

Making Contacts to Single Molecules: Are We There Yet?

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Abstract. The problem of connecting two wires to a single molecule has several practical solutions, varying from break junctions, to gaps formed by controlled evaporation and self-assembled structures. Here, we focus on gold nanoparticle self-assembled junctions, and break junctions, two techniques that allow the number of molecules in the gap to be determined. We show that the nanoparticle junctions are affected by the electronic properties of the nanoparticles, and that corrections for these effects tend to bring the data into closer agreement with both break-junction measurements and *ab initio* calculations.

1 Introduction

How well do we understand charge transport through a molecule connected at each end to conducting electrodes? Modern computational techniques make quantitative predictions about molecular conduction, yet, to take one controversial example, experiments show DNA to be an insulator [1], semiconductor [2], conductor [3] and even superconductor [4] (though the issue is now probably resolved [5]).

A reliable method for contacting molecules is needed, and, if quantitative comparison with theory is the goal, then the number of molecules that are contacted should be countable. Methods for contacting molecules include scanning tunneling microscopy (STM) [6–8] conducting atomic force microscopy (AFM) [9, 10], break junctions [11–13] (and see the discussion by Wang, Lee and Reed in [38]), fixed-gap nanojunctions [14, 15], nanopores [16, 38], mercury drop contacts [17] and crosswire assemblies [18]. Each method has some particular advantage [16] but the difficulty of counting the number of contacted molecules, and the characterization of their bonding, remain difficult problems. These problems probably underlie the wide range of data reported for similar molecules [19], though a *tour-de-force* assembly mechanism for placing molecules into nanojunctions has produced some striking results [20, 21].

We chose to study simple (and already much studied) molecules, the alkane dithiols [10, 22], using a self-assembled system in which a well defined number of molecules are connected, by covalent bonds, to metal electrodes. A self-assembled monolayer of (in this case) octanethiol is placed in contact

with a solvent so that some molecules leave (taking a gold atom with them, such is the lability of the gold surface covered with thiols [23]). Thus, such a surface, when placed in a solution of dithiolated molecules, will open up spaces for the dithiolated molecules to enter the monolayer [24]. The result is dithiolated molecules inserted into a monolayer of monothiols in a well-defined orientation, and bonded at their lower end to the gold substrate. It is still not easy to make an electrical contact to the inserted molecules, because the atoms of a top contact must line up correctly with the (now fixed) upper thiol, so that a chemical bond can form. To solve this problem, the monolayer is next incubated with a suspension of gold nanoparticles (NPs). We used 1.5 nm diameter gold stabilized with triphenylphosphine [25] as this ligand is readily displaced by the more reactive thiol. The NPs find the protruding thiols and attach to them. The attached NPs then make excellent “large” targets for a conducting atomic force microscope probe. A gold-coated probe is pushed into the NP to complete a circuit. The result is highly reproducible data showing a quantized series of current-voltage curves that are multiples of the current-voltage curve for a single molecule [22]. Importantly, the single molecule data are quite close to the results of first-principles calculations [22]. This rosy picture is clouded by further studies of transport as a function of alkane chain length [26] which yield a value for the inverse electronic decay length, β , that are too small and too voltage-dependent.

Xu and Tao [27] have recently introduced an elegant extension of the break-junction method. They operate an STM as an automated break junction, pushing a gold tip (under computer control) into a gold substrate immersed in a solution of dithiolated molecules. The bias between tip and substrate is fixed and the current recorded as the tip is pulled away from the surface. The current plotted vs. distance shows discrete plateaus (regions of constant current over a significant distance of the pull). When these values of current plateau are histogrammed, distinct peaks are seen in the conductance, probably corresponding to 1, 2, 3 etc. molecules bridging the gap [27]. The plateaus in the current vs. distance plots form because gold filaments are very ductile, so a single molecule dominates the gap resistance as the gold to which it is attached is drawn out from the tip and substrate [28]. This method is simple to carry out and gives reproducible data, though complete current-voltage curves must be obtained through repeated experiments at different biases. These measurements are made in solution and we expect that the environment matters considerably for redox active molecules, but we doubt that this is critical for simple tunnel transport.

