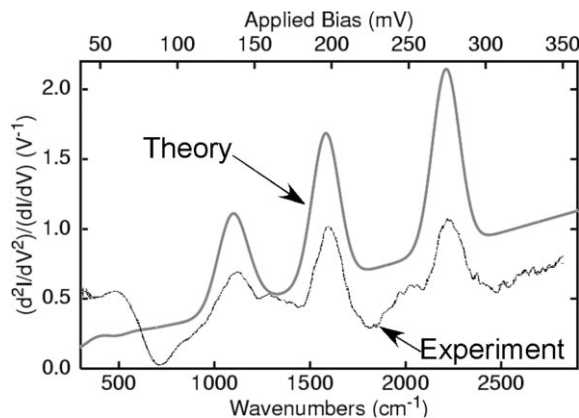


Figure 3. Experimental^[45] and calculated^[46] IETS spectra for the trimer of phenylene ethynylene between gold electrodes.

transfer rates based originally on Marcus theory. When vibronic coupling (effectively, the amount of reorganization energy) is relatively weak, one sees co-tunneling and inelastic electron tunneling spectra at low temperatures. When it becomes very strong, one can see trapping, hopping, loss of phase, and activated transport. This is the regime of organic electronics (effectively because the interelectrode distances there are much too long to permit coherent tunneling).

Time scale arguments based on the so-called Landauer–Buttiker tunneling time, generalized to the molecular level, yield in a particular approximation the formula^[52]

$$t_{\text{LB}} \equiv \frac{N\hbar}{\Delta E_{\text{G}}} \quad (6)$$

where t_{LB} is the Landauer–Buttiker tunneling time, which is best interpreted as the time for which the electron is actually localized on the tunneling center (in this case the molecule), N is the number of sites on the molecular bridge, and ΔE_{G} is the injection energy, that is, the energy gap between the Fermi level and the nearest frontier molecular orbital. For many situations, when the ΔE_{G} is on the order of volts, t_{LB} is on the order of sub-femtoseconds and there is insufficient time for the molecule to undergo vibronic distortions. Clearly, as the molecule gets longer (N increases) and as the injection gap gets smaller either because a gate voltage has been used to push a frontier orbital near the Fermi level or because a source–drain voltage begins to include the level, this tunneling time becomes longer. Regardless, strong vibronic coupling is required to see trapping because there are simply not enough modes in really small molecules (such as in 1,4-phenyldithiol) to couple effectively.

7. Electrochemical Gating

Some functional devices will surely exploit the redox chemistry of molecules, that is to say, modulation of conductance through alteration of the charge state of the molecule. The

easiest and most controllable way to do this is through electrochemistry, measuring the electronic properties of molecules that are attached to a surface maintained under potential control in a conducting electrolyte. This has the advantage that the potential at the molecule is well-defined because the potential drop at each electrode is maintained by a double layer established with respect to an electrode of constant polarization (a reference electrode). What is learnt from measurements of this sort will surely be useful in establishing design rules for “dry” molecular devices. At the moment, electrochemical control offers by far the easiest route to gating molecular conductance,^[4] as first demonstrated in pioneering work by Tao.^[53] Solid-state gating has been measured in mechanical break junctions^[5–9] but the required gate voltages are large because of geometric reasons.

The repeated break-junction method is easily adapted to making measurements of molecules that are held under potential control. All that is required is that one of the electrodes be insulated almost all the way to its apex to minimize leakage currents into the supporting electrolyte.^[54,55] An example of single-molecule conductance data obtained as a function of the oxidation state of a molecule^[56] is shown in Figure 4. These data were obtained with an aniline heptamer (entry 12 in Table 1) in a 50 mM sulfuric acid electrolyte, and show the expected increase of conductance on oxidation of the oligoaniline (Fig. 4a). The measured peak conductance (ca. 6 nS) corresponds to a state that is far from simple metallic (expected to show the conductance quantum, 77 μ S), possibly because of strong charge localization from vibronic coupling or image trapping but more likely illustrating the role of 3D transport in metallic conduction in this system.^[57] Interestingly, the dependence of conductance on the potential results in weak negative differential resistance (NDR) when the ap-

plied bias is swept over an appreciable range (Fig. 4b), because, in this microscopic junction the applied bias can change the local potential appreciably.^[56]

8. Coulomb Blockade

In the Coulomb blockade (CB) regime, mean-field models fail. An appropriate formulation involving Fock space (essentially a full configuration interaction methodology) has been developed by Datta and co-workers to deal with this problem;^[58] such calculations (which require major numerical effort) have been very successful in describing the line shape for CB transport.

