

# Introduction to Molecular Conductor

Guorong Li\*

Course: Solid State II, Spring Semester 2008; Instructor: Elbio Dagotto  
Department of Physics Astronomy, University of Tennessee, Knoxville, TN 37996

(Dated: April 16, 2008)

Molecules, particularly organic molecules, are not normally thought of as conductors, and their conducting behavior are quite distinct. From last decade, research on molecular conductance and molecular electronic, has drawn increasingly more attention. This paper will first introduce the background of molecular electronics, then followed by the analysis of measurements of the molecular conductance in typical metal-molecule-metal(MMM) junction. At last, one example will demonstrate the application of molecule conductor and the other one will illustrate the arising nano-phenomena, for example, kondo effect and coulomb blockade, occurring in molecule transistor.

Keywords: molecular conductor, molecular electronics, molecular wire, test bed

## I. INTRODUCTION

The rapid miniaturization of electronics to the micrometer scale has been a key force driving scientific and economic progress over the past three decades. The smaller of the electronics, the bigger of the number of transistors that can be fabricated on a silicon integrated circuit and therefore the computing speed of such a circuit is doubling every 18 to 24 months (Moore's Law). In nowadays, solid-state microelectronics has advanced to the point at which 100 million transistors, with feature size measuring 180 nm can be put onto a few square centimeters of silicon. However, that is not sufficient to allow microprocessors to do the things expected for them.

However, in recent years, researchers have reported a variety of molecular-scale wires and switches[1], including molecular-scale transistors based on carbon nanotubes [2], semiconductor nanowires [3], small organic molecules [4] and biomolecules[5]. In fact, these four categories represent the four types of molecule or molecular-scale structure used to make electronic devices, see figure 1.

Figure 1A demonstrates that diodes and transistors

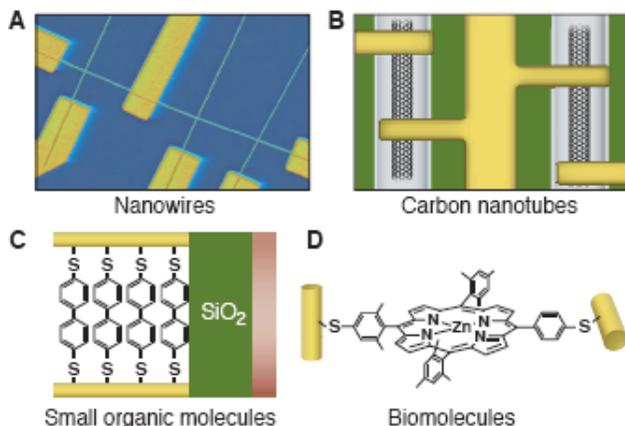


FIG. 1: Four approaches to molecular-scale electronics[6]

based on semiconductor nanowires are assembled with microfluidics to form logic AND, OR, NOR, and XOR circuits and logic functions. Figure 1B is about carbon nanotube transistors connected by gold interconnects to construct logic circuits such as a NOT circuit, NOR circuit, static random access memory (RAM) cell, and ring oscillator. Figure 1C is about field-effect transistors based on self-assembled monolayers of polyphenylene molecules combined to create a NOT circuit. Last, figure 1D is that porphyrin molecules store digital information as electrical charges like dynamic RAM cells.

From bottom up, why people prefer molecules? Based on W.Grant McGimpsey[7], there are several reasons. As follows:

1. Molecules are small — With transistor size at 180 nm on a side, molecules are some 30,000 times smaller.
2. Electrons are confined in molecules — Whereas electrons moving in silicon have many possible energies that will facilitate jumping from device to device, electron energies in molecules and atoms are quantized - there is a discrete number of allowable energies
3. Molecules have extended pi systems — Provides thermodynamically favorable electron conduit - molecules act as wires.
4. Molecules are flexible — Pi conjugation and therefore conduction can be switched on and off by changing molecular conformation providing potential control over electron flow
5. Molecules are identical — Can be fabricated defect-free in enormous numbers.
6. Some molecules can self-assemble — Can create large arrays of identical devices.