Do these plateau regions really correspond to integer numbers of molecules in well-defined geometries? Values of conductance measured in this way [27] are close to, but systematically higher than, those measured by the method of self-assembled junctions [22, 26]. Importantly, the Xu-Tao method yields much more realistic values for β [27]. It is the aim of this paper to show that electronic effects of the nanoparticle contact account, at least qualitatively,

for differences between the two techniques (which are relatively small in any case). This lends credence to the interpretation of the current-plateaus as corresponding to integer numbers of molecules in the gap. Thus the method of Xu and Tao [27] represents a significant improvement over our self-assembly based method [22], yielding data that is quite close to the results of first-principles simulation and resolving the issue of anomalous values for the electronic decay constant [26]. Some issues remain to be resolved, but these are minor relative to the scale of recent progress.

2 Contact Resistance in NP Contact Experiments

Our original, probably naive, interpretation of our experimental data assumed that the contact between the gold-coated AFM probe and the NP was good (i.e., the system acts like a bulk metal). Yet this is surely not true. The particle probably remains coated with triphenylphosphine (as evidenced by a low measured adhesion force between the AFM probe and the NP). Any significant resistance (i.e., greater than the resistance quantum, $h/2e^2 \approx 12.6 \text{ k}\Omega$) would lead to independent charging of the NP, with consequent Coulomb blockading [29]. The matter is complicated further by the possibility that very small ($< 5 \text{ nm}$ diameter) gold NPs may suffer from an intrinsic gap as a consequence of quantum size effects [30].

The current-voltage curves taken via a gold NP show clear evidence of a zero-bias gap (Fig. 1). This shows the mean, and standard deviation (as vertical bars) for current data points for about 1000 measurements of octanedithiol molecules between a gold NP ($d = 1.5 \text{ nm}$) and a gold (111) surface. The derivative, dI/dV , is shown on the same plot, illustrating a zero bias gap on the order of 0.5 V . It is tempting, and probably partially correct, to attribute this gap to a Coulomb blockade caused by charging of the gold NP. Interpretation is, however, complicated by the fact that gold NPs of this size show evidence of electronic structure with level spacings on the order of 100 meV [30]. Unfortunately, this problem is difficult to circumvent, as the NP technique relies on the use of (easily-displaced) triphenylphosphine ligand, limiting the particle size to 1.5 nm [25] (or smaller, see below). Note that this ligand is probably not important from a strictly electronic viewpoint as it is not easily reduced or oxidized.

The problem is not easily dealt with from a theoretical viewpoint either. This is because it requires a detailed electronic structure calculation for the NP with explicit inclusion of electron-electron interactions in order to deal with the Coulomb charging problem. Simple estimates, based on “particle in a box” pictures do not give a good account of the details of the observed structure [30]. We therefore proceed to treat the Coulomb blockade aspect the simplest way we can, using the results of the fits to assess the degree to which this approach is flawed in practice.

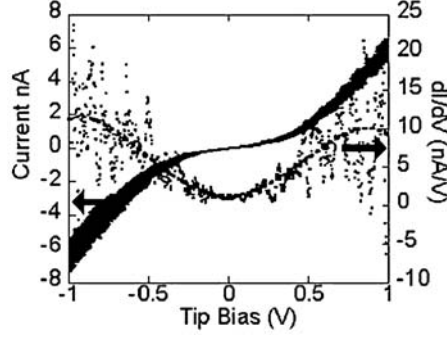


Fig. 1. Current vs. bias ($T = 300\text{K}$) for octanedithiol in a gold-molecule-gold junction (*left axis*) with the corresponding derivative (*right axis*). Data are averages for 1000 molecules with the standard deviation on each current shown by a vertical bar (giving the curve its width). Despite the averaging process, noise dominated the numerical derivative, so a 4th order polynomial fit is shown as the *dashed line*

At its simplest, this problem can be treated by considering the junction as a resistance (proportional to inverse tunneling rate) in parallel with a capacitor to represent the AFM to gold particle contact and a second parallel resistor-capacitor combination in series with the first to represent the gold particle to gold substrate contact (illustrated in the inset in Fig. 2a). Such an arrangement has been treated in detail by Hanna and Tinkham [31] and the current-voltage characteristic is calculated as follows:

With R_1 corresponding to the probe-to-particle tunnel junction resistance, C_1 to its capacitance, R_2 corresponding to the particle-to-substrate tunnel junction resistance and C_2 its capacitance, and allowing for a charge accumulation Q_0 on the nanoparticle, the current is obtained from

$$I(V) = e \sum_{n=-\infty}^{\infty} \sigma(n) [\Gamma_2^+(n) - \Gamma_2^-(n)] = e \sum_{n=-\infty}^{\infty} \sigma(n) [\Gamma_1^-(n) - \Gamma_1^+(n)]. \quad (1)$$

Here,

$$\Gamma_j^\pm(n) = \frac{1}{R_j e^2} \left(\frac{-\Delta E_j^\pm}{1 - \exp(\Delta E_j^\pm / k_B T)} \right), \quad j = 1, 2 \quad (2)$$

and

$$\Delta E_1^\pm = \frac{e}{C_1 + C_2} \left(\frac{e}{2} \pm (ne + Q_0) \pm C_2 V \right) \quad (3)$$

$$\Delta E_2^\pm = \frac{e}{C_1 + C_2} \left(\frac{e}{2} \pm (ne + Q_0) \pm C_1 V \right). \quad (4)$$

The residual charge on the nanoparticle, Q_0 , was set to zero in the fits that follow as non-zero values give asymmetric I-V curves, contrary to experiment. In (2), the electron distribution abides by the following ratios and equations:

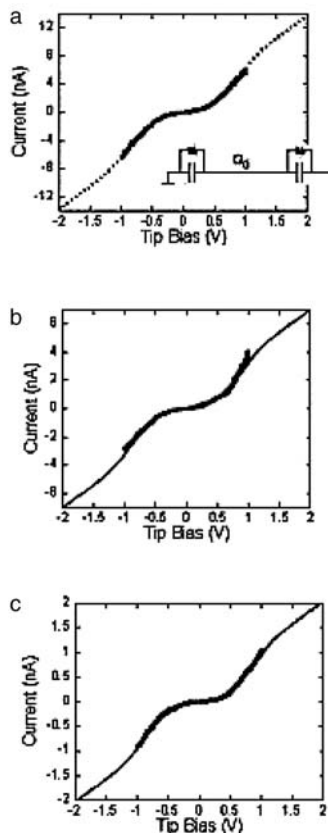


Fig. 2. Experimental single molecule current-voltage data (averages for many molecules) are shown as the *thick lines* superimposed on the theoretical Coulomb-blockade fits (*thin lines*) for (a) octanedithiol, (b) decanedithiol and (c) dodecanedithiol. Fitting parameters are listed in Table 1

$$\frac{\sigma(n)}{\sigma(n+1)} = \frac{\Gamma_1^-(n+1) + \Gamma_2^-(n+1)}{\Gamma_1^-(n) + \Gamma_2^+(n)} \quad (5)$$

and

$$\sum_{n=-\infty}^{\infty} \sigma(n) = 1. \quad (6)$$

C_2 should be at least equal to the free space capacitance of the sphere, $4\pi\epsilon_0 R$ where $R \approx 1.5$ nm, giving 0.08aF ($1\text{aF} = 10^{-18}\text{F}$). Fits to averaged data for octane, decane and dodecanedithiol are shown in Fig. 2 (for details of the statistical distribution of this data see [26]). The fits are good, but we

Table 1. Fitting parameters for the Coulomb blockade model for the various n-alkanes with 1.5 nm Au contacts (C_8 = octanedithiol, C_{10} = decanedithiol, C_{12} = dodecanedithiol)

