Measurement of Single-Molecule Conductance

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Abstract
What is the conductance of a single molecule? This basic and seemingly simple question has been a difficult one to answer for both experimentalists and theorists. To determine the conductance of a molecule, one must wire the molecule reliably to at least two electrodes. The conductance of the molecule thus depends not only on the intrinsic properties of the molecule, but also on the electrode materials. Furthermore, the conductance is sensitive to the atomic-level details of the molecule-electrode contact and the local environment of the molecule. Creating identical contact geometries has been a challenging experimental problem, and the lack of atomic-level structural information of the contacts makes it hard to compare calculations with measurements. Despite the difficulties, researchers have made substantial advances in recent years. This review provides an overview of the experimental advances, discusses the advantages and drawbacks of different techniques, and explores remaining issues.
Molecular electronics: science and technology related to the understanding, design, and fabrication of electronics devices based on molecules

Contact geometry: the atomic-scale geometry of an electrode, and the binding site and orientation of a molecule on the electrode

1. INTRODUCTION

The ability to measure and control electrical current through a molecule is a critical requirement toward the goal of building electronic devices using individual molecules (1, 2). This ability also offers us a unique opportunity to understand charge transport, an important phenomenon that occurs in many chemical and biological processes (3, 4), on a single-molecule basis. Furthermore, it allows us to read the chemical information of a single molecule electronically (5), which opens the door to chemical and biosensor applications based on the electrical detection of individual molecular binding events (6).

The most fundamental quantity that describes the electrical properties of a bulk material is conductivity, based on which materials are often divided into conductors, insulators, and semiconductors. Conductivity is defined as $\sigma = (I/V) \times L/A$, where $I$ is the electrical current, $V$ is the applied bias voltage, $L$ is the length, and $A$ is the cross sectional area of the material. For a small molecule, $A$ and $L$ are difficult to define precisely, and a more well-defined quantity is the conductance, $G$, given by $G = I/V$. So a basic question in molecular electronics is, what is the conductance of a single molecule?

To determine the conductance of a molecule, one must first bring it into contact with at least two external electrodes (Figure 1). The contact must be robust, reproducible, and able to provide sufficient electronic coupling between the molecule and the electrodes (7–11). One way to meet the contact requirements is to attach the molecule covalently to the electrodes via proper anchoring groups at two ends of the molecule. Clearly, the measured conductance depends not only on the molecule, itself, but also on the properties of the electrodes and the atomic-scale molecule-electrode contact geometry (12–17). Another factor that may affect the measured conductance is the local environment of the molecule, which includes solvent molecules (vacuum or air), pH, and ions (18, 19). Finally, an electron traversing through the molecule...
may exchange energy with the vibration modes of the molecule or surrounding solvent molecules (20, 21). Consequently, the measured conductance may be sensitive to temperature (22–24). Precisely controlling these measurement details, especially the molecule-electrode contacts, has been a difficult task, which is a major reason for the large disparities between different measurements for even a relatively simple molecule, such as alkanedithiols (25, 26). In this chapter, we review recent experimental advances and discuss remaining issues in measuring single-molecule conductance.

A related problem is to determine the conductance of a single metal atom or a linear chain of metal atoms bridged between two electrodes made of the same metal as the atoms in the chain (27–32). This system is known as a quantum point contact. For metals, such as Au, the conductance of a quantum point contact is close to \( G_0 = \frac{2e^2}{h} = 77.4 \mu \text{S} \), where \( e \) is the electron charge, \( b \) is the Planck constant, and \( S \) is the conductance unit. \( G_0 \) is the conductance quantum unit corresponding to 100% transmission of electrons from one electrode to the other through the point contact. Therefore, the conductance of a molecule given in units of \( G_0 \) tells us how conductive the molecule is in comparison with a metal atom, which is why we use \( G_0 \) as the unit of conductance here.

Molecular electronics is a diverse and rapidly growing field, and many excellent reviews have appeared in recent years, covering general concepts (4, 33–36), theoretical aspects (21, 37, 38), and experimental methods (39–42). In the present review, we mainly focus on the measurements of single molecules covalently bound to two electrodes. We refer the readers interested in molecule-film measurements to recent reviews by Metzger (42) and Wang et al. (41). The remainder of the chapter is arranged as follows: Section 2 provides a brief overview of experimental tools that measure the conductance of molecular thin films, and Section 3 describes techniques and methods for single-molecule conductance measurements, in which we discuss both the advantages and difficulties of different techniques. Section 4 addresses some critical issues that affect single-molecule conductance, and Section 5 provides a summary and outlook.

## 2. Measurements of Molecular Films

To date, many experimental techniques have been developed to measure and control current through molecules. We can divide these techniques into two broad categories: molecular film and single-molecule measurements. We briefly describe the first category in this section, whereas we discuss single-molecule conductance measurements in more detail in Section 3.

### 2.1. Bulk Electrodes

The basic idea of the bulk electrode approach is to sandwich a molecular film, either a monolayer or multiple layers, between two electrodes. The molecules are typically first immobilized on one electrode surface, via self-assembly or Langmuir-Blodgett methods (40, 42). Both self-assembly and Langmuir-Blodgett methods provide ordered molecular films, which are highly desired for successful measurement and data
Molecular junction: a molecule is attached to two electrodes to form an electrode-molecule-electrode structure.