This paper is mainly interested in small organic molecules as a conductor. Molecular conductors represent the ultimate in device miniaturization, with the

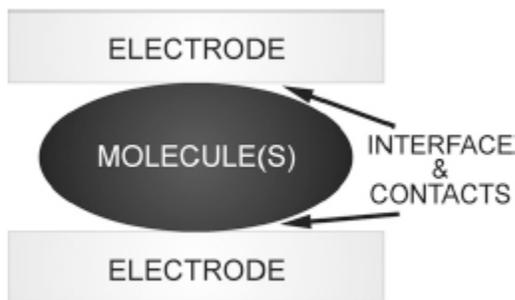


FIG. 2: Schematic representation of a molecular Junction

added advantages of spontaneous self-assembly, unprecedented mechanical flexibility and chemical tenability.

### III. METAL-MOLECULE-METAL JUNCTION

Many experiments about molecule conductor are done through a metal-molecule-metal junction. In order to analysis different testbeds used in experiments, we need to simplify the junctions and obtain different elements of the junction. Because we need to investigate what role the different elements play in molecular conductance measurements and find out the most critical or dominant influence. A schematic drawing of a molecular junction is shown in figure 2 where one or more molecules are sandwiched between two electrodes. The junction can be divided into 3 major regions, i.e., the electrodes, the molecule(s), and the interfaces between each contact and molecules.

#### A. The Electrodes

When come to consider electrodes, we need to know how do we to fabricate a junction. Except for the break junction technique[8], all other types of molecular junctions do not have both electrode fabricated simultaneously. First, one electrode is fabricated, then a self assembly molecule(SAM) is formed on this electrode, and the final step involves the formation of a second electrode.

There are lots of aspects of electrodes such as electrode compositions, shape, surface cleanness and topography etc and these aspects are always easy to influence the junction properties.[9][3] We usually use metals such as Au, Ag, Pt, Pd, Hg, etc, but sometimes use semiconductor substrate like GaAs. The roughness and cleanness of these metal types are very important in determining the conductance and the number of molecules in the junction. Since the molecules are in nano-regimes, the surface topography of electrodes are also influent the final configuration of the junctions. If we consider the SAM forming on the electrode, electrodes status are critical in

determining the packing density and tilt angle of SAM. Because the local contact geometries in nanoscale junctions for single molecule or a group of molecules are never identical. However, with a larger junction, large assemblies of molecules are measured simultaneously, which means, large collection of different local geometries in one junction are measured statistically. This results in an average conduction value. Therefore, single molecules experiments and measurements on SAMs results often in different conductance values.

The second or top electrode is even more critical than the bottom electrode. People evaporate metals on top of SAMs and results are always unreliable and irreproducible.[10][11] The majority of the wide range of experimental testbeds I will introduced in Section V can be subdivided based on their top contact and the method of applying this top contact.

#### B. The Molecules

The molecules studied can vary in length, composition, orientation and packing. From aspect of composition, Dustin K.James and James M. Tour in Rice University give a chapter with categories of molecular wires[12]. Base on their idea, they are two kinds of molecular wires, Organic Molecular Wires and Organometallic Molecular. In this paper I will mainly focus on organic molecular wires such as polyphenylene-based molecules, carbon Nanotubes, and alkane-based molecules.

In another dimension, if we consider the role of molecules play in junction, we can divide molecules into three parts:

1. The surface-active head group that anchors the molecule to the first electrode
2. The backbone of the molecule, and
3. The functional end group that might contain the proper functionality to ensure a good contact to the top electrode.

In order to get a idea about the configuration of molecules in junction, we take alkane(di)thiols for an example, see figure 3. A flat phase with the molecules parallel to the surface.

This is 220 Å constant-current STM image showing molecular resolution of the striped phase of HS-C6-SH prepared by in vacuo gas-phase deposition.

However, figure 4 give us a schematic of a standing-up phase with only one thiol bonded to gold, a looped phase with both thiols attached or a combination of both looped and standing-up molecules.