Sample	C_1 (aF)	C_2 (aF)	R_1 (M Ω)	R_2 (M Ω)
C_8	0.318 ± 0.02	0.085 ± 0.02	<1	128 ± 5
C_{10}	0.318 ± 0.02	0.085 ± 0.02	<1	252 ± 10
C_{12}	0.318 ± 0.02	0.085 ± 0.02	<1	875 ± 40

show the modeled curves over a higher bias range than the experimental data to emphasize the fact that structure in the curves lies beyond the range of experimental observation (set by sample stability). The parameters for these fits are listed in Table 1. Once the octanedithiol data were fitted, the remaining data could be fitted with the same values for the tip-NP capacitance, C_1 , and NP-surface capacitance C_2 , to yield values for the molecular resistance, R_2 . The tip-to-NP resistance was too low to be determined accurately by the fits. The values of R_2 are closer to those that have been calculated [22,32–35] and the value of C_2 is of the right order, but too low, given that the appropriate relative dielectric constant must be > 1 . The essentially constant value for C_2 is reasonable, given the small changes in the relatively large NP-surface distance. Of more concern is the failure of the corrected data to produce a reasonable value for β . A plot of the values of R_2 vs. chain length (in units of methylene groups) is shown in Fig. 3. The best exponential fit is shown by the dashed line. The fit is clearly quite poor, and the corresponding value of β (0.48) anomalously low [26]. How might the intrinsic electronic properties of the sphere interfere with an otherwise exponential decay? A simple, if utterly classical, representation would be to introduce a “contact resistance”.

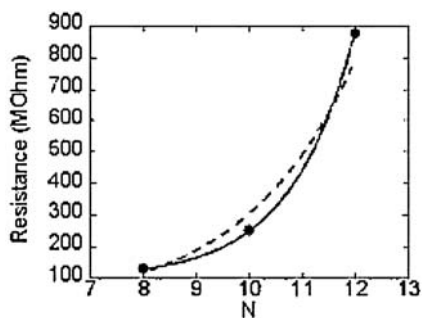


Fig. 3. Resistance vs. chain length (N = number of methylene groups) shown as the black dots. Best-fit exponential ($b = 0.48$) is shown by the *dashed line*. The modified decay (exponential plus constant) is shown by the *solid line*

This concept has no validity in a quantum system, but might be valid if the tunneling steps (tip to NP, NP to surface) were incoherent, perhaps as a consequence of thermal vibrations. Fitting to $R_0 + R_1 \exp(\beta N)$ produces a much better fit and improved value for β of 0.83 (solid line in Fig. 3.) with $R_0 = 98 \text{ M}\Omega$. We point this out to raise the possibility that a resolution of the remaining inconsistencies lies with the electronic properties of the NP. A definitive answer awaits development of an electronic structure calculation incorporating electron interactions properly.

3 Changing the NP Size

Given the need for triphenylphosphine stabilization, the only experimentally accessible procedure is to go down in size, and we used the method of Woerhle et al. [36] to synthesize NPs of nominal diameter 0.7 nm. HRTEM showed that the resulting particles were smaller than the 1.5 nm NPs originally used, but resolution and contrast were too poor for a quantitative size distribution to be determined. Nonetheless, it proved possible to attach these particles to octanethiol monolayers containing inserted octanedithiols. STM images of a monolayer with attached NPs and a control sample (no inserted dithiols and hence no attached NPs) are shown in Fig. 4 (experimental procedures were

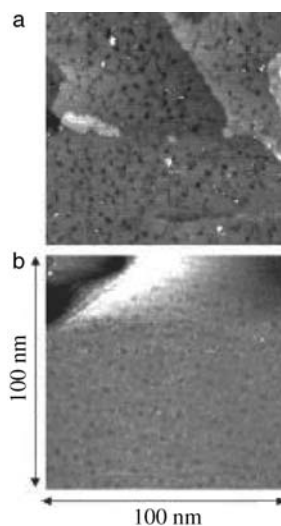
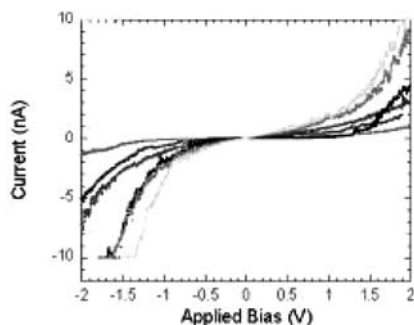