Several distributional aspects have been seen, that is, it has been noted by several workers that fluctuations in geometry, both static and dynamic, leads to major changes in the conductance spectrum. The experiments of Tao's group are particularly revealing here because the electrochemical break junction provides such an extensive dataset. Single-molecule transport, in this sense, is closely related to single-molecule spectroscopy. Two sorts of characteristic fluctuations are expected: one corresponding to irreproducibility at different times on the same sample (spectral diffusion in single-molecule spectroscopy) and the other corresponding to different values for different measurements on different molecules (inhomogeneous broadening). A clear example of inhomogeneous broadening is given in Figure 4 of the paper by Chen et al. that reported NDR in aniline oligomers.^[56] This shows repeated sweeps of the current–voltage (I – V) characteristics of different single molecules. The sweeps are fairly reproducible but there are significant differences between the responses of each molecule.

In the CB regime, it is possible to do real electrochemistry, that is, to charge the molecule. Such charging processes have been seen in single-molecule transport break-junctions in an aqueous solution, with the usual double layer and solvation polarizations that lower the energy of the charged state, which can also be stabilized by the presence of ions and by vibronic coupling.^[33]

In this regime, very small currents are expected (generally in the order of nanoamperes) and quite different conductance signatures such as diamonds are observed in the contour plot of current as a function of gate voltage and source–drain voltage (Fig. 5). The positions of these diamonds, and their shapes, reveal a great deal about the parameters characterizing the transport junction. So-called vibrational co-tunneling events, in which there are parallel lines to the diamond sides displaced by the energy of the normal mode, closely correspond to the IETS.^[9] There have been a lot less calculations in the CB regime than in the Landauer–Imry coherent tunneling regime, and therefore, comparison between theory and experimental results is more difficult.

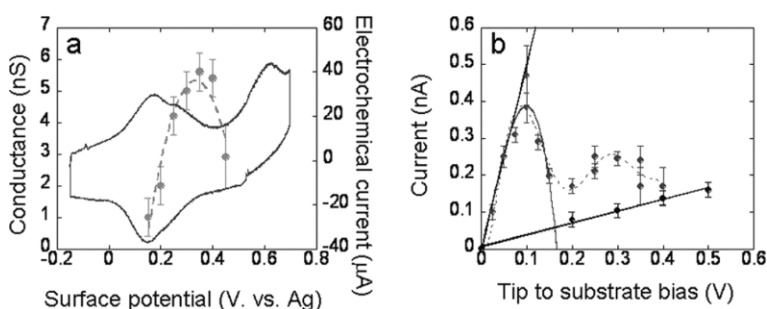


Figure 4. a) Single-molecule conductance as a function of the charge state of an oligoaniline molecule measured in an electrochemical break junction in 50 mM sulfuric acid. The solid line is a cyclic voltammogram showing the first (ca. 0.2 V) and second (ca. 0.6 V) oxidations with a reduction peak at ca. 0.15 V on the return sweep. The first oxidation is reversible, and conductance data taken in this potential range (with a small applied tip-to-substrate bias) shows that the molecule is most conductive just after the first oxidation. The dashed line is a fit of the single-molecule conductance to a parabola. b) The current–voltage characteristics for the oxidized molecule. The data points connected by the dashed line fall with increasing bias (above 0.1 V) as the applied bias reduces the molecule. The corresponding negative differential resistance peak is well-fitted using the measured dependence of conductance on the potential (solid curve). In contrast, when a nonconducting medium is used, the current–voltage data are linear (points connected by the straight line). (Data from Reference [56].)