Several aspects during of the self assembly will affect the final phase formed, like the molecules length, the use of solvent, the type of metal or semiconductor surface,

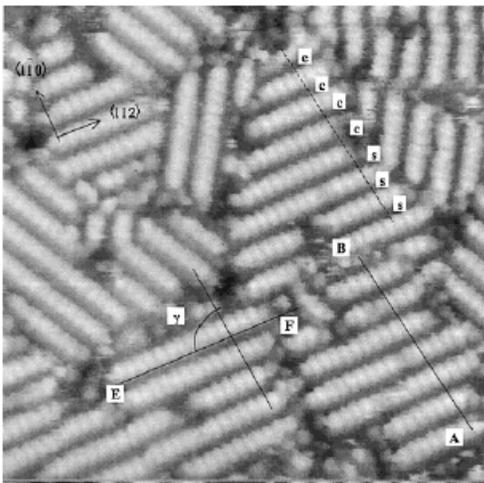


FIG. 3: A Flat Phase[13]

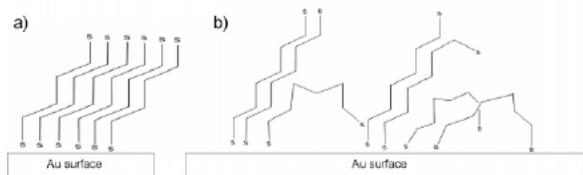


FIG. 4: Schematic of standing-up phase

the temperature and so on. Clearly, these phase change might lead to a significant changes in conduction.

### C. The molecule-electrode interface

There are two types of contact, one is chemisorbed and the other is physisorbed. Although the formation is not fully understood, the Au-S bond is known to be a chemisorbed contact. The difference between a chemisorbed contact and physical contact can lead to a change of a few orders of magnitude in conduction of the junction. Basically, this difference can be described in terms of the current through the molecular junction with the Landauer formula, stating that the conductance  $G$  is given by:

$$G = \frac{2e^2}{h} \times T_1 \times T_{mol} \times T_r \quad (1)$$

Where  $e$  is the elementary charge,  $h$  plancks constant and  $T_1$   $T_r$  and  $T_{mol}$  are the transmission coefficients of the left contact, right contact and the molecule, respectively. It is easy to see that from this formula, that a change in transmission of one of the contacts will change the absolute value of the current with the same factor. Therefore, to make a good comparison between the con-

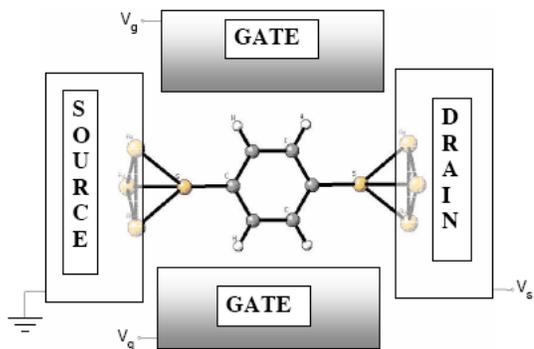


FIG. 5: Schematic representation of a molecular transistor[17]

tained currents per molecule, the differences in transimission of the second contact must be accounted for.

## IV. ELECTRON TRANSPORT IN MMM JUNCTION

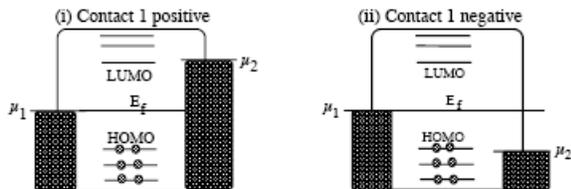
Several experimental groups have reported measurements of the current-voltage(I-V) characteristics of individual or small numbers of molecules. [1][10][14][11][15]A molecule represents a quantum dot, at least an order of magnitude smaller than semiconductor quantum dots. So like quantum dots, we have done some research about the electron transport, what about molecules? More specifically, what is the resistance of a molecule? Or what do we see when we connect a short molecule between two metallic contacts as shown in figure 5 and measure the current(I) as a function of the voltage(V). This has been observed using many different approaches including break junctions, scanning probes, nanopores, and a host of other methods. A number of theoretical models have been developed for calculating the I-V characteristics of molecular wires using semi-empirical as well as first principles theory. [9][16]This section will provide an intuitive explanation for the observed I-V characteristics using simple models to illustrate the basic physics.

First, as an example, figure 5 shows a utility of MMM junction as a molecular transistor in which a short molecule (Phenyl dithiol, PDT) sandwiched between source and drain contacts. However, most experiments so far lack good contacts and do not incorporate the gate electrodes.

In order to understand the basic principles of electron transport in molecular conductor or in a molecular transistor, the first thing we need to consider is to draw the energy diagram as follows.