The placement of the top electrode is often the most difficult part of the measurement, and many methods have been developed (43). One is to evaporate a metal layer onto the molecular film in vacuum. To avoid a short circuit between the top electrode and the bottom electrode, one must ensure that energetic metal atoms do not damage the molecular film and the deposited metal does not penetrate into the molecular film via defect sites to reach the bottom electrode (44, 45). To minimize the short-circuit problem, Akkerman et al. (46) put a conducting polymer layer onto the molecular film before the deposition of the top electrode. Another method is to print a metal layer onto the molecular film by transferring a metal film evaporated on a stamp via direct contact (47, 48).

Electrodeposition methods have also been investigated (49–51). For example, Manolova et al. (52) used a 4,4′-dithiodipyridine-modified Au electrode to allow Pd or Pt ions to adsorb preferentially onto the pyridine moiety of the molecules. The adsorbed metal ions were then reduced electrochemically to metallic Pd or Pt that could serve as the second electrode in a metal ion-free acidic solution (52). Angle-resolved X-ray photoelectron spectroscopy showed that the second electrode was indeed on top of the molecular film without penetrating into the molecule film via defect sites. Instead of using a solid metal as the top electrode, an alternative approach is to place a drop of mercury onto the molecular layer (53–57). The mercury approach is relatively simple and has shown high device yields.

2.2. Nanoelectrodes

The molecular film measurements described above involve many molecules, which can be reduced using nanoscale electrodes. For example, a conducting atomic-force-microscope tip with a radius of curvature on the nanometer scale can serve as the top electrode to measure conductance of a relatively small number of molecules (58, 59). Another method is the cross-wire junction, which sandwiches a molecular layer between two perpendicular metal wires (60–62). The contact area between the two wires is small, so a relatively small number of molecules is measured.

One may also reduce the number of molecules by confining the molecular film inside a nanopore fabricated in a thin solid membrane (63, 64). One side of the membrane is first covered with a metal layer, and molecules are allowed to form a monolayer on the metal surface inside of the nanopores. A second metal layer is then deposited on top of the molecular film in the nanopores. Nanopores can also be used as templates to fabricate nanoscale metal-molecule-metal junctions (65). Metal is first deposited electrochemically into the nanopores in an alumina membrane to partially fill up the nanopores. Sample molecules are then allowed to adsorb on the metal surface inside of the nanopores, which is followed by the chemical deposition of a top metal layer into the nanopores to form nanoscale molecule junctions. After dissolving the alumina, these molecular junctions in a solution are assembled onto electrode arrays for conductance measurements.
The molecular film measurements have played an important role in the understanding of the electron-transport properties of molecules (66, 67) and for demonstrations of many device functions, including rectification (44, 68–70), molecular switching (62, 71, 72), and negative differential resistance effects (56, 63, 73). When applying these techniques to a particular sample molecule, one needs to consider the following factors: First, not all the molecules of interest can form well-ordered films, which limits the choice of molecules for the studies. Second, molecular films often have defects, and additional defects may be created during the fabrication of the top electrode (51) and application of bias voltage (61). It is important to ensure that the defects and electromigration-induced effects do not dominate the measured conductance. Third, in a close-packed film, a molecule interacts with the neighboring molecules, which may suppress its conformational change and affect its electron-transport properties (74). As a result, the average conductance per molecule calculated from the molecular film measurements may not be directly comparable with single-molecule conductance measurements. Finally, the molecules in the films are not exposed to the outside world, which makes it difficult to introduce a gate electrode and prevents one from studying molecular binding processes between the sample molecules and analytes.

3. MEASUREMENTS OF SINGLE MOLECULES

To determine the conductance of a single molecule, one must (a) provide a signature to identify that the measured conductance is a result of not only the sample molecules, but also a single sample molecule, (b) ensure that the molecule is properly attached to the two probing electrodes, and (c) perform the measurement in a well-defined environment. The current methods fall into three categories: scanning probe methods, fixed electrodes, and mechanically controlled molecular junctions.

3.1. Scanning Probe Techniques

Scanning tunneling microscopy (STM) has played a unique role in the field of molecular electronics (75). This is because it allows one to image individual molecules adsorbed on a conductive substrate with submolecular resolution. By placing a scanning-tunneling-microscope tip over a molecule, one can perform tunneling spectroscopy measurements on the molecule (76–78). In addition, the tip can be used to manipulate atoms and molecules on surfaces (79). A closely related technique is atomic force microscopy (AFM). Although AFM has typically a lower resolution than STM, it measures both the mechanical and electrical properties of molecules when a conducting tip is used (80, 81). To date, STM and AFM have revealed many interesting phenomena important to the development of molecular electronics. Examples include reversible redox switching (82–85), an electromechanical molecular amplifier (86), the negative differential resistance-like effect (59, 87–89), molecular switching (90, 91), and the study of field effects on electron transport in molecules (92).

In the STM or AFM method, a molecule adsorbs onto a substrate to form a well-defined molecule-substrate contact, but the tip-molecule contact is often less well defined, which prevents one from determining the absolute conductance of the
molecule. One way to reduce this problem is to embed a molecule of interest into the matrix of another, often less conducting molecule (Figure 2a). Bumm et al. (90) used this approach to study current through molecular wire candidates inserted into an insulating alkanethiol monolayer and observed much higher current through the molecular wires than through the surrounding alkanes. Tao (82) studied Fe-porphyrin coadsorbed in the ordered array of porphyrin molecules in an electrochemical cell. Fe-porphyrin is redox active, whereas porphyrin is similar in structure but redox inactive. The work shows that the current through the redox active molecule is much higher than that through the redox inactive molecule when the electrode potential is tuned near the redox potential of Fe-porphyrin.