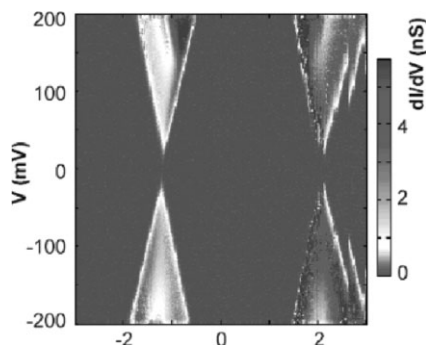


Figure 5. A typical Coulomb diamond figure illustrating both multiple charge states and vibrational side bands. The vertical and horizontal axes are the source-drain voltage and the gate voltage, respectively. Reproduced from [8], with permission; copyright 2006, the American Chemical Society.

Because, for a given molecule, one can go from the coherent tunneling regime to the CB just by changing the geometry at the interface (and therefore the relative sizes of Γ and U), we expect that measurements on multiple copies of (putatively) the same junctions might exhibit very different conductance signatures. This has indeed been seen using both electrochemical and mechanical break-junctions.^[8,9]

9. Conclusions

The title of this paper arises because in the coherent tunneling, Landauer–Imry regime, the agreement of good DFT calculations, compared to the measurements using repeated break-junctions is really quite satisfactory (see Table 1). All of the different approaches based on the DFT scheme in the coherent, elastic situation agree fairly well, with the remaining disagreements coming from such issues as basis set, nature of the extended molecule, approach to the band lineup problem, and choice of geometry.^[28]

It has been pointed out that with increased voltage, the onset of peaks in the conductance (that arise from resonances between molecular levels in the extended molecule and the electrode levels) are often predicted to occur at much higher voltages (by as much as 1 V). Again, one can blame the usual suspects (basis functions, approach to the band lineup problem). However, there may be something a bit more insidious here—clearly, the molecule can readjust its geometry within the junction, and with field gradient in the order of 10^8 V cm⁻¹, that might well happen. Indeed, we know that molecule–metal transport junctions are generally unstable at voltages above 1–2 V; such instabilities have been studied extensively, and they correspond with another aspect of the geometrical variation that both bedevils and enriches transport measurement.

The use of IETS and the associated propensity rules helps to understand the presence and geometry of molecules in the junction. The geometry issue remains poorly defined, and it

has been demonstrated both experimentally and theoretically that geometric variations lead to the sort of stochastic switching^[59] and multivalued conductance numbers^[2,41] observed in measurements using many different test beds.

The distributions obtained for measurements such as the electrochemical or mechanically controlled break junctions should be understood as arising from different geometries in the junction. As in single-molecule spectroscopy, actual observations of these distributions should permit an understanding of structure function relationships at the interface.

Experimental measurements in the Coulomb blockade limit have been reported,^[8,9] including the study of the Coulomb diamonds in large molecules (and occasionally in small molecules) with aberrantly weak electrode coupling (Γ). With gating, one can arrange for injection onto the molecule, even when the Coulomb blockade condition $\Gamma/U \ll 1$ does not apply.

There has been formal work that is developing vibronic coupling theory for junctions, but the strong vibronic coupling limit that demonstrates both hysteresis and charge trapping (and is a good picture for negative differential resistance) has not been extended toward an actual numerical study. This will clearly be a major avenue of research in molecular transport junctions in the next decade.

Similarly, some difficulties involved in metal–molecule junctions are avoided by using semiconductor electrodes. Even though these pose some of their own difficulties (band bending, impurity states), the covalent bonding associated with the C–C,^[38] C–Si,^[34–36] or C–Ga^[37] structures at semiconductor interfaces is highly attractive both for stability and for reproducibility.

The first decade of molecular junction transport measurement and modeling is almost over, and major advances have been made. Although there was much concern when the initial calculations of transport differed by orders of magnitude from the initial experiments, it is clear from Tables 1 and 2 that this situation is very much improved—mists are clearing in our understanding of transport in metal–molecule–metal junctions in the coherent tunneling regime.

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