Figure 6 represent the schematic energy level diagram of metal-molecule-metal structure when contact 1 is (i) positively biased and when contact 1 is (ii) negatively biased with respect to contact 2. (a)  $u = 0$ : Molecu-

(a)  $\eta=0$ : Molecular levels remain fixed with respect to contact 1.



(b)  $\eta=0.5$ : Molecular levels shift with respect to contact 1 by half the applied bias.

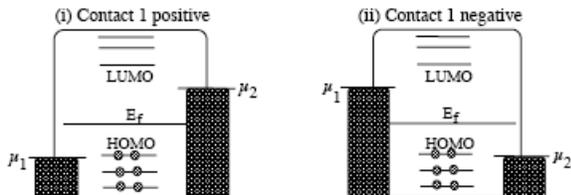


FIG. 6: Energy Diagram Of MMJ Junction

lar energy levels remain fixed with respect to contact 1, and (b)  $\eta = 0.5$ : Molecular energy levels shift by half the applied voltage, with respect to contact 1. When in a MMJ junction, the current will be mixed with two types. One is the hopping current, which is due to electron transfer through different energy levels, and the other is tunneling current which exponentially decreases with the increasing gap. These two currents can also be called the incoherent current and coherent current.

## V. MOLECULAR ELECTRONIC TESTBEDS

### 1. STM

Scanning Tunneling Microscopy scans over a surface with a preferably, atomically sharp conducting probe. A bias is applied between the STM tip and the conducting substrate and tunneling current between both is monitored. See figure 7.

In Figure 7, the second connection to the MW candidate was achieved via the probe tip of an STM. The height that the 1 molecule extends above the DT film. If normal to the surface, is  $7.3 \text{ \AA}$ , the trajectory of the STM tip traces out a surface of constant current. The relatively flat DT layer can be imaged by an atomic scale asperity on the end of the STM tip with resolution of the molecular lattice.

The STM is capable of recording very small currents. This is also a necessity because of the presence of a tunneling gap between the STM tip and the surface studied, that severely lowers the total current between both electrodes. The major advantage of an STM is to record simultaneously the current and morphology of the sam-

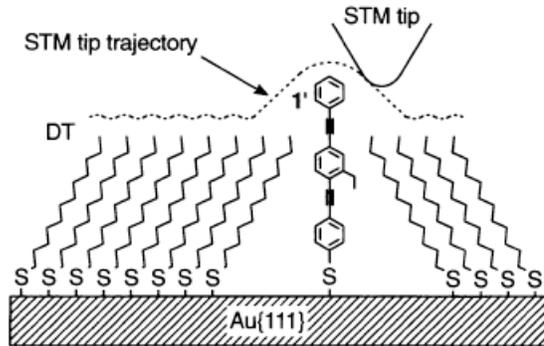


FIG. 7: The Molecule wire is anchored to Au(111) substrate with a SAM of n-dodecanethiol(DT)[5]

ple at the atomic level and, therefore, the tip can be used to address and measure at specific locations or molecules. This also implies that single molecules can be measured, but in densely packed SAMs it is never exactly clear how many molecules will be measured since the exact size and morphology of the tip is unknown. Xu, Bingqian and Tao, Nongjian J[15] observed three peaks in STM topography which is most likely due to two and three molecules bridging the junction. However, it is not easy to know. To circumvent this problem, conducting molecules embedded in an insulating SAM matrix have been studied just as figure 7. However, this creates other challenges like circumventing the inherent instability of the inserted molecules pack at less dense areas in the SAM, originating from defect sites on the substrate surface and grain boundaries.

The major disadvantage of the STM arises from its major advantage. Since the STM operates in constant current mode, constant height mode or a combination of both, it is actually unclear that the distance is between the tip and the surface and whether changes in current are due to changes in height or due to change in conduction of the molecules. Furthermore, because of the additional tunneling distance due to the gap between the molecules and the tip together with the extremely small device areas, lower currents are measured. For example, there is a limiting factor for the maximum measurable length of the insulating alkane(di)thiols, no more than 14 carbon atoms in length, otherwise, it will become extremely difficult to measure. The advantages of using STM are the possibility for studying in site the assembly and performing measurements in solution. This gives rise to the opportunity to measure molecules bridging the gap with both endgroups anchored to the tip and substrate. The chemisorbed contact at both ends greatly reduces the influence of contact resistance on the total resistance. Furthermore, since the tip can be moved repeatedly up and down to fabricate each time a new single molecule junction, statistics can be done and fluctuations due to