Another STM approach demonstrated by Langlais et al. (93) is to attach one end of a molecule to a step edge on a metal substrate. The STM image of the molecule and the metal substrate provides spatially resolved electronic penetration of the metallic electronic states from the step edge into the molecule, which the researchers used to determine the electron tunneling decay constant along the molecule.

A third approach is to attach one end of a molecule onto a substrate and the other end to an Au nanoparticle covalently (Figure 2b). One then places a scanning-tunneling-microscope tip (94) or a conducting atomic-force-microscope tip (7) on top of the nanoparticle. Because Au nanoparticles are typically coated with an organic surfactant layer, the tip and the nanoparticle form a tunneling junction. Consequently, the nanoparticle behaves similar to a Coulomb island, and the electron transport between the tip and the substrate via the nanoparticle exhibits Coulomb blockade effect (7, 94). By fitting the measured I-V curves with the Coulomb blockade model, one can extract the conductance of the sample molecule between the nanoparticle and the substrate (95, 96).
Ho et al. (97) recently made a significant step toward the goal of creating a metal-molecule-metal junction with atomic-scale precision. They assembled a copper(II) phthalocyanine molecule bound to two Au atomic chains on an NiAl(110) surface by manipulating individual Au atoms and copper(II) phthalocyanine molecules with a scanning-tunneling-microscope tip. The spatially resolved electronic spectroscopy revealed that the electronic states of the metal-molecule-metal junction change significantly when varying the number of Au atoms in the chains one by one. The NiAl(110) is conducting, so the electronic coupling between the molecule and the substrate is strong. To reduce the electronic coupling, Repp et al. (98) introduced an insulating layer of NaCl between the sample molecule (pentacene) and a Cu substrate. By manipulating an Au atom with a scanning-tunneling-microscope tip, they created an Au-pentacene contact and studied the dependence of the molecule’s electronic states on the formation of the Au-molecule contact (Figure 3). These STM studies not only provided the atomic-scale structural information of the metal-molecule contacts but also determined the mixing of the electronic states of the molecules with those of the metal electrodes.

![Figure 3](image_url)

**Figure 3**
Making and breaking a chemical bond between a single pentacene molecule and an Au atom on an NaCl bilayer supported by a Cu(100) substrate. (a) Scanning tunneling microscopy (STM) image showing the molecule and the Au atom before bond formation. (b) Image showing a molecule-metal complex (6-Au-pentacene) after resonant tunneling through the lowest unoccupied molecular orbital of the pentacene molecule. (c) Calculated geometry of the adsorbed 6-Au-pentacene complex. C, H, and Au atoms are represented by gray, white, and gold spheres, respectively. Reprinted with permission from Reference 98.
In both examples described here, the metal electrodes, consisting of a single or several Au atoms, are too small to develop full continuous density of states of metallic character. The coupling between the molecule and metal substrate is reduced by the thin NaCl layer, but it is still finite as it is needed for STM imaging. Therefore, the results may not be compared directly with the molecular conductance measurements that use large or bulk metal electrodes. Another challenge is to connect the metal electrodes to two external electrodes to carry out electron-transport measurements on the molecular junctions created by STM.

3.2. Fixed Electrodes

A conceptually simple method to measure single-molecule conductance is to fabricate a pair of facing electrodes on a solid substrate and then bridge the electrodes with a molecule terminated with proper anchoring groups that can bind to the electrodes (Figure 4a). A key requirement of this method is to fabricate electrodes with a molecular-scale gap, which has been a difficult task. This is because most molecules are a few nanometers or less, and fabrication of such a small gap between electrodes is beyond the reach of conventional micro- and nanofabrication facilities. Unconventional
fabricsation techniques—such as electromigration (99, 100), electrochemical etching or deposition (101–104), and other novel methods (105–109)—have been developed to create electrodes separated with a molecular-scale gap.

One attempt to avoid the requirement of molecular-scale gaps is to use metal nanoparticles as bridges (Figure 4b). This technique starts with a pair of electrodes separated with a gap that is much larger than a sample molecule. After covering the electrodes with a layer of sample molecules, one drives a metal nanoparticle with a diameter greater than the electrode gap into the gap to bridge the two electrodes, either using dielectrophoresis (110) or a magnetic field when Au-coated Ni particles are used (71). This results in two metal-molecule-metal junctions in series, which may complicate the data analysis. Dadosh et al. (111) reported another strategy based on synthesizing a dimer structure, consisting of two Au nanoparticles connected by a dithiolated organic molecule, and electrostatically trapping the dimer structure between two metal electrodes (Figure 4c).

Because the fixed electrodes are supported on a solid substrate, the molecular junctions are mechanically stable, which is ideal for studying electron transport through molecules as a function of temperature, magnetic field, and other external parameters. Another advantage of this approach is that one can use the substrate (e.g., heavily doped Si) as a gate electrode to control the electron transport through the molecules. Researchers have applied this approach to study various interesting phenomena, including single-electron charging (99, 100, 107, 112) and Kondo effects (99, 100, 113) in molecules at low temperatures.