Fig. 4. STM image of (a) octanethiol monolayer with inserted octanedithiol molecules after incubation with 0.7 nm gold particles followed by rinsing. Similar treatment of an octanethiol monolayer (no inserted octanedithiol) results in a clean surface with no gold clusters adhering (b)

Table 2. Apparent heights and widths of the bare thiols and the two gold NPs in STM images

Sample	Height (nm)	Width (nm)
Protruding thiol	0.69 ± 0.08	2.4 ± 0.4
0.7 nm particle attached	2.4 ± 0.4	5.0 ± 1
1.5 nm particle attached	2.8 ± 0.4	6.1 ± 1.5

as described in [22]). The measured dimensions of the small NPs differ from those measured for the 1.5 nm NPs and the bare thiols (Table 2). These data were obtained from STM images and important role of electronic structure in the contrast is evident: The changes in dimensions trend in the right direction, but the absolute numbers do not correspond to physical size differences.

**Fig. 5.** A representative sample of the range of current-voltage curves obtained using the 0.7 nm gold spheres as contacts. Though the data are spread considerably, the zero-bias gap is consistently larger than that obtained with a 1.5 nm diameter contact

Current-voltage data obtained with these NPs were quite variable, and we were unable to construct meaningful distributions corresponding to multiples of a fundamental curve (as was done for the larger NP [22]). However, the curves were broadly similar, as shown by the representative sample in Fig. 5. Comparison with Figs. 1 and 2 shows quite clearly that the low bias region of suppressed (or partially suppressed) current is roughly doubled (± 1 V cf. ± 0.5 V) as the particle size is halved. Wang et al. [30] did not explore the effect of particle size in the region (>5 nm) where the electronic structure of the NP becomes important, so this observation of a Coulomb-blockade-like behavior (blockade scaling with $1/\text{radius}$) is novel, and suggests that elements of the Coulomb blockade model apply in this small size regime also.

4 Status of Single Molecule Measurements

The results and analysis presented above suggest that (a) measurements on NP-contacted junctions are distorted by the electronic properties of the NP, (b) the distortions are partially explained with classical Coulomb blockade theory, though substantial deviations indicate the importance of the intrinsic electronic structure of the NP and (c) the consequence is a reduction of measured current in the low bias region corresponding to the Coulomb blockade and/or low bias gap of the NP states. While not fully quantitative, these factors could explain the discrepancies between the data obtained with NP contacts [22, 26] and those obtained with break junctions [27]. Values of the low-bias resistance for octanedithiol connected between gold contacts are summarized in Table 3. The theoretical values come from initial DFT simulations [22], refined calculations that dealt with the interfacial dipole self-consistently [32, 35] and simple estimates based on the known value of β [32, 34]. These simple estimates might be expected to work quite well for the wide HOMO-LUMO gap of the alkane, so it appears that the break junction data and the latter two theoretical values are in reasonable agreement. The NP raw data disagree with these data by a factor of nearly 20, improved to about a factor 2 with the Coulomb blockade correction.

Table 3. Measured (top three entries) and calculated (lower three entries) resistances at low bias for octanedithiol connected to gold electrodes

Method (Reference)	Resistance ($M\Omega$)
Self-assembled junction [22]	900 ± 50
Coulomb-blockade-corrected, this work.	128 ± 5
Break junction [27]	51 ± 5
DFT [22]	150
DFT [32,33]	40
Simple estimate [32,33]	38.5

Thus, we conclude that rather good single molecule data are available from the method of Xu and Tao [27]. The molecule is under some strain in these junctions, though electromechanical measurements indicate that these effects do not dominate the data for a number of molecules [28]. In addition to being easier to interpret, the new approach is experimentally quite simple and flexible. For example, the use of partially-insulated STM probes [37] permits measurement in aqueous electrolytes, a feature exploited in the measurement of the electronic properties of DNA molecules in their native state [5].

Thus, in answer to the question posed in our title, reliable single molecule measurements of conductance are at hand. The measurement of temperature

dependence [16] for a well-defined single molecule junction remains as an important experimental challenge.

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