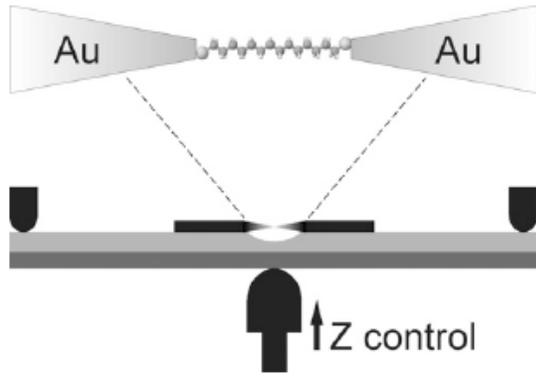


FIG. 8: Schematic depiction of a mechanical break junction set-up[16]

different contacts will be excluded from the results[15]. Research to develop the STM is still in progress.

## 2. Break Junction

In figure 8, a piezo controlled pushing rod bends the substrate with  $\mu\text{m}$  control. The large reduction factor between the Z-movement and the elongation in-plane allows for sub-nm control of the electrode distance.

Break junctions can be divided in two classes, mechanically controllable break junctions and electromigration break junctions. Fig 7 is a demonstration of mechanically controllable break junctions. This technique consists of a lithographically defined metallic free suspended bridge or a notched wire above a gap etched in an insulating (polymer or oxide) layer on a, preferably, bendable substrate. A piezo controlled pushing rod bends the substrate with micrometer precision in z-direction, while the counter supports at the sides of the sample keep the sample at a fixed position. Bending the substrate leads to an elongation in the plane of the electrodes causing the metallic bridge to break. Due to the high reduction factor between the piezo micrometer precision in z-direction and the in-plane elongation, the gap between the electrodes can be altered with sub-nm control. This ensures a well-defined distance between the electrodes and a stable configuration of the junction, down to  $0.2 \text{ pm h}^{-1}$ . It is more stable when we perform measurements at low temperatures. In the final step the molecules can be assembled between the leads. This can be done by different methods: breaking the electrodes while molecules are present either in solution or in the gas phase, or by adding a solution with the self-assembling molecules after the contacts are broken.

An example see figure 9.

In figure 9A, the gold wire of the break junction before breaking and tip formation. In figure 9B, after addition of benzene-1,4-dithiol, SAMs form on the gold wire sur-

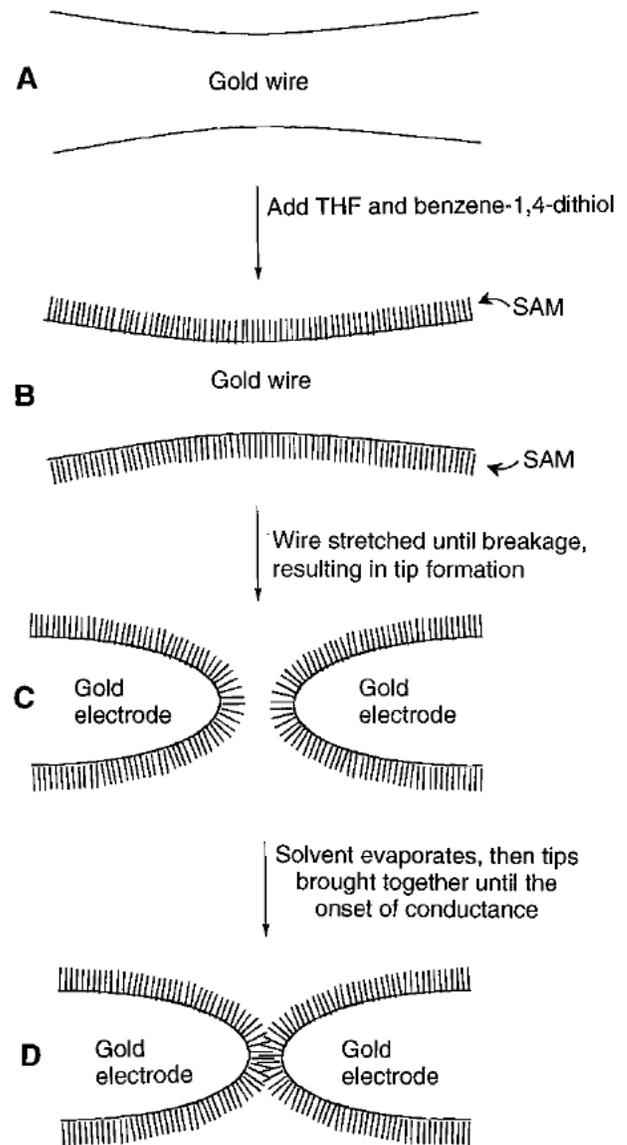


FIG. 9: Schematic of the measurement process[8]