Further improvements are desired to address the following issues. First, the device-to-device variation is large, which calls for statistical analysis. However, the fabrication yield is usually rather low, making it difficult to perform statistical analysis (104, 105). Second, for redox molecules, the single-electron charging effect was used as a signature to identify measurements attributed to a single molecule (99, 100, 107, 112). But, in general, it is difficult to determine how many molecules are bridged across the electrodes and how many contribute to the measured current. Because metal-nanoparticle complexes often form during the fabrication processes of the molecular-scale gaps, it is important to distinguish that the measured transport properties are a result of the sample molecule rather than the nanoparticles or a nanoparticle-molecule complex (114). Third, even though the molecules have two linker groups, it is difficult to determine if the molecules are indeed covalently bound to the two electrodes. Finally, the structure of the electrodes and the position of the molecule are not precisely known, so a technique that can provide atomic-scale structural information of the molecular junction is highly desired.

3.3. Mechanically Formed Molecular Junctions

It is difficult to fabricate electrodes separated with a gap that can fit a sample molecule precisely. This difficulty may be overcome by bringing two electrodes together or separating them apart mechanically. Using a piezoelectric transducer (PZT) or other mechanical actuation mechanisms, one can control the gap with subangstrom precision, making it possible to fabricate molecular junctions and measure the conductance.
of various molecules. Several techniques based on this concept have been developed, which are described below.

### 3.3.1. Mechanically controllable break junction

The basic principle of the mechanically controllable break junction (MCBJ) method (115, 116) is to break a thin metal wire supported on a solid substrate into a pair of facing electrodes (32). The process is controlled by bending the substrate with a mechanical actuator, such as a PZT and stepping motor (Figure 5a). An MCBJ device can be built manually by fixing a metal wire with a notch near the middle of the wire (116). An alternative method is to create a nanobridge connecting two microelectrodes on a substrate using electron-beam lithography (Figure 5b) (117). Because the bending is achieved by fixing two ends of the substrate while pushing the middle part of the substrate vertically, the vertical movement of the PZT is demagnified when the substrate is thin compared to its width. This allows one to accurately control the width of the gap.

Moreland & Ekin (115) first used the MCBJ to study electron tunneling, and Muller et al. (116) pioneered the technique to create metallic quantum point contacts and to demonstrate conductance quantization (29). Reed et al. (118) applied MCBJ to measure electron transport in molecules. They first formed a molecular-scale gap between two electrodes and then exposed the electrodes to a solution containing benzenedithiol. After evaporation of the solvent, they measured a finite current between the electrodes and attributed it to electron transport through the molecules. Kergueris et al. (119) measured electron transport through oligothiophenes terminated with dithiols using an MCBJ in a similar way. These pioneering works demonstrate the feasibility of studying electron transport in molecules using the MCBJ; however, how many molecules were involved in the conduction and whether the molecules were bound to both electrodes were not clear.

Reichert et al. (120) provided strong evidence of single-molecule conductance measurements using an MCBJ setup. In their experiment, they first applied a droplet of a solvent containing dithiol molecules to the electrode pair formed with the MCBJ to allow the molecules to adsorb onto the electrodes. The gap was then closed while maintaining a fixed voltage across the electrodes, during which time they recorded the current (Figure 5c). Initially, the current grew exponentially, owing to electron tunneling across the gap. When the gap was decreased to a certain width, sometimes the current locked into a stable value weakly dependent on the gap width (121). At that point, the first molecule was presumably attached to the opposite side. The measured I-V (Figure 5d) curves were asymmetric for asymmetric molecules, which suggests a single or a small number of molecules bridging the gap. Smit et al. (122) reported that a hydrogen molecule forms a stable bridge between platinum electrodes in their quantum point contact measurements in the presence of H₂. The measured conductance determined from the hydrogen bridge is close to 1G₀, nearly perfect conductance or 100% transmission through H₂. They also studied the vibrations of the molecules using point contact spectroscopy (123).

### 3.3.2. Scanning-tunneling-microscopy-based break junction

Xu & Tao (124) developed an STM–break junction method that quickly creates thousands of
molecular junctions by repeatedly moving a scanning-tunneling-microscope tip into and out of contact with the substrate electrode in the presence of sample molecules (Figure 6). The molecules in the study have two end groups that can bind to the tip and the substrate electrodes, respectively. The process can be divided into three steps: (a) A PZT drives the tip toward the substrate surface until it contacts the molecules bound to the substrate. During the contact period, one or more molecules may bind to the tip via the second end group. (b) The tip is pulled away from the substrate, and then the molecules break contact with one of the two electrodes individually, which

Figure 5
(a) Schematics of a microfabricated mechanically controllable break junction (MCBJ) (88). (b) Scanning-electron-microscope picture of the lithographically fabricated break junction (92). (c) Change of current recorded during the formation of a molecular junction. After a region of roughly exponential increase of the current, the current suddenly locks into a remarkably stable value (plateau), nearly independent of the distance. (d) I-V and dI/dV of a molecular junction. Images reprinted with permission from References 32, 117, 120, and 121.
Conductance histogram: a statistical distribution of conductance values of a large ensemble of molecular junctions with microscopically different contact geometries.

Figure 6

(a) Measurement of single-molecule conductance using a scanning tunneling microscopy (STM) break junction. A scanning-tunneling-microscope tip is pushed into contact with molecules adsorbed on an electrode with a piezoelectric transducer (PZT) in a solution containing the sample molecules, during which the molecules have a chance to bridge the tip and substrate electrodes. The tip is then pulled away from the substrate to break the molecules from contacting the electrodes. (b) The current (conductance) for viologen dithiol (N,N′-bis(6-thiohexyl)-4,4′-bipyridinium bromide) recorded during the pulling process shows stepwise features. Bias voltage = −0.1 V. These curves reflect the typical current features for thousands of molecular junctions repeatedly formed under the same conditions. (c) Conductance histogram constructed from the individual measurements reveals well-defined peaks near integer multiples of a fundamental value, ~1 nS, which is identified as the conductance of a single molecule. Reprinted with permission from Reference 85.

is shown as a series of stepwise decreases in the current (Figure 6b). (c) The process is repeated until a large number of molecular junctions are created and measured. The conductance histogram of these molecular junctions exhibits peaks located near integer multiples of a fundamental value, which is used as a signature to identify a single-molecule conductance. During the approaching stage, one may control the tip to either make contact with the substrate to form a quantum point contact or avoid the formation of a point contact between the tip and the substrate.
Unlike most of the MCBJ experiments that record the approaching processes, this method focuses on the separation process. Because only those molecules bound to two electrodes can be stretched until breakdown during the separation process, this method selectively measures the conductance of those molecules bound to both electrodes. Another difference is that the creation of the molecular junctions and the measurement of the conductance are performed in an organic solvent or aqueous electrolyte, so one can easily introduce the sample molecules via the solution and control the electron transport through the molecules electrochemically. Finally, the scanning-tunneling-microscope tip images the substrate surface before performing the electron-transport measurement, so one can place the tip on an atomically flat area or move the tip laterally to a fresh area of the substrate during the measurement. This freedom comes at the cost of mechanical and thermal stability, however, which is typically not as good as the MCBJ. Different groups have used this or similar approaches to determine the conductance of many molecules (85, 125–127). Despite the success, several issues remain to be resolved and understood (see Section 4).

3.3.3. Conducting atomic-force-microscopy break junction. The stepwise change in the conductance curves shown in Figure 6b was attributed to the breakdown of individual molecules during the separation of the electrodes. Xu et al. (80) confirmed this by measuring the electromechanical properties of the molecular junctions with a conducting atomic force microscope (Figure 7). Each abrupt conductance decrease is accompanied by an abrupt decrease in the force, corresponding to the breakdown of a molecule from contacting the electrodes. Further pulling causes only a slight change in the conductance but an approximately linear increase in the force. When the force reaches a certain threshold, another molecule junction breaks.

![Figure 7](http://www.annualreviews.org/aojournals/annualreviews.org/)

(a) Simultaneous conductance and force measurements of a molecular junction during breakdown using a conducting atomic force microscope setup. (b) As the individual molecules break, the conductance decreases in a stepwise fashion (red), and associated with each conductance step, the force (blue) also decreases abruptly (83).
down, resulting in additional abrupt decreases in the conductance and the force. The average breakdown force required to break Au-octanediithiol junctions is \(~1.5\) nN (128), which is about the same as the force required to break an Au-Au bond under the same conditions, indicating the breakdown probably takes place at the Au-Au bond. The conducting AFM break junction method also allows one to study the electromechanical properties of single molecules.

3.3.4. Other scanning-tunneling-microscopy-controlled point contact measurements. The STM break junction method described above forms a molecular junction by first contacting the molecules with the tip and then pulling the tip away. Haiss et al. (129) developed an STM trapping method to bridge molecules between the tip and the substrate. The tip was brought close to but not into contact with the substrate covered with the dithiol molecules. They observed sudden jumps in the tunneling current, which they attributed to the spontaneous chemical-bond formation between the tip and the molecule.

Yasuda et al. (130) showed recently that one can form a molecular junction by moving the tip toward a given molecule until a chemical bond formed between the tip and the molecule. They first imaged isolated target molecules \(\alpha,\omega\)-bis-(acetylthio)terthiophene and \(\alpha,\omega\)-bis-(acetylseleno)terthiophene] embedded in an octanemonothiol monolayer. The target molecules are terminated either with two thiol or selenium groups that can bridge the substrate and the tip, but the octanemonothiols are bound to the substrate via its sole thiol group. They first located the target molecules and then placed the tip above a molecule and moved it toward the chosen molecule. When the tip formed a chemical bond with the terminal group (S or Se) of the molecule, the conductance jumped to a much higher conductance.

4. CRITICAL ISSUES IN SINGLE-MOLECULE CONDUCTANCE MEASUREMENTS

The mechanical methods, especially when combined with force measurements and statistical analysis, have the following distinctive features: (a) Peaks in the conductance histogram located at integer multiples of a fundamental value can be used as a signature to identify the conductance of a single molecule. (b) The simultaneously measured force tells us if a molecule is properly bound to two electrodes. (c) Statistical analysis reduces the chances of mistaking impurities as sample signals. (d) Mechanical methods work in solution and in vacuum, which not only makes it easy to introduce various sample molecules into the measurement, but also provides a controlled and inert environment for the measurement. However, there are several issues that require further study.

4.1. Molecule-Electrode Contact Geometry

In STM– or conducting AFM–break junction methods, a large number of molecular junctions are repeatedly created, but these molecular junctions differ in their contact geometries (Figure 8). In fact, the conductance of the last step, corresponding to
Figure 8

(a) Different contact geometries of a 1,6-hexanediithiol molecule bound to two Au electrodes. 
(b) Calculated conductance values of the molecule for the different contact geometries plotted versus the number of atoms protruding out of the crystal planes of the electrodes. 
(c) Distribution of conductance values with 1296 different contact geometries. Reprinted with permission from References 14 and 16.