faces. In figure 9C, mechanical breakage of the wire in solution produces two opposing gold contacts that are SAM-covered. In figure 9D, after the solvent is evaporated, the gold contacts are slowly moved together until the onset of conductance is achieved. Steps figure 9C and figure 9D (without solution) can be repeated numerous times to test for reproducibility.

The main advantage of this technique is the sub-nm control of the contacts with the possibility to measure single molecules. Furthermore, the back and forth bending of the substrates allows for doing statistics on a large number of measurements with a single junction.

In a break junction formed by electromigration, the gap between two electrodes is created by passing a

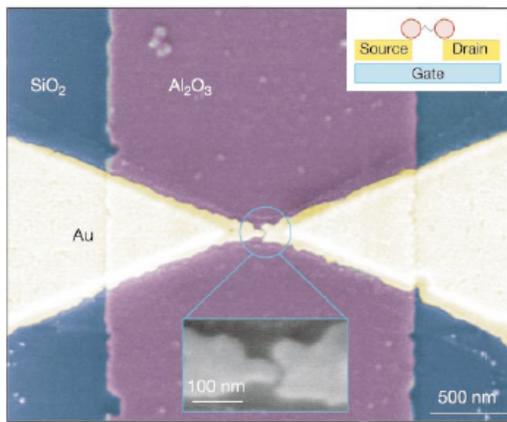


FIG. 10: Three Terminal Junction[18]

large electrical current through a lithographically defined nanowire.

### 3. Others

For other methods, Hylke B Akkerman and Bert de Boer have already made a summary. There are as follows:

1. Conducting Probe atomic force microscope
2. Nanotransfer printing
3. Hanging mercury drop junction
4. Nanopores
5. Crossed wires
6. 2D nanoparticle array
7. Large area molecular junction
8. Nanoparticle bridge molecular junction
9. Soft contact deposition
10. Metal evaporated molecular junction

## VI. RESEARCH

### Coulomb blockade and Kondo effect

With simple cathode/anode analysis, we cannot well understand the factors that affect the conductance of a molecule. However, the further advance in break junctions work came in 2002, one group[18] prepared electrochemical break junctions on a silicon oxide/silicon back plane see figure 10.

This is different with cathode/anode experiment. This permits measurement of molecular transport in a

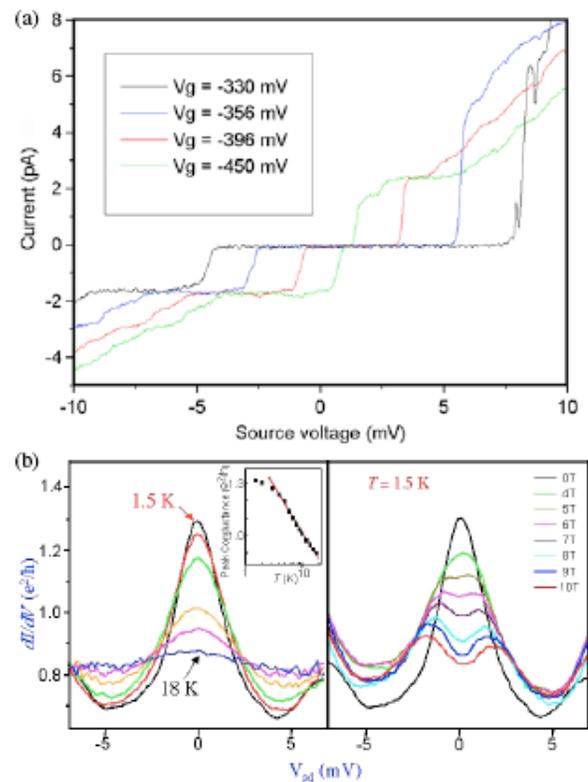


FIG. 11: Coulomb Blockade and Kondo Effect[16]