The formation of a single-molecule junction, varies considerably from one junction to another, which reflects atomic-scale variations in the contact geometries (13, 14, 16, 17). Guo and colleagues (16) calculated the conductance values of molecules with hundreds of different contact geometries (Figure 8c). By assuming that the statistical weight of each geometry is equal, they obtained a distribution of the conductance values...
HOMO: highest occupied molecular orbital
LUMO: lowest unoccupied molecular orbital

values. The distribution for 1,6-hexanedi thiol bound to Au electrodes has a peak near $\sim 2 \times 10^{-3} \ G_0$, which is in good agreement with the experimental peak position at $\sim 1.2 \times 10^{-3} \ G_0$ (124). In addition to various binding sites of the anchoring groups (e.g., S) on Au electrodes, Muller (14) considered the possibility that the anchoring groups may bind to one or more Au atoms protruding out of the electrode crystal planes (Figure 8a). For 1,6-hexanedi thiol, most of the 16 different contact geometries have conductance values close to $\sim 2 \times 10^{-3} \ G_0$ (Figure 8b), in close agreement with both the experiment and the calculations by Guo et al. (16).

In the case discussed above, pronounced peaks appear in the conductance histogram, which are used to identify the conductance of single molecule. This method fails if the distribution is too broad, as shown by Ulrich et al. (131). We also found in our lab that some molecules, especially small conjugate molecules, exhibit well-defined steps in the individual conductance traces, but the conductance histograms display only broad distributions (132). Another possibility is that for (at least) some molecules, more than one set of conductance peaks appear in the histograms. Li et al. (133) studied the conductance of single N-alkanedithiols ($N = 6, 8$ and $10$) covalently bound to Au electrodes. For each molecule, the conductance histogram reveals three sets of well-defined peaks near integer multiples of different conductance values. The two higher conductance sets can be described by the tunneling model with an identical decay constant of 0.84 $\text{Å}^{-1}$ and interpreted in terms of different molecule-electrode contact geometries (134). The lowest one is thermally activated, which was previously reported by Haiss et al. (23), and is attributed to the thermal fluctuation of the molecular conformation.

The distribution of different contact geometries appears to depend on the way the molecular junctions are formed. For example, Wandlowski and colleagues (85) measured the conductance of dithiol molecules using an STM break junction by carefully avoiding the contact of the tip with the Au substrate. They found one set of pronounced peaks in the conductance histograms. Conversely, Venkataraman et al. (127) reported that diamine-terminated molecules gave well-defined peaks in the conductance histograms by forcing the two electrodes to form a point contact during the approaching stage. In their case, the formation of point contacts was believed to be crucial for the formation of an amine-Au bond.

4.2. Molecule-Electrode Energy-Level Alignment

The conductance of a molecule depends on the alignment of the molecular energy levels, especially the highest occupied molecular orbital (HOMO) and lowest occupied molecular orbital (LUMO), relative to the Fermi levels of the electrodes. Typically, the Fermi level is positioned in the LUMO-HOMO gap of the molecule because if the HOMO or LUMO is close to the Fermi level of an electrode, electrons transfer between the molecule and the electrode, and consequently the molecules are oxidized or reduced spontaneously. The energy-level alignment is determined by the intrinsic properties of the molecule and the electrodes, and also by the interactions between the molecule and the two electrodes, which are often difficult to determine for both theory and experiment (135, 136).
Surface spectroscopy techniques, such as ultraviolet photoelectron spectroscopy and X-ray photoelectron spectroscopy, can provide useful information about the energy-level alignments of molecules adsorbed on surfaces (137). STM tunneling spectroscopy has also been used to study the electronic states of molecules adsorbed on surfaces. Hipps and colleagues combined the tunneling spectroscopy with ultraviolet photoelectron spectroscopy to study metallo-porphyrins and phthalocyanines on Au (138) and resolved different molecular energy levels and their relative positions to the Au Fermi level (77).

In electrolytes, one may gain valuable insights into the energy-level alignment by measuring the oxidization or reduction potentials (Figure 9) (139). One may even tune the alignment by adjusting the potentials of the electrodes relative to a reference electrode inserted in the electrolyte. When the LUMO or HOMO is brought close to the Fermi levels, electrochemical oxidation or reduction occurs. For molecules that can be reversibly oxidized or reduced, significant changes in the conductance occur. This has lead to electrochemical gate control of the conductance of single redox molecules that is analogous to field effect transistors (82, 140–142). This behavior has been observed in several redox systems (82, 140–143). For example, Haiss et al. (140) reported an interesting potential-dependent conductance in viologen derivatives. Another example is perylene tetracarboxylic diimide terminated with thiol groups (Figure 9c) (141). The conductance of a single perylene tetracarboxylic diimide molecule covalently bound to two Au electrodes increases reversibly over nearly three orders of magnitude as one shifts the LUMO of the molecule toward the Fermi level of the electrodes.

### 4.3. Effect of External Force

The mechanical methods can create a molecular junction by controlling the separation between two electrodes. It is natural to ask how the applied force affects the measured conductance of the molecules. In the individual conductance traces recorded during the breakdown of the molecular junctions, the step is rather flat, which means the force does not significantly affect the measured conductance until the contact breaks down. However, carefully examining the steps, one can see a finite decrease, on average, in the conductance upon stretching. In the case of alkanedithiols, the decrease is only 10%–20% before breakdown (81). Another observation is that the distance over which a molecular junction can be stretched is typically several angstroms. Clearly a small molecule cannot be stretched over such a large distance without tearing the molecule apart. The reason for such a large stretching distance is that most of the stretching actually takes place in the Au atoms near the molecule-electrode contact rather than in the molecule, itself. When the force reaches ~1.5 nN, the contact breaks, and the maximum force that one applies to the molecule is ~1.5 nN. For molecules such as alkanedithiols, such a force is not sufficient to change the electronic states of the molecules or distort the structure of the molecule significantly. However, for conjugated molecules, such as oligothiophenes, the force can cause a much greater change in the conductance, owing to a stronger coupling between the electronic states and the structures of the molecule than that for alkanedithiols (81).
4.4. Effect of Environment

The local environment (such as solvent molecules, ions, pH, and dopants) of a molecule can significantly affect the conductance of the molecule. Xiao et al. (144) measured conductance on several oligopeptides terminated with dithiols as a function of solution pH and observed the dependence of the conductance on pH (Figure 10).
They traced the pH dependence to the protonation or deprotonation of NH$_2$ and COOH in the peptides, which changes electronic states and local charge distributions of the molecules. The conductance of a molecule may also depend on the surrounding ions (6). For example, the presence of Cu$^{2+}$ and Ni$^{2+}$ in solution changes the conductance of cysteamine-Gly-Cys by $\sim$300 and $\sim$100 times, respectively, owing to strong binding of the metal ions to the molecule. In a recent study by STM in an ultrahigh vacuum environment, a charged dangling bond of Si induced a large change in the electronic states of a nearby adsorbed molecule, and the researchers attributed this observation to the electric field by the charge (92). In the case of peptides, the binding of Ni$^{2+}$ and Cu$^{2+}$ is strong and known to induce conformational changes in the peptides. Therefore, in addition to an electrostatic effect, conformational changes may be responsible for the change in conductance.

For certain molecules, the dependence of conductance on local environment may be traced to the change in doping. Chen et al. (145) measured the conductance of a hepta-aniline oligomer attached to Au electrodes in toluene and in electrolyte. The single-molecule current-voltage characteristic is linear in toluene but displays negative differential resistance in an acidic electrolyte. The conductivity of bulk polyaniline increases dramatically when it is oxidized in an acidic medium, in which acid plays the role of doping the polymer materials. Similar to the bulk polyaniline, the conductance of a single aniline oligomer also increases in the oxidized form in acid. These results show the sensitive dependence of the conductance of the redox molecule on the solvent, and on the doping condition.

### 4.5. Current-Induced Local-Heating Effects

Local heating is known to be a critical factor in the design of conventional silicon-based microelectronics. When current passes through a single molecule, how hot it gets is an important question. In a nanoscale junction, the inelastic electron mean free
path is often large compared with the size of the junction, so each electron is expected to release only a small amount of its energy to phonons (heat) during transport in the junction (66, 67). However, substantial local heating may still arise owing to the large current density and thus power per atom.

Recently, researchers have reported experimental studies of local-heating effects in quantum point contacts (146, 147). In the case of molecules, the current density is much lower, but the thermal conduction of molecules may also be poorer than that of the metal contacts. Theoretical calculations have found a finite increase in the temperature of the molecules as a result of the inelastic scattering of electrons (148, 149). Huang et al. (150) reported on an experimental approach to determine the local temperature in a single molecule covalently bound to two Au electrodes. They measured the force required to break the attachment of the molecules to the electrodes. Because the breakdown process is thermally activated, the average breakdown force is sensitive to the local temperature of the molecule-electrode contact and can be used to estimate the effective local temperature of the molecular junction. For octanedithiol, the temperature with a bias voltage of 1 V (current $\sim 20$ nA) increases by $\sim 25$ K above room temperature.

5. OUTLOOK

The conductance of a single molecule depends not only on the intrinsic properties of the molecule and the probing electrodes, but also on the molecule-electrode contacts and its local environment. To determine the conductance unambiguously, one wishes to fabricate a molecular junction with molecule-electrode contacts that are well defined on the atomic scale and carry out the measurement in a controlled environment. Fabricating such contacts reproducibly has been a challenge. Despite the difficulty, researchers have made solid advances recently. For example, STM has been used to create a well-defined metal-molecule-molecule junction by precisely placing individual metal atoms into contact with a molecule adsorbed on a substrate. To measure the conductance, the remaining challenges are to wire the two metal ends to an external circuit and to ensure that the electronic coupling between the molecular junction and the underlying substrate is negligible.

Another important development is various break junction techniques. By combining a mechanical break junction with simultaneous force and conductance measurements, one can determine if the measured conductance is a result of a single molecule and how the molecule is bound to the probing electrodes. The approach also allows one to create a large ensemble of molecular junctions with microscopically different molecule-electrode contacts and to perform statistical analysis on the conductance values of the molecular junctions. A peak in the distribution gives an averaged conductance of the molecule. The approach is simple and has been used to measure the electron-transport properties of many different molecules in vacuum and in solutions. However, the exact molecule-electrode contact geometries created by the break junction methods are usually unknown, and techniques that can provide atomic-scale structural information of the molecule-electrode contact will be of great importance to the field.
SUMMARY POINTS

1. Determining the conductance of single molecule is a basic task in molecular electronics.

2. To measure the conductance of a molecule, one must provide a reliable and reproducible contact between the molecule and two probing electrodes.