source/drain two electrode-junctions, but with partial gating provided by the silicon back plane. Because using three electrodes provide much better information since the reference electrode fixes the reference potential. So the effective gating of a source/drain molecular junction provide external control of the electrostatic potential with the junction. This kind of experiment represents a major advance in the capability to characterize the voltage dependence of transport through an MMM junction. Initial measurements utilizing this technique concentrated of so-called Coulomb blockade behavior(see figure 11a) and kondo effect behavior(see figure 11b). With lectures XSDX given on class, we know that both of these are highly nonohmic signatures, the first arising from capacitive charging of a molecular or atomic dot, the second from a splitting off of an isolated resonant state, producing a current maximum at zero voltage, with any nonzero-spin molecule.

### Dynamic Random Access Memory

The group in Yale University[19] investigate an electronically programmable memory devices utilizing molecular self-assembled monolayers. The devices exhibit electronically programmable and erasable memory bits compatible with conventional threshold levels and a memory

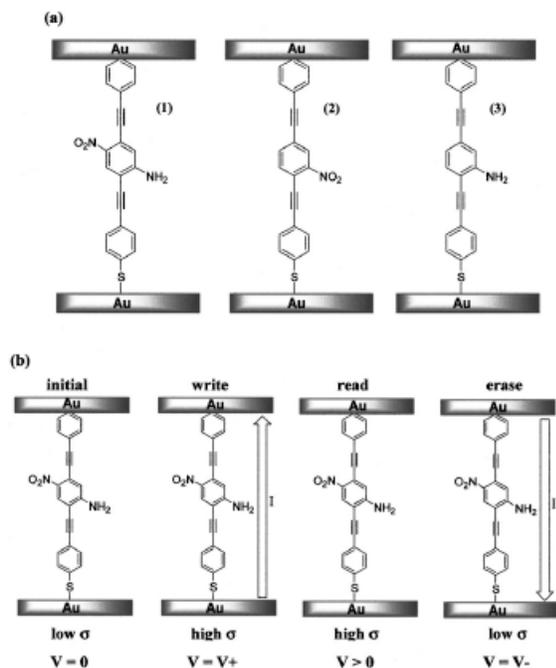


FIG. 12: Dynamic Random Access Memory[19]

cell applicable to a random access memory is demonstrated in their paper. See figure 12

This devices consist of a nanoscale nearly 30-50 nm diameter area of a self assembled monolayer contacted on both ends by metallic contacts. The system are like Au-molecules-Au and the type of molecules are be checked in the reference. This device operates by the storage of high or low conductivity state. figure 12 shows the write, read, and erase sequence. An initially low conductivity state (low  $\sigma$ ) is changed (written) into a high conductivity state (high  $\sigma$ ) upon application of a voltage pulse. The direction of current that flows during this write pulse is diagrammed. The high  $\sigma$  state persists as a stored bit, which is unaffected by successive read pulse.

## VII. SUMMARY AND PROSPECT

This paper first reviews the factors influent molecule conductance by investigating different roles of electrode, molecules, and contact interaction in a typical MMM junction. Then this paper introduces how conductance experiment done in terms of different test beds and with comparisons. In research section, this paper first demonstrates a research about the new phenomenon Coulomb blockade and Kondo effect happening in a single atom bond to molecule in a MMM junction which is hot recently. At last, with considering molecule electronics, a application on memory was introduced. This area involves molecule diode, molecule switch, and molecule

transistor that will be used in extremely small electronics like nanoscale devices which is promised leading to nanocomputers.

\* gli6@utk.edu

- [1] E. G. Emberly and G. Kirczenow, Phys. Rev. Lett. **91**, 188301 (2003).
- [2] A. Bachtold, P. Hadley, T. Nakanishi, and C. Dekker, Science **294**, 1317 (2001), <http://www.sciencemag.org/cgi/reprint/294/5545/1317.pdf>, URL <http://www.sciencemag.org/cgi/content/abstract/294/5545/1317>.
- [3] C. Joachim and M. A. Ratner, Nanotechnology **15**, 1065 (2004), URL <http://stacks.iop.org/0957-4484/15/1065>.
- [4] D. James and J. Tour, Chemistry of Materials **16**, 4423 (2004), ISSN 0897-4756, URL [http://pubs3.acs.org/acs/journals/doilookup?in\\_doi=10.1021/cm049648r](http://pubs3.acs.org/acs/journals/doilookup?in_doi=10.1021/cm049648r).
- [5] L. A. Bumm, J. J. Arnold, M. T. Cygan, T. D. Dunbar, T. P. Burgin, I. Jones, L., D. L. Allara, J. M. Tour, and P. S. Weiss, Science **271**, 1705 (1996), <http://www.sciencemag.org/cgi/reprint/271/5256/1705.pdf>, URL <http://www.sciencemag.org/cgi/content/abstract/271/5256/1705>.
- [6] G. Y. Tseng and J. C. Ellenbogen, Science **294**, 1293 (2001), <http://www.sciencemag.org/cgi/reprint/294/5545/1293.pdf>, URL <http://www.sciencemag.org>.
- [7] W. G. McGimpsey, *Ppt:molecular electronics, past, present, future?*
- [8] M. A. Reed, C. Zhou, C. J. Muller, T. P. Burgin, and J. M. Tour, Science **278**, 252 (1997), <http://www.sciencemag.org/cgi/reprint/278/5336/252.pdf>, URL <http://www.sciencemag.org/cgi/content/abstract/278/5336/252>.
- [9] J. Taylor, M. Brandbyge, and K. Stokbro, Phys. Rev. Lett. **89**, 138301 (2002).
- [10] S. Kohale, S. Molina, B. Weeks, R. Khare, and L. Hope-Weeks, Langmuir **23**, 1258 (2007), ISSN 0743-7463, URL [http://pubs3.acs.org/acs/journals/doilookup?in\\_doi=10.1021/la062441n](http://pubs3.acs.org/acs/journals/doilookup?in_doi=10.1021/la062441n).
- [11] S. Datta, W. Tian, S. Hong, R. Reifenberger, J. I. Henderson, and C. P. Kubiak, Phys. Rev. Lett. **79**, 2530 (1997).
- [12] J. M. T. Dustin K. James, *Molecular Wires*, vol. 257 (Springer-Verlag Berlin Heidelberg, 2005).
- [13] T. Leung, M. Gerstenberg, D. Lavrich, G. Scoles, F. Schreiber, and G. Poirier, Langmuir **16**, 549 (2000), ISSN 0743-7463, URL [http://pubs3.acs.org/acs/journals/doilookup?in\\_doi=10.1021/la9906222](http://pubs3.acs.org/acs/journals/doilookup?in_doi=10.1021/la9906222).
- [14] A. Labonte, S. Tripp, R. Reifenberger, and A. Wei, Journal of Physical Chemistry B **106**, 8721 (2002), ISSN 1520-6106, URL [http://pubs3.acs.org/acs/journals/doilookup?in\\_doi=10.1021/jp0256261](http://pubs3.acs.org/acs/journals/doilookup?in_doi=10.1021/jp0256261).
- [15] B. Xu and N. J. Tao, Science **301**, 1221 (2003), <http://www.sciencemag.org/cgi/reprint/301/5637/1221.pdf>, URL <http://www.sciencemag.org/cgi/content/abstract/301/5637/1221>.
- [16] H. B. Akkerman and B. de Boer, Journal of Physics: Condensed Matter **20**, 013001 (20pp) (2008), URL [http://pubs3.acs.org/acs/journals/doilookup?in\\_doi=10.1021/la062441n](http://pubs3.acs.org/acs/journals/doilookup?in_doi=10.1021/la062441n).

- [//stacks.iop.org/0953-8984/20/013001](http://stacks.iop.org/0953-8984/20/013001).
- [17] F. Z. S. D. Magnus Paulsson, *Nanoscience, Engineering and Technology Handbook*, Resistance of a Molecule (CRC Press, 2003).
- [18] W. Liang, M. P. Shores, M. Bockrath, J. R. Long, and H. Park, *Nature* **417**, 725 (2002), URL <http://dx.doi.org/10.1038/nature00790>.
- [19] M. A. Reed, J. Chen, A. M. Rawlett, D. W. Price, and J. M. Tour, *Applied Physics Letters* **78**, 3735 (2001), URL <http://link.aip.org/link/?APL/78/3735/1>.