3. Measurement of single-molecule conductance has been difficult owing to the lack of a technique that can provide reliable and well-defined molecule-electrode contacts.

4. STM-based methods can place metal atoms into contact with a single molecule on a substrate with atomic precision. Remaining challenges are to connect the metal atoms to the external electrodes for conductance measurements and to ensure the electronic coupling between the molecule and the substrate does not interfere with the conductance measurement.

5. Break junction methods can create a large number of molecular junctions with different contact geometries. Although these contact geometries are not known precisely, the methods allow one to perform statistical analysis and to determine an average conductance of a molecule.

6. The conductance of a molecule depends also on its local environment.

7. By carrying out the measurement in an electrochemical environment, one can tune the alignment of the molecular energy levels relative to the Fermi energy levels of the electrodes and thus control the conductance of the molecule.

8. Future techniques that can fabricate molecular junctions with molecule-electrode contacts that are well defined on the atomic scale and that can characterize the atomic-scale structures of the molecule-electrode contacts will contribute enormously to the field of molecular electronics.

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LITERATURE CITED


22. Presents a tutorial review of fundamental aspects of electron transport through molecules and different approaches to compute molecular conduction properties.


Contents

Frontispiece
  C. Bradley Moore ................................................................. xvi

A Spectroscopist's View of Energy States, Energy Transfers, and Chemical Reactions
  C. Bradley Moore ........................................................................ 1

Stochastic Simulation of Chemical Kinetics
  Daniel T. Gillespie ........................................................................ 35

Protein-Folding Dynamics: Overview of Molecular Simulation Techniques
  Harold A. Scheraga, Mey Khalili, and Adam Liwo ............................ 57

Density-Functional Theory for Complex Fluids
  Jianzhong Wu and Zhidong Li ....................................................... 85

Phosphorylation Energy Hypothesis: Open Chemical Systems and Their Biological Functions
  Hong Qian .................................................................................... 113

Theoretical Studies of Photoinduced Electron Transfer in Dye-Sensitized TiO₂
  Walter R. Duncan and Oleg V. Prezhdo .......................................... 143

Nanoscale Fracture Mechanics
  Steven L. Mielke, Ted Belytschko, and George C. Schatz .................... 185

Modeling Self-Assembly and Phase Behavior in Complex Mixtures
  Anna C. Balazs ............................................................................. 211

Theory of Structural Glasses and Supercooled Liquids
  Vassily Lubchenko and Peter G. Wolynes ....................................... 235

Localized Surface Plasmon Resonance Spectroscopy and Sensing
  Katherine A. Willets and Richard P. Van Duyne ............................... 267

Copper and the Prion Protein: Methods, Structures, Function, and Disease
  Glenn L. Millhauser ....................................................................... 299
Aging of Organic Aerosol: Bridging the Gap Between Laboratory and Field Studies
Yinon Rudich, Neil M. Donahue, and Thomas F. Mentel .............................................. 321

Molecular Motion at Soft and Hard Interfaces: From Phospholipid Bilayers to Polymers and Lubricants
Sung Chul Bae and Steve Granick ................................................................. 353

Molecular Architectonic on Metal Surfaces
Johannes V. Barth .......................................................... 375

Highly Fluorescent Noble-Metal Quantum Dots
Jie Zheng, Philip R. Nicovich, and Robert M. Dickson ........................................ 409

State-to-State Dynamics of Elementary Bimolecular Reactions
Xueming Yang .......................................................... 433

Femtosecond Stimulated Raman Spectroscopy
Philipp Kukura, David W. McCamant, and Richard A. Mathies ......................... 461

Single-Molecule Probing of Adsorption and Diffusion on Silica Surfaces
Mary J. Wirth and Michael A. Legg ................................................................. 489

Intermolecular Interactions in Biomolecular Systems Examined by Mass Spectrometry
Thomas Wyttenbach and Michael T. Bowers ........................................ 511

Measurement of Single-Molecule Conductance
Fang Chen, Joshua Hihath, Zhifeng Huang, Xiulan Li, and N. J. Tao .................. 535

Structure and Dynamics of Conjugated Polymers in Liquid Crystalline Solvents
P. F. Barbara, W. - S. Chang, S. Link, G. D. Scholes, and Arun Jethiraj ............ 565

Gas-Phase Spectroscopy of Biomolecular Building Blocks
Mattanjah S. de Vries and Pavel Hobza .......................................................... 585

Isomerization Through Conical Intersections
Benjamin G. Levine and Todd J. Martinez ......................................................... 613

Spectral and Dynamical Properties of Multiexcitons in Semiconductor Nanocrystals
Victor I. Klimov .......................................................... 635

Molecular Motors: A Theorist’s Perspective
Anatoly B. Kolomeisky and Michael E. Fisher .................................................. 675

Bending Mechanics and Molecular Organization in Biological Membranes
Jay T. Groves .......................................................... 697

Exciton Photophysics of Carbon Nanotubes
Mildred S. Dresselhaus, Gene Dresselhaus, Riichiro Saito, and Ado Jorio ........